Nano-Engineering Geology of clay-leachate interactions

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The title page:
Les armoiries de l'Université de Liège lui ont été octroyées par le Roi Baudouin en 1967, à l'occasion du 150e anniversaire de l'Institution, à la requête de Marcel Dubuisson, Recteur, agissant en qualité de Président du Conseil d'Administration.
Les armoiries veulent rappeler «la participation plus que séculaire de l'Université à la vie de la Cité de Liège» et rattacher l'Institution à l'histoire du Sart Tilman, où l'Université s'est implantée en grande partie.
C'est ainsi qu'on trouvera sur le blason, en 1 et 4, le perron liégeois, entouré du L et du G, du mot LièGe, en or sur fond rouge.
En 2 et 3, en rouge sur fond or, se détache un grill rectangulaire à cinq barres, avec une tige annelée, entouré de quatre coquilles Saint-Jacques.
Le domaine du Sart Tilman était jadis la possession de l'Abbaye de Saint-Jacques et de l'Abbaye de Saint-Laurent.
Les coquilles de Saint-Jacques, que l'on retrouve dans les écus de l'ancienne Abbaye liégeoise, étaient portées par les pèlerins du Moyen-Age, à Saint-Jacques de Compostelle.
L'écu est surmonté par la couronne royale.
Enfin, l'inscription latine «Universitas leodiensis» (Université de Liège), figure dans un bandeau, en dessous de l'écu (www.ulg.ac.be).

L'Université de Liège des origines à nos jours:
Dix siècles de tradition intellectuelle, gage de la qualité de notre enseignement
La fondation de l'Université de Liège en 1817, à l'initiative du roi Guillaume 1er des Pays-bas (qui a aussi fondé la Technische Universiteit Delft), est l'aboutissement d'une longue tradition intellectuelle qui remonte aux origines de la Principauté. A partir du XIe siècle, sous l'impulsion des princes-évêques, les écoles liégeoises constituent, en effet, un pôle d'attraction pour les étudiants et les chercheurs qui viennent y conquérir leurs premiers grades ou, comme Pétrarque, exploiter les richesses des bibliothèques.
La réputation des écoles médiévales valut à Liège le nom de nouvelle Athènes (www.ulg.ac.be).

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Symbol list

If variables are used only locally they do not appear in this overview.

Symbol	Name	Units
A	Area	(m^2)
A	Cross-sectional area perpendicular to the flow	(m^2)
BS	The basal spacing of an oriented clay sample. These values can be found in literature (*e.g.* Mitchell 1993). If not stated differently, the value of an air-dried sample.	(Å)
$BS_i^{(001)FOA}$	The basal spacing of clay species i; FOA sample preparation	(Å)
BS_{BSBH}	Basal spacing before heating and before percolation	(Å)
BS_{AS}	Basal spacing after percolation of permeate	(Å)
BS_{AH}	Basal spacing after heating	(Å)
C_c	Compression index	(-)
CF	Clay mineral fraction (all clay minerals, not only fraction <2 micrometer) determined from a TRP plot	(% total mass sample)
CF_i^{FOA}	Fraction of a clay mineral type i determined during a FOA analysis	(% total mass sample)
C_s	Swelling index	(-)
C	Concentration cations	(mol/unit volume)
CEMC	Concentration equivalent monovalent cations	(mol/unit volume)
$CEMC_{ini}$	Concentration equivalent monovalent cations of the fluid contained in the clay before permeation	(mol/unit volume)
$CEMC_{fin}$	Concentration equivalent monovalent cations of the leachate	(mol/unit volume)

con	Electric conductivity fluid	(S/m)
COV	Coefficient of variation = standard deviation/mean	(-)
C_v	Coefficient of consolidation	(m^2/s)
C_{vh}	Coefficient of variation describing the natural heterogeneity	(-)
C_{st}	Constant used in double layer effective stress relationship = 1	(mol/m^3)
$2D_{BSBH}$	Distance between clay particles before heating or percolation with salt	(Å)
$2D_{AS}$	Distance between clay particles after percolation with salt solution	(Å)
$2D_{AH}$	Virtual distance between clay particles after heating to 500°C	(Å)
$2D_{meca\ 0}$	Distance between clay particles when the external stress → 0 at the initial double layer thickness	(unit length)
D_{meca}	Half-distance between two clay particles	(unit length)
$2D_{meca}$	Distance between two clay particles = Mechanical aperture	(unit length)
$2D_{flow}$	Hydraulic aperture between two clay particles	(unit length)
e_1	Distance between clay particles parallel to the maximum exterior compressive stress	(m)
$e_{1\ ini}$	Distance between clay particles parallel to the maximum exterior compressive stress before percolation of leachate	(m)
$e_{1\ fin}$	Distance between clay particles parallel to the maximum exterior compressive stress after leachate percolation	(m)
e_2	Distance between clay particles perpendicular to the maximum exterior compressive stress	(m)
EBS	Equivalent basal spacing	(Å)
EBS_{ini}	Equivalent basal spacing before fluid/leachate contact	(Å)

EBS_{fin}	Equivalent basal spacing after fluid/leachate contact	(Å)
e	Void ratio	(-)
e_{lab}	Void ratio of a clay sample in the laboratory	(-)
e_{field}	Void ratio of a clay barrier in the field	(-)
$+e$ or $-e$	Elementary charge = $1.6021773 \cdot 10^{-19}$ (Binas 1986)	(C)
e_d	Void ratio of parallel clay particles at equilibrium based only on voids present in the interparticle space.	(-)
Eh	Standard electrode potential of the reference redox reaction: $2H^+ + 2e^- \leftrightarrow H_2$	(V)
F	Faraday's constant = $9.64853 \cdot 10^4$	(C/mol)
g	Gravitational acceleration	(m/s^2)
G_S	Specific gravity	(-)
h	Settlement of an oedometer clay sample	(mm)
h_{TOT}	Thickness of a TOT/TO-layer	(Å)
H or ΔH	Hydraulic head	(m)
H_{lab}	Hydraulic head exerted on a clay sample in the lab	(m)
H_{field}	Hydraulic head exerted on a clay barrier in the field	(m)
Δh	Settlement due to the interaction clay - leachate	(mm)
i	Hydraulic gradient	(-)
I_C	Consistency index $I_C = \frac{LL - W_c}{PI} = 1 - LI$ (DIN 18122)	(-)
K_0	Coefficient of neutral earth pressure	(-)
K_{hc}	Hydraulic conductivity	(m/s)
$K_{hc\ ini}$	Hydraulic conductivity before percolation with leachate	(m/s)
$K_{hc\ fin}$	Hydraulic conductivity after leachate percolation	(m/s)

$K_{hc\ lab}$	Hydraulic conductivity measured on a clay sample in the laboratory	(m/s)
$K_{hc\ field}$	Calculated hydraulic conductivity of a clay barrier	(m/s)
$K_{intrinsic}$	Intrinsic permeability (1 Darcy = $9.87 \cdot 10^{-13}$ m^2)	(m^2)
K_p	Normal rigidity	(N/m^3)
K_τ	Tangential rigidity	(N/m^3)
L_1	Length flow tube 1 or height clay particle, parallel to the maximum exterior compressive stress	(m)
L_2	Length flow tube 2 or width clay particle, perpendicular to the maximum exterior compressive stress	(m)
LI	Liquidity Index: $LI = \frac{W_c - PL}{PI} = 1 - I_C$	(-)
LL	Liquid limit	(% fluid content)
LL_{Casa}	Liquid limit determined using the Casagrande cup	(% fluid content)
LL_{Casa*}	Liquid limit determined using the cone penetrometer but transformed to the LL_{Casa} value using expression (**A4 - 2**)	(% fluid content)
LL_{cone}	Liquid limit determined using the cone penetrometer	(% fluid content)
LL_{cone*} or $LL_{equi\text{-}cone}$	Liquid limit determined using the Casagrande cup but transformed to the LL_{cone} value using expression (**A4 - 2**)	(% fluid content)
LL_s	Standard liquid limit of a homogenised clay tested with demineralised water	(% fluid content)
m	Number of particles in width of sample	(-)
M	$M = 6 \cdot \sin\phi' / (3 - \sin\phi')$	(-)
M_f	Mass fluids	(unit weight)
M_s	Mass solids	(unit weight)
MBA	Methylene Blue Adsorption value	(g/100g)
n	Number of particles in height of sample	(-)

n	Porosity	(-)
N_{int}	Number of clay - clay interfaces per clay sample	(-)
N_{layers}	Number of TOT/TO-layers per clay particle	(-)
OCR	Overconsolidation ratio	(-)
pH	power of H$^+$ cations, $pH = -\log(H^+)$; concentration of H$^+$ in mol/l	(-)
PL	Plastic limit	(% fluid content)
PI	Plasticity index: PI = LL - PL	(% fluid content)
P_i	Injection pressure fluid during hydraulic conductivity test	(Pa)
p'	Mean effective pressure	(kPa)
p'_f	Mean effective pressure at failure	(kPa)
q	Deviatoric stress	(kPa)
q_f	Deviatoric stress at failure	(kPa)
Q	Flow	(m^3/s)
Q	Width clay particle or sample	(micrometer)
$Q_{I\ ini}$	Combined flow through flow conduits influenced by clay - permeate interaction before permeation	(m^3/s)
$Q_{I\ fin}$	Combined flow through flow conduits influenced by clay - permeate interaction after permeation	(m^3/s)
Q_{II}	Combined flow through inert flow conduits not influenced by clay - permeate interaction before or after permeation	(m^3/s)
Q_{tot}	Total flow through a clay sample or barrier: $Q_I + Q_{II}$	(m^3/s)
R	Gas constant = 8.3145	(J/mol·K)
res	Electric resistiviy fluid	(Ohm·m)
r	Width sample / height sample	(-)

r	Correlation coefficient	(-)
s	L_2/L_1	(-)
S	Empirical standard deviation	(f(variable))
SL	Shrinkage limit	(% fluid content)
S_{rp}	Standard deviation characterising the reproducibility	(f(variable))
S_h	Standard deviation characterising the natural heterogeneity	(f(variable))
S_a	Specific surface	(m^2/kg)
S_r	Degree of saturation, saturation index	(-)
S_u	Undrained shear strength	(kPa)
t	Time	(s)
$t_{min\ val\ lab}$	Up to this time $t_{min\ val\ lab}$ (minimum validity) and possibly beyond, the results of the laboratory tests and numerical simulation are valid	(unit time)
$t_{min\ val\ field}$	Up to this time $t_{min\ val\ field}$ (minimum validity) and possibly beyond, the results of the laboratory tests and numerical simulation extrapolated to field values, are valid	(unit time)
T	Temperature	(°K) or (°C)
TCF^{TRP}	Total amount of clay minerals determined in a total random powder plot (TRP)	(% total mass sample)
TCF_{ini}	Total fraction of clay minerals in a clay sample before fluid/leachate contact	(% total mass sample)
TCF_{fin}	Total fraction of clay minerals in a clay sample after fluid/leachate contact	(% total mass sample)
u	Pore pressure	(kPa)
V	Closure of an interparticle void = $-2D_{0\ meca} + 2D_{meca}$	(m)

V	Breadth clay particle or clay sample	(micrometer)
val	Valence of an ion	(-)
v/p	A ratio to measure the swelling capacity of Smectites (Thorez 1976)	(m)
V_{fluid}	Volume fluid	(unit volume)
V_{solids}	Volume solids	(unit volume)
V_{voids}	Volume voids	(unit volume)
V_{total}	Total sample volume	(unit volume)
V_{lim}	If a volume of leachate equal to V_{lim} has been percolated through the clay, all measured reactions e.g. decrease/increase of hydraulic conductivity or chemical settlement have taken place (up to $t_{min\ val}$)	(m^3)
W_{lab}	Height or thickness of a clay sample	(micrometer)
W_{field}	Height or thickness of a clay barrier	(micrometer)
W	Breadth flow tubes or height sample or height clay particle	(m)
w_{OPT}	Fluid content at optimum Proctor density	(-) or (%)
w or W_c	Fluid content expressed as percentage or fraction water loss at 105°C during 12h, in terms of dry weight	(-) or (%)
w_{nat}	Natural fluid content	(-) or (%)
α	Coefficient relating strain to concentration	(-)
ε	Strain of the interparticle void	(-)
ε_a	Axial strain	(-)
ε_0	Permittivity of vacuum = $8.85419 \cdot 10^{-12}$ (Binas 1986)	(F/m)
ε'	Relative dielectric constant (water = 80; ethanol = 25; oil = 2; Binas 1986)	(-)
ε'_{ini}	Relative dielectric constant of the fluid contained in the clay before permeation	(-)

ε'_{fin}	Relative dielectric constant of the leachate	(-)
ϕ	Angle of internal friction	(°)
ϕ'	Effective angle of internal friction	(°)
γ_b	Bulk unit weight; unit weight of the moist soil $\gamma_b = (1 + w) \cdot \gamma_d$	(kN/m^3)
γ_d	Dry unit weight $\gamma_d\left(\frac{kN}{m^3}\right) = 9.81 \cdot \rho_d\left(\frac{g}{cm^3}\right)$ *e.g.* (Prinz 1997)	(kN/m^3)
γ_γ	Unit weight of the saturated soil	(kN/m^3)
γ_s	Unit weight of clay solid matter	(kN/m^3)
γ_w	Unit weight of water or any other fluid contained in the clay	(kN/m^3)
λ_{ddl}	Reactivity coefficient	(-)
η	Dynamic viscosity	(Pa·s)
ρ_b	Bulk density, density of the moist soil	(g/cm^3)
ρ_d	Density of the dry soil	(g/cm^3)
ρ_f	Density of the fluid	(g/cm^3)
ρ_{Pr}	Proctor density	(g/cm^3)
ρ_γ	Density of the saturated soil	(g/cm^3)
ρ_s	Density of clay solid matter	(g/cm^3) or (kg/m^3)
ρ_w	Density of water or any other fluid contained in the clay	(g/cm^3)
ρ_{OPT}	Optimum Proctor density	(kN/m^3)
σ_l', σ_s'	Effective stress between clay particles at equilibrium	(Pa)
σ	Exterior compressive stress (perpendicular to ddl and/or interlayers)	(Pa)
σ_3	Confining stress during triaxial test	(Pa)

θ	Angle of incidence of the X-ray beam	(°)
θ_{ddl}	Thickness of the centre of mass of the double layer to the clay particle surface	(m)
ν	Poisson's ratio	(-)
ν_{kin}	Kinematic viscosity	(m^2/s)
Ψ	Electrostatic potential in the midplane between two clay particles	(V)

Abbreviations

(001), (040)	Indicate the Miller symbols for crystal faces (h,k,l). In clay minerals, variations in the union and stacking of standard layers produce the different clay species. To identify clay minerals one can measure the repeat distance of these stacks. This distance, which can be measured by X-ray diffraction analyses, is called the basal (001) spacing (Battey 1994).
(10-14c)	Illite-Chlorite mixed-layers.
(10-14m)	Illite-Smectite mixed-layers (Sm*s.s.* is a (10-14m).
500 or 500°C	XRD analysis of a clay sample heated to 500°C.
300 or 300°C	XRD analysis of a clay sample heated to 300°C.
0.5	Factor times the LL; in character - number code used to describe the curing conditions of homogenised clay samples in contact with fluids like genuine landfill leachates. See **Table: Code** for more details.
1	Factor times the LL; in character - number code used to describe the curing conditions of homogenised clay samples in contact with fluids like genuine landfill leachates. See **Table: Code** for more details.
2	Factor times the LL; in character - number code used to describe the curing conditions of homogenised clay samples in contact with fluids like genuine landfill leachates. See **Table: Code** for more details.
Al-hydroxides	See Sm_{Al}.
Al-pillar	See Sm_{Al}.
A-line	PI = 0.73·(LL-20) (Casagrande 1947).
ARC	Action de Recherches Concertée n° 99/04-243: Confinement de centres d'enfouissement technique à l´aide de barrières argileuses.
ASTM	American society for testing of materials.
BOAC	Before or after consolidation? The first question engineer A should ask engineer B when B is trying to explain a certain type of physical or/and chemical reaction he observed when a certain fluid was added to the clay to engineer A. Depending on the order in which *e.g.* brines are added to the clay and the consolidation phase take place, opposite results can be found (*e.g.* both an increase and decrease of the hydraulic conductivity) see Schmitz *et al* 2004b.

BOD	Biological Oxygen Demand.
BS	British standard.
“C”	Secondary Chloritisation, not a Chloritisation in *s.s.* but a look alike of Chloritisation in the XRD.
C	Chlorite in a X-ray diffractogram.
C	Temperature during curing: 50°C; in character - number code used to describe the curing conditions of homogenised clay samples in contact with fluids like genuine landfill leachates. See **Table: Code** for more details.
C = Sm_{ref}	Reference Bentonite; in character - number code used to describe the curing conditions of homogenised clay samples in contact with fluids like genuine landfill leachates. See **Table: Code** for more details.
Ca or Ca^{2+}	Calcium cation.
CAC	Cation exchange capacity.
CE	Extremely plastic clay, BS 5930
CH	Clay of high plasticity, BS 5930
CI	Clay of intermediate plasticity, BS 5930
Cl^-	Chlorite anion.
C/N ratio	Carbon to nitrogen ratio.
Chlo	Chlorite.
Leachate-C	See C.
Clino	Indicates clinoptilolite, a zeolite mineral.
COD	Chemical oxygen demand.
cold	Stored at room temperature.
cor.	*(as subscript)* if a value has been corrected for dilution *etc.*
CWBI	Centre Wallon de Biologie Industrielle.
CU	Consolidated undrained triaxial test.

ddl	Diffuse double layer.
DIG	Département d'Infrastructures et de Géomécanique, Université de Liège (at present part of GéomaC).
DIN	Deutsche Industrie-Norm.
E	Demineralised water; in character - number code used to describe the curing conditions of homogenised clay samples in contact with fluids like genuine landfill leachates. See **Table: Code** for more details.
EG	Ethylene glycol.
EG	XRD analysis of a sample treated with ethylene glycol.
EGME	Measurement of the specific surface using ethylene glycol monoethyl ether.
ESEM	Environmental scanning electron microscope.
F	Temperature during curing: 20°C; in character - number code used to describe the curing conditions of homogenised clay samples in contact with fluids like genuine l landfill leachates. See **Table: Code** for more details.
FOA	Forced oriented aggregate, an oriented sample used for XRD analyses taking the whole clay fraction into account (not only the fraction smaller than 2 micrometer).
FNRS	Fonds National de la Recherche Scientifique.
GéomaC	Géoressources, Géotechnologies & Matériaux de Construction, department at the ULg.
GSD	Grain size distribution.
H	A landfill leachate; leachate-H2 for Atterberg, leachate-H1 for hydraulic conductivity tests; in character - number code used to describe the curing conditions of homogenised clay samples in contact with fluids like genuine landfill leachates. See **Table: Code** for more details.
(h,k)	Means any crystal plane in mineralogy except for the in clay mineralogy important crystal plane (0,0,1), the basal spacing (BS).
Leachate-H	See H.

• LCPC	Laboratoire Central des Ponts et Chaussées.
• I	Illite.
• “I”	Open Illite.
• K or K^+	Potassium cation.
• Kao	Kaolinite.
• K	Kaolinite in X-ray diffractograms
• K	Kruibeke clay; in character - number code used to describe the curing conditions of homogenised clay samples in contact with fluids like genuine landfill leachates. See **Table: Code** for more details.
• K	Saturated KCl solution; in character - number code used to describe the curing conditions of homogenised clay samples in contact with fluids like genuine landfill leachates. See **Table: Code** for more details.
• K0.67	A 0.67 mol/l KCl solution; in character - number code used to describe the curing conditions of homogenised clay samples in contact with fluids like genuine landfill leachates. See **Table: Code** for more details.
• Kao_{ref}	The reference Kaolinite used in this thesis.
• KCl_{sat}	Saturated KCl solution.
• LGIH	The former: Laboratoire de Géologie d'Ingénieur d'Hydrogéologie et de Prospection Géophysique, Université de Liège (at present part of GéomaC).
• LIG	The former: Laboratoire d'Infrastructure et de Géomécanique, Université de Liège (at present part of GéomaC).
• LST	Limestone.
• Lit rev	Literature review by the cited author.
• M	An old, mature landfill leachate; leachate-M; in character - number code used to describe the curing conditions of homogenised clay samples in contact with fluids like genuine landfill leachates. See **Table: Code** for more details.

M	Montmorillonite.
M^{x+}	Cation with a valence of x times 1.
MBA	Methylene blue adsorption value.
MSW	Municipal solid waste.
MY	Million years
Leachate-M	See M.
Na or Na^+	Sodium cation.
N	XRD analysis of a natural (untreated) clay sample.
N	A saturated NaCl solution; in character - number code used to describe the curing conditions of homogenised clay samples in contact with fluids like genuine landfill leachates. See **Table: Code** for more details.
$NaCl_{sat}$	Saturated NaCl solution.
N_2-BET	Measurement of the specific surface based on the Brunauer, Emmett, and Teller gas adsorption theory (nitrogen as gas).
nat.	i) As subscript: Test using the natural clay, not dried, ground or sieved but remoulded if necessary. ii) The XRD analysis of a sample without the addition of ethylene glycol or K^+ cation or Li^+ cation, in fact the clay as it was delivered to the clay laboratory plus the necessary minor sample preparation needed for XRD analyses.
NOA	Normal oriented aggregate (of the fraction less than 2 micrometer), the “standard” sample preparation used for XRD analyses.
NF	Normes Françaises
nor.	As subscript: The normal, standard Atterberg limit values of the homogenised clay as powder in contact with demineralised water.
Note:	Information added within a statement of the cited author.
O	A mix of young landfill leachates; leachate-C; in character - number code used to describe the curing conditions of homogenised clay

	samples in contact with fluids like genuine landfill leachates. See **Table: Code** for more details.
O-sheet	Octahedral-sheet.
oedo	Oedometric boundary conditions.
oedo$_C$	Consolidometer.
PC	Personal communication.
Pillar	See Sm_{Al}.
pow.	As subscript: The Atterberg limits of the homogenised clay, dried at 30°C, ground and sieved.
Q	Quartz in X-ray diffractograms.
RMR	Rock mass rating.
S	Soignies clay; in character - number code used to describe the curing conditions of homogenised clay samples in contact with fluids like genuine landfill leachates. See **Table: Code** for more details.
sat	Saturated solution.
Sm or Sm*s.s.*	Smectite.
Sm$_{Al}$	Smectite with a substance in the interlayer space that prevents collapse of this interlayer space upon heating. This substance can be an Al-hydroxide (Sm$_{Al}$) or other sesquioxide pillars.
Sm$_{org.}$	Smectite with organic matter in the interlayer space that prevents collapse upon heating (to 500°C).
Sm$_{ref}$	The reference Smectite used in this thesis.
Standard sample	Indicates samples stored 1 month at room temperature with an initial fluid content equal to the liquid limit.
SEM	Scanning electron microscope.
Sm$_{tot}$	The total amount of Smectite *e.g.*: Sm+ Sm$_{Al}$ + Sm$_{org}$.
ST	Silt-clay mixture, DIN 18196

• T	Tournai clay; in character - number code used to describe the curing conditions of homogenised clay samples in contact with fluids like genuine landfill leachates. See **Table: Code** for more details.
• TA	Distinct plastic clay, DIN 18196
• TL	Slightly plastic clay, DIN 18196
• TM	Medium plastic clay, DIN 18196
• TOC	Total organic carbon (total bonded organic carbon).
• TO-layer	Tetrahedral-octahedral layer, the basic unit of two-layer mineral like Kaolinite.
• TOT-layer	Tetrahedral-octahedral-tetrahedral-layer, the basic unit of three-layer minerals like Smectite and Illite.
• triax	Triaxial boundary conditions.
• TRP	Total random powder, an XRD plot of a non-orientated clay sample.
• T-sheet	Tetrahedral-sheet.
• TW	Tap-water
• U(1)	Humic acid Fluka Chemika (N°53680), Steinheim (CH), concentration 1g/l; in character - number code used to describe the curing conditions of homogenised clay samples in contact with fluids like genuine landfill leachates. See **Table: Code** for more details. Used in letter combination: Humic acid, concentration 1g/l.
• U(5)	Humic acid Fluka Chemika (N°53680), Steinheim (CH), concentration 5g/l; in character - number code used to describe the curing conditions of homogenised clay samples in contact with fluids like genuine landfill leachates. See **Table: Code** for more details. Used in letter combination: Humic acid, concentration 5g/l.
• ULg	Université de Liège.
• V	Vermiculite.
• warm	Stored at 50°C.
• XRD	X-ray diffraction.

Table: Code

Code used to describe the homogenised clay samples in contact with genuine landfill leachates
e.g. TOC1;3 indicates that a Tournai clay was mixed with a melange of young landfill leachates, that this mixture was stored at 50°C at a fluid content equal to the liquid limit of the clay during 3 months.

First letter; Clay type	Second letter; Fluid type added to homogenised clay or clay consistency		Third letter; temperature during curing	First number; Initial fluid content during curing expressed in terms of the LL of the clay	Second number; Storage time in months	Additional letter combination; special curing conditions
T Tournai clay	E demineralised water	K0.67 a 0.67 mol/l KCl solution	F 20°C	0.5 times the LL	1	out. During curing the clay was stored in an open recipient exposed to a sea climate
S Soignies clay	O mix of young landfill leachates; leachate-C	U(1) Humic acid, concentration 1g/l	C 50°C	1 times the LL	2	-C Sample permeated by leachate-C
K Kruibeke clay	M old landfill leachate; leachate-M	U(5) Humic acid, concentration 5g/l		2 times the LL	3	-H1 Sample permeated by leachate-H1
C = Sm_{ref} Reference Bentonite	H landfill leachate; leachate-H2 for Atterberg, leachate-H1 for hydraulic conductivity tests	nat. Natural clay which was not homogenised		etc. up to 8 times the LL	etc. up to 3 years	etc.
Kao_{ref} Reference Kaolinite	N saturated NaCl solution	pow. Natural homogenised clay				
	K saturated KCl solution					
X either: T, S, K or C	X any of the variables mentioned in these columns		X either: C or F	X and/or: 0.5, 1 or 2	X and/or: 0.5, 1 or 2	

Definitions

• Activity	The activity is defined by: $Activity = \frac{PI}{\%mass < 0.002mm}$ (Skempton 1953).
• Beidellite	A clay mineral of the Smectite group in which Si atoms have been replaced by Al atoms and in which there is virtual absence of Mg or Fe replacing Al atoms (DGM 1994). The electric charge is thus located predominantly in the tetrahedral-sheet close to the gegenions in contrast to Montmorillonite.
• Bentonite	Bentonite is a rock name referring to compacted shale containing a large portion of Smectite (usually Montmorillonite) (Fam and Dusseault 1999). A Bentonite, as defined by Prof. Thorez is an assemblage of neoformed volcanogenic Montmorillonite clay minerals (PC Thorez).
• Ca-Montmorillonite	Montmorillonite in which the cations held by the electrostatic forces are dominantly Ca^{2+} cations.
• Combination	The way in which the following variables are combined: Tournai clay, Soignies clay, Kruibeke clay, the leachate-C, -H or -M, warm storage, cold storage, at an initial fluid content of 0.5·LL, 1·LL or 2·LL, during 1 or 2 months.
• Cristobalite	Structure: Cubic or tetragonal SiO_2 mineral. Habit: Small octahedra often aggregate into tiny rounded groups. Optics: Colourless, transparent. Occurrence: In cavities of volcanic rocks. (Battey 1994)
• Eluviation	Eluviation is the translocation (movement by water) of weathering products out of one horizon to a lower horizon (Singer and Munns 1996).
• Geological barrier	The *in situ* material located surrounding (*e.g.* under) the (future) landfill, not pretreated (Prinz 1997).
• Illuviation	Illuviation is the accumulation of eluviated materials (Singer and Munns 1996).
• Kaolin	TO-minerals like: Kaolinite, Nacrite, Dickite and Anauxite.
• Kaolinite	The principal mineral of the Kaolin group of clay minerals (DGM 1994).
• Kruibeke clay	Rupelian clay, Oligocene. Obtained near Kruibeke.

• Level of analysis	Is given by the type and number of variables that are known. Analysis at another level actually means that the effect of a certain variable like the effect of the leachates is taken out. Variables in this sense are: Tournai clay, Soignies clay, Kruibeke clay, leachate-C, leachate-H, leachate-M, warm storage, cold storage, initial fluid content of 0.5·LL, 1·LL or 2·LL, during x months.
• (Clay-) Liner	Artificial layer (engineered barrier) of natural or pretreated clay material usually alien to the site of the future landfill that supports or takes over the function of the geological barrier.
• Methylene blue	3.9-bis-dimethylamino-phynazothionium-chloride, molecular weight 319.6 g/mol. (Merck 2000).
• Montmorillonite	Montmorillonite is the high-alumina end member of the Smectite group. Some replacement of the Al by the Mg atom has taken place (DGM 1994). The electric charge is weak and located in the octahedral-sheet, quite far from the gegenions.
▪ Na-Montmorillonite	Montmorillonite in which the cations held by the electrostatic forces are dominantly Na^+ cations.
• Niggli numbers	Niggli numbers are ratios of (component percentage)/(100-x), wherein x is the component percentage of the major constituent. This method removes the dilution effect of component x. One has to take care that there may be other components which have a diluting effect on the remaining space after component x has been "removed" (Swan and Sandilands 1995).
• Octahedral-sheet	When external ions are attached to the apical oxygen of the tetrahedral-sheet, each of them is bonded to two apical oxygens and to an OH^- ion which lies in the centre of the hexagonal ring of the apices. The bonding of the external ions will be completed by attachment to a sheet of anions on the other side which might be another set of opposed tetrahedral apices (thus another tetrahedral-sheet) or a sheet of OH^- ions. In either case the external ions are now in a set of octahedral co-ordinated polyhedrons, the octahedral-sheet (Battey 1994).
• Ponza Bentonite	Clay used in the experiments by Di Maio and Fenelli (1994) and Di Maio (1996), predominantly Na-Montmorillonite.
• Podzol	Podzols are characterised by a grey subsoil which has been leached, with accumulation of amorphous iron-aluminium sesquioxides and humus. Podzols occur under coniferous forests in humid and subhumid areas (Bell 1998).

• Pillaring	The process of inserting Al-hydroxides into the interlayer of *e.g.* a Smecite is called Al-hydroxilisation or Al-pillaring. Smectite + Al-hydroxide = (10-14c) (PC Thorez).
• Plastic limit (PL)	The plastic limit is the fluid content at which the remoulded clay passes from the plastic state to a friable or brittle state (Skempton 1970).
• Plasticity index (PI)	The plasticity index is defined by: PI = LL - PL (Skempton 1970). The plasticity index shows how much water a clay can render before it looses its plasticity (Atterberg 1911).
• Secondary Chlorite	Not a Chlorite in *s.s.* but a look alike of Chlorite in the XRD analysis.
• Soignies clay	Ypresian clay, Eocene. Obtained near Soignies.
• Smectite	Smectite is the clay family name for swelling clays. For the Tournai, Soignies and Kruibeke clay the Smectite/Montmorillonite fraction is either: a) Pure Montmorillonite (Sm), the v/p must be > 0.95 b) Mixed-layer Montmorillonite-Illite (10-14m) with a v/p smaller than <0.95 simply called Montmorillonite in this thesis (PC Thorez).
• Synthetic seal	An artificial seal like geomembranes or bitumen, usually located between the drainage layer and the engineered clay barrier.
• Tetrahedral-sheet	The structure of layer silicates is based upon layers of SiO_4 tetrahedrons. The tetrahedral layer comprises three sheets of atoms, the basal O^{2-}, the central Si^{4+} atom and the apical O^{2-} atom. The bases of the tetrahedral are located in one plane, sharing the three corners of the base with neighbours and with their apices all pointing in the same direction (Battey 1994).
• Tournai clay	Ypresian clay, Eocene. Obtained near Tournai.

Abstract

How can the suitability of a clay to act as a barrier to the flow of a specified fluid be determined? This question is directly related to the different mechanical and chemical stresses to which a clay barrier will be exposed. In spite of these mechanical and chemical stresses it must be guaranteed that the clay will fulfil its barrier function during the entire required containment period. This required technical life could be very long in engineering terms: 100-10000 years. During this period the clay barrier can neither be repaired nor maintained. Therefore it must be known which chemical or physical reactions will occur and how these reactions will influence the geomechanical properties of the clay.

Because there was no standard approach to test the suitability of natural clays as barrier on the long-term, this had to be developed. Based on literature it was shown that the reactions between clays and fluids could be decomposed in reactions on the particle level, the interlayer level and the TOT/TO level of clay minerals:

- Micrometer: Reactions on the particle level are the most frequent, the fastest to accomplish (instantaneous when leachate arrives) and have the least impact on the geomechanical properties of clays. It was shown that the double layer theory presents a valuable framework to analyse the changes in geomechanical properties upon clay-leachate contact. The properties of the fluid that are taken into account are the concentration of cations and the relative dielectric constant. Other processes on the particle level not captured by the double layer theory are *e.g.* the dissolution of calcitic cement and the oxidation of pyrites. The acids produced by the latter process influence reactions on the lower interlayer and TOT/TO level as well. It was shown that the natural clays possess themselves a rich variety of cations. These concentrations must be included in the analysis.

New tools developed on the particle level were:

- Integration of the chemical composition of the natural fluid contained in the clay in further analyses.
- The discretisation of clay samples into a discontinuous but homogeneous assembly of discrete clay particles (finite element mesh) with the use of information from petrographical studies of thin sections and oedometer tests.
- The implementation of a constitutive law into a numerical code to simulate the interparticle distance to interparticle fluid chemistry and mechanical stress.

- Nanometer: Reactions on the interlayer level include clay mineral alteration processes. To link these processes to geomechanical properties, the clay mineral sample preparation was modified to include all clay minerals and not only the fraction smaller than two micrometers. Next a method was developed to link clay mineralogy to geomechanical properties (equivalent basal spacing).

New tools developed on the interlayer level were:

- The equivalent basal spacing (EBS)
- Relation between the equivalent basal spacing and the liquid limit

With these tools a link can be made between the clay mineralogy and geomechanical properties. Leachate - clay interactions can be analysed as well as other processes like the mixing of clays and the reactions of clays upon heating *etc.*

- Ångström: Reactions on the TO/TOT level include the disintegration of TO arrangements, which will result in a complete destruction of a clay mineral. Of all three levels considered, changes on the TO/TOT level will cause the greatest change in geomechanical properties. Fortunately the processes on this TOT/TO level take a long history of subsequent physical and chemical reactions (hundreds to thousands of years *in situ*). Because changes on this level fail to be reproduced in the laboratory one must rely on natural analogues.
New tools developed on the TO/TOT level were:
- The link between the clay leached in the laboratory to natural analogues using thin sections and XRD diffraction analysis.

Examples are shown that the aforementioned approach can be applied in any geomechanical problem involving clays.

Samenvatting

Kan iedere klei gebruikt worden als een barrière die weerstand biedt tegen stroming van vloeistoffen? Tijdens zijn functie als barrière wordt klei blootgesteld aan een aantal mechanische en scheikundige belastingen. Desondanks moet gegarandeerd worden dat klei zijn functie als barrière waarneemt gedurende de gehele vereiste isolatie periode. Deze vereiste technische levensduur is erg lang vanuit het oogpunt van een ingenieur: honderden tot tienduizenden jaren. In deze periode kan de klei noch gerepareerd noch onderhouden worden. Daarom moet vooraf bekend zijn, welke scheikundige of natuurkundige reacties optreden en op welke wijze deze reacties de geomechanische eigenschappen van klei beïnvloeden.

Omdat er geen standaard benadering bestond om de toepasbaarheid van natuurlijke klei als barrière op de lange termijn te testen, moest deze eerst ontwikkeld worden. Gebaseerd op vakliteratuur werd aangetoond dat reacties tussen klei en vloeistoffen gescheiden kunnen worden in reacties op het kleideeltjes, kleimineraal en TOT/TO niveau:

- Micrometer: Reacties op het kleideeltjes niveau komen het meest voor. Deze zijn het snelst te bewerkstelligen (vrijwel gelijktijdig met de aankomst van het loogwater) en hebben de geringste invloed op de geomechanische eigenschappen van klei. De diffuse dubbellaag theorie vormt een waardevol kader om de veranderingen van geomechanische eigenschappen door klei-loogwater contact te analyseren. De eigenschappen van de vloeistof waarmee rekening gehouden wordt, zijn de concentratie van kationen en de relatieve diëlektrische constante. Andere processen die de dubbellaag niet in aanschouw neemt zijn *b.v.* het oplossen van calciet cement of de oxidatie van Pyriet. De zuren die door dit laatstgenoemde proces gevormd worden beïnvloeden ook reacties op de kleinere tussenlaag en TOT/TO niveaus. Het is aangetoond dat de natuurlijke klei zelf een grote variëteit aan kationen bezit. Deze concentraties moeten in de analyse betrokken worden.

Nieuwe methoden die ontwikkeld werden op het kleideeltjes niveau waren:

- Integratie van de vloeistof die van nature in de klei aanwezig is bij verdere analyse.
- De keuze van het eindige elementennet dat kleimonsters representeert als een discontinu maar homogeen netwerk van onafhankelijke kleideeltjes, door informatie welke vergaard werd tijdens de petrografische analyse van dunne doorsneden en oedometer tests.
- De toevoeging van een natuurkundige wet in een numerieke code met het doel de afstand tussen kleideeltjes te simuleren als functie van de scheikundige samenstelling van de vloeistof tussen de deeltjes en de mechanische belasting op de deeltjes.

- Nanometer: Kleimineraal omzettingsprocessen maken deel uit van de reacties op het tussenlaag niveau.

Om deze omzettingsprocessen uit te drukken als verandering van de geomechanische eigenschappen moest de preparatie van kleimineraal monsters aangepast worden om niet enkel de fractie kleiner dan 2 micrometer maar de gehele kleifractie te kunnen analyseren. Vervolgens werd een methode ontwikkeld om de kleimineralogie met geomechanische eigenschappen te verbinden (EBS, "equivalen basal spacing").

Nieuwe methoden die ontwikkeld werden op het tussenlaag niveau waren:

- De "equivalent basal spacing" (EBS)

- Verbinding tussen de equivalente basis afstand en de vloeigrens

Met deze methodes kan een verbinding gelegd worden tussen kleimineralogie en geomechanische eigenschappen. Loogwater - klei interacties kunnen hiermee geanalyseerd worden maar ook andere processen, zoals het mengen van verschillende kleimineralen en de reacties van klei op verhitting *enz.*

- Ångström: Het verlies van de TO samenhang die tot een vernietiging van de kleimineralen leidt, behoort tot de reacties op het TO/TOT niveau. Van alle onderzochte niveaus zullen veranderingen op het TO/TOT niveau de grootste veranderingen in geomechanische eigenschappen teweegbrengen. Gelukkig is er een lange "geschiedenis" van opeenvolgende scheikundige en natuurkundige reacties voor nodig (honderd tot duizend jaren *in situ*). Omdat het niet gelukt is deze processen in het laboratorium na te bootsen moest men informatie vergaren door een vergelijk met natuurlijke analogieën.

Nieuwe methoden die ontwikkeld werden op het tussenlaag niveau waren:

- Een verbinding werd gemaakt tussen klei, geloogd in het laboratorium, met natuurlijke analogieën gebruik makende van dunne doorsneden en Röntgen diffractie analyse.

Dat de beschreven aanpak in elk geomechanisch probleem toegepast kan worden, wordt met talrijke voorbeelden aangetoond.

Zusammenfassung

Lässt sich jeder Ton als Barriere gegen strömende Flüssigkeiten einsetzen? Während seiner Barrierefunktion wird der Ton unterschiedlichen physikalischen und chemischen Belastungen ausgesetzt. Es muss aber garantiert warden, dass der Ton während der gesamten Zeit seiner Funktion nachkommen kann. Die technische Lebensdauer ist von einem ingenieurtechnischen Blickwinkel aus gesehen sehr lang: hunderte bis hundertausende Jahre. Während dieser Zeit kann die Tonbarriere weder repariert noch gewartet werden. Deshalb muss im Voraus bekannt sein, welche chemischen und physikalischen Prozesse auftreten können und wie diese Prozesse auf die geomechanischen Eigenschaften der Tone Einfluss nehmen.

Weil es keine Norm gibt, eine Langzeitgebrauchsfähigkeit natürlicher Tone als Dichtungsbarriere zu definieren, musste diese erst entwickelt werden. Auf der Grundlage von Literaturrecherchen wurde gezeigt, dass die Interaktion zwischen Ton und Sickerflüssigkeit in Reaktionen auf Tonteilchen, Zwischenschicht und TOT/TO Ebene eingeteilt werden kann:

- Mikrometer: Reaktionen auf der Tonteilchenebene sind am häufigsten, am schnellsten (unmittelbar nach Ankunft der Sickerflüssigkeit) nehmen aber den geringsten Einfluss auf die geomechanischen Parameter des Tones. Es wurde dargelegt, dass die Theorie der diffusen Doppelschicht die Interaktionen zwischen Ton und Flüssigkeit auf der Teilchenebene beschreibt. Die Eigenschaften, die in Betracht genommen werden, sind die Kationenkonzentration und die relative dielektrische Konstante der Flüssigkeit. Andere Prozesse, die auf der Tonteilchenebene stattfinden und die nicht von der diffusen Doppelschicht-Theorie beschrieben werden, sind z.B. die Lösung von Kalkzement oder die Oxidation von Pyrit. Die Säuren, die durch den letztgenannten Prozess entstehen, beeinflussen auch die kleineren Zwischenschicht und TOT/TO-Ebenen. Es wurde gezeigt, dass die natürlichen Tone selber eine reiche Ansammlung von Kationen besitzen. Diese Konzentration muss in der Analyse berücksichtigt werden.

Neue Methoden, die auf der Tonteilchenebene entwickelt wurden, sind:

  - Die Analyse der Ton-Sickerwasser Interaktion mit Berücksichtigung der Zusammensetzung der natürlichen Tonflüssigkeit.
  - Tonproben als homogene, anisotrope Ansammlung diskreter Tonteilchen im Finite-Elementen-Gitter zu beschreiben, stützend auf der Information von Dünnschliffen und Oedometer-Versuchen.
  - Die Einführung eines Stoffgesetzes in einem Finite-Elementen-Programm, welches die Tonteilchenabstände als Funktion der chemischen Zusammensetzung der Sickerflüssigkeit und der externen mechanischen Belastung beschreibt.

- Nanometer: Reaktionen auf der Zwischenschichtebene schließen alle Tonumwandlungsprozesse mit ein. Um diese Prozesse in geomechanische Eigenschaften auszudrücken, wurde zuerst die Probenaufbereitung umgewandelt, so dass alle Tonminerale und nicht nur die in der Fraktion kleiner als 2 Mikrometer analysiert werden konnten. Danach wurde ein System entwickelt, um Tonmineralogie an die Geomechanik zu koppeln ("Equivalent Basal Spacing").

Neue Methoden, die auf der Zwischenschichtebene entwickelt wurden, sind:

  - Der "Equivalent Basal Spacing" (EBS)
  - Zusammenhang zwischen der Fliessgrenze und dem "Equivalent Basal Spacing".

Mit diesen Methoden kann eine Verbindung zwischen der Geomechanik und der Tonmineralogie hergestellt werden. Sickerwasser-Ton-Interaktionen sowie andere Prozesse: Mischung verschiedener Tonminerale, die Reaktionen der Tonminerale bei Erhitzung usw., können hiermit vorhergesagt werden.

- Ångström: Reaktionen auf der TO/TOT Ebene schließen Prozesse wie die Zerstörung der TO Verbindung mit ein, welche zu einer kompletten Vernichtung der Tonminerale führt.

Von den in Betracht genommenen Ebenen erzeugen Reaktionen auf der TO/TOT Ebene die größten Änderungen der geomechanischen Eigenschaften. Auf der TOT/TO Ebene verlaufen die Reaktionen nur nach einer langen Aufeinanderfolgung von chemischen und physikalischen Prozessen (hundert bis tausend Jahren *in situ*). Diese Prozesse konnten im Labor nicht nachvollzogen werden. Es besteht aber die Möglichkeit, auf Basis natürlicher Analoge Bewertungen zu erlangen.

Neue Methoden, die auf der TO/TOT Ebene entwickelt wurden, sind:

- Die Verbindung zwischen Tonproben, welche im Labor durchsickert wurden und natürlichen Analogen, wurde auf der Basis der Dünnschliffanalyse und der Röntgendiffraktometrie hergestellt.

Beispiele zeigen, dass die obgenannte Methodik bei jedem geomechanischen Problem, das Tone involviert, angewendet werden kann.

Résumé

Comment peut-on déterminer la capacité de l’argile à se comporter comme une barrière efficace à l’écoulement d’un fluide donné ? Cette question est directement reliée aux différentes contraintes mécaniques et chimiques auxquelles la barrière argileuse sera exposée. En dépit de ces sollicitations mécaniques et chimiques, il faut être capable de garantir la pérennité de l’étanchéité de l’argile durant la durée totale de l’ouvrage. Cette durée de vie nécessaire peut être très longue (par rapport à la durée de vie d’ouvrages du Génie Civil) : de 100 à 10000 ans. Durant cette période, aucune intervention au niveau de la barrière ne peut être effectuée (ni réparation ni maintenance). C’est pourquoi il faut connaître quelles réactions physiques et chimiques peuvent prendre place et comment ces réactions vont influencer les propriétés géomécaniques de l’argile.

Vu qu’il n’existe pas d’approche standard pour tester la capacité de l’argile à constituer à long terme des barrières d’étanchéité, il a été nécessaire de la développer. Se basant sur un relevé de la littérature, il a été montré que les réactions entre l’argile et les fluides peuvent être décomposées en trois catégories : celles qui se déroulent à l’échelle de la particule de minéraux argileux, à l’échelle de l’espace interfoliaire et à celle du TOT/TO.

- Micromètre : Les réactions à l’échelle de la particule sont les plus fréquentes, les plus rapides à s’effectuer (instantanément quand le lixiviat arrive) et ont l’impact le plus faible sur les propriétés géomécaniques de l’argile. Il a été montré que la théorie de la double couche constitue un cadre valable pour évaluer les changements des propriétés géomécaniques lors du contact argile-lixiviat. Les propriétés du fluide qui sont prises en compte sont la concentration en cations et la constante diélectrique relative. D’autres processus à l’échelle de la particule ne sont pas pris en compte par la théorie de la double couche : par exemple, la dissolution d’une cimentation calcitique et l’oxydation des pyrites. Les acides produits par ce dernier processus influencent aussi les réactions à une échelle inférieure, comme celui de l’espace interfoliaire et du TOT/TO. Il a été montré que les argiles naturelles possèdent en leur sein une riche variété de cations. Ces concentrations doivent être incluses dans l’analyse.

Les nouveaux outils qui ont été développés à l’échelle de la particule:

- Intégration du fluide de constitution de l’argile pour les analyses ultérieures.
- Modélisation d’un échantillon d’argile en un assemblage discontinu mais homogène de particules discrètes d’argile (Maillage éléments finis) grâce à l’utilisation des informations obtenues à l’aide des analyses pétrographiques de lames minces et des tests oedométriques.
- L’implémentation d’une loi constitutive dans un code numérique pour simuler la distance interparticulaire en fonction de la chimie du fluide interparticulaire et de l’état de contrainte.

- Nanomètre : Les réactions à l’échelle de l’espace interfoliaire incluent tous les processus d'altération minéralogique. Pour relier ces processus aux propriétés géomécaniques, la préparation des échantillons des minéraux argileux a été modifiée pour inclure tous les minéraux argileux et non pas seulement la fraction plus petite que deux micromètres. Ensuite une méthode a été développée pour relier la minéralogie des argiles aux propriétés géomécaniques ("equivalent basal spacing").

Les nouveaux outils qui ont été développés à l’échelle de l’espace interfoliaire:

- L' "equivalent basal spacing"
- La relation entre l' "equivalent basal spacing" et la limite de liquidité.

Avec ces outils, un lien peut être fait entre la minéralogie des argiles et les propriétés géomécaniques. Les interactions lixiviats-argile peuvent être analysées aussi bien que d'autres processus comme le mélange des argiles et les réactions de celles-ci à la chaleur.

- Ångström : Les réactions à l'échelle TO/TOT incluent la désintégration des arrangements TO, qui résultera en une destruction complète du minéral argileux. Des trois échelles considérées, les changements à l'échelle TO/TOT causeront les plus importantes modifications sur les propriétés géomécaniques. Les processus à l'échelle TO/TOT concernent (heureusement) un grand enchaînement d'événements physiques et chimiques (de centaines ou milliers d'années in situ). Au laboratoire, ces changements n'ayant pas pu être reproduits, on doit les relier à des processus analogues dans la nature.

Les nouveaux outils qui ont été développés à l'échelle TO/TOT:

- Le lien entre la lixiviation de l'argile au laboratoire avec les processus analogues dans la nature sur la base de l'analyse pétrographique des lames minces et de l'analyse de la diffraction aux RX.

Des exemples ont montré que l'approche des trois échelles mentionnées précédemment peut être appliquée dans n'importe quel problème géomécanique en présence d'argiles.

Jury

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Preface

From October 2000 till October 2001 I worked at the Université de Liège towards my Diplôme d'études approfondies. In the following period from October 2001 to this date, I worked as research fellow of the National Scientific Research Fond (FNRS) at the Université de Liège on this thesis.

These periods coincide with the ARC (Action de Recherches Concertée) project: Confinement of landfill sites with clay barriers. It was in the same domain that I conducted the tests, interpreted the results and made the advances in understanding clay mineralogy in geomechanical terms and clay - leachate interaction described in this thesis.

In order to perform the tests:

- Suitable clays were acquired in different quarries.
- Suitable landfill leachates were acquired at existing landfills.
- Special sample testing equipment was designed and built.
- New sample testing methods were tested and adopted.
- New methods to interpret clay mineralogy in geomechanical terms were developed.
- Appropriate laws were introduced into a numerical code.

The experimental work at the Université de Liège was presented by me on a regular basis (four times a year) to the partners of the ARC project, on many international conferences and workshops and occasionally as guest lecturer:

- Geomechanical tests were discussed with Prof. R.Charlier (Univ. Liège), Prof. A.Bolle (Univ. Liège), Prof.Ch.Schroeder (Univ. Libre Bruxelles and Univ. Cath. Louvain), Prof.J-C.Verbrugge (Univ. Libre Bruxelles and Univ. Gembloux), Dr.A-S.Ourth (Univ. Gembloux), ir.M.Demanet (Bureau Seco) and Prof.T.Hueckel (Duke Univ.) during his sabbatical stay in Liège.
- The clay mineral analyses campaigns were set-up and performed, interpreted and discussed in cooperation with Prof.J.Thorez and Mrs.D.Dosquet from the Liège clay laboratory.

Laboratory experiments shown in this thesis were obtained as raw data in any of the ARC associated laboratories and are marked as such, either directly or by reference to the publication in which they appeared first. The thesis as a whole was supervised by Prof.R.Charlier.

I would like to thank the persons below, who were of great help thanks to their special abilities in different fields of applied geology:

- The research technicians in the geomechanical laboratory of the Geomac department: Mr.Ph.Demoulin, Mr.R.Vandezande, Mr.A.Geurts, Mr.A.Cornette, Mr.M.Frédérick and ir.P.Illing for their assistance during the numerous tests.
- The constitutive laws were introduced into the numerical code *LAGAMINE* with the help of Dr.F.Collin and ir.J-P.Radu of the Geomac department.
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- Thin sections were prepared with the cooperation with Mr.X.Boes and Mr.Culus of the clay laboratory, Université de Liège.
- Prof. Jacobs of the Katholieke Universteit Leuven tested the specific surface of the clays.
- Dipl.-Ing.M.Schmitz, Mrs.D.C.P.A.H.Defesche and especially Dipl.-Physiol.Dd.J.Marquardt for the uncountable informative discussions and for the review of the text.

Liège, February 2004, Glück Auf,

Robrecht M Schmitz

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1 Introduction

1.1 Waste containment with clay barriers[1]

Every day more and more waste is produced. This waste needs to be isolated from the biosphere with barriers. There are several reasons why clay can be used as a barrier. One of them is the low hydraulic conductivity of clay. During its function as a barrier the clay will be exposed to different mechanical and chemical stresses. Nevertheless it must be guaranteed that the clay will fulfil its barrier function during the necessary waste containment period.

Questions

How can the suitability of a clay to act as barrier to the flow of a specified fluid be determined? Which physical or chemical reactions occur once this barrier is permeated by different fluids such as *e.g.* leachates? How will these reactions affect the geomechanical properties, like the hydraulic conductivity, of the clays? Will these reactions cause such large changes that the clay barrier cannot stand to the required task, the confinement of hazardous materials? These are the questions that needed to be answered and guided the direction of research.

Materials

To be nearer to real construction practice it was decided not to use pure monomineralic clays and synthetic landfill leachates but natural clays (representative of the clays found in general in Belgium and which can actually be used as a barrier) and genuine landfill leachates to analyse the clay barrier-waste interaction. To analyse some of the observed reactions in more detail a reference Smectite (supposed to be the most active clay), a reference Kaolinite (supposed to be the least active clay) and various fluids with a simpler composition than genuine landfill leachates were used as well.

Tools

How natural clay changes its properties under these barrier conditions was not known. Tools often used to analyse clay-fluid interactions are in fact poorly understood in geomechanical terms:

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[1] *Where in this thesis reference is made to stress conditions in domestic landfill barriers these conditions were deduced from the multitude of landfill design regulations applied in various countries in Europe and separately the regulations imposed by the European Union. In Schmitz (2001a) a summary of various regulations is given.*
The most stringent regulation (e.g. the requirement that barriers should be constructed above the groundwater table) found in any of the regulations was supposed to be appropriate, assuming that the adaptation of less developed landfill design regulations will follow, as it happened during the last 20 years, the more developed ones in due time. For general geomechanical aspects in landfill construction see Polo-Chiapolini (et al 1992) or Verbrugge (2000).

- Batch tests like the Atterberg tests are often thought to represent the long-term behaviour (Arrhenius principle) of clay - fluid interaction. *Perhaps even on long-term these interactions will not occur in barriers percolated by fluids.*

- The results of clay mineral analyses are vaguely interpreted referring only to a qualitative presence or absence of Smectite. *Perhaps other minerals equally play an important role.*

- Results obtained on commercial Bentonites (nice, pure and easy to interpret in the laboratory) are thought to be representative of natural clays (actually used on-site). *Perhaps some processes do not occur at all or occur differently in other clays.*

Therefore not only the interactions between natural Tertiary clay and genuine landfill leachates needed to be interpreted. Additionally it had to be determined how:

- Clay mineralogy is actually related to geomechanics.
- Batch tests like the Atterberg tests actually function and how their result can be interpreted correctly.
- Natural complex clays behave with respect to the monomineral clays used predominantly in literature.

How these questions were tackled and which solutions were found will be described in this thesis.

In addition new geological and geomechanical information of the clay deposits and suggestions related to the construction of a barrier will be given.

1.2 Waste containment, a solution?

If the goal is to find out if clay barriers contain leachate on long-term despite clay-leachate interactions, one could ask the question, why not?
A response could be that clay is reactive and that various substances can modify clay and its mechanical properties.
Does this matter? Yes, it does. Especially the hydraulic conductivity of a clay barrier should remain low, now and in x years. In which x is a function of the waste that needs to be contained (see **Figure: I-1**).

Approach followed
Tests with clays and leachates should preferably be performed during a thousand years. Thousand years do not only exceed the financial support for a thesis but also the likely life expectancy of a scientist. During a thesis the durations of tests are probably restricted to 3-4 years. During this short time interval the analysis of the reactions between clay and leachate must reveal the relevant physical and or chemical processes. If these can be recognised, the physical laws can provide the extrapolation to x years. Additionally it must be determined if other physical and or chemical reactions can occur outside the time frame of the thesis but within the time frame a clay barrier needs to function *e.g.* the supernova of the sun in our solar system will certainly affect the clay barrier but this physical process is likely to take place outside the time frame of the thesis and outside the time frame of the requested life of the clay barrier.

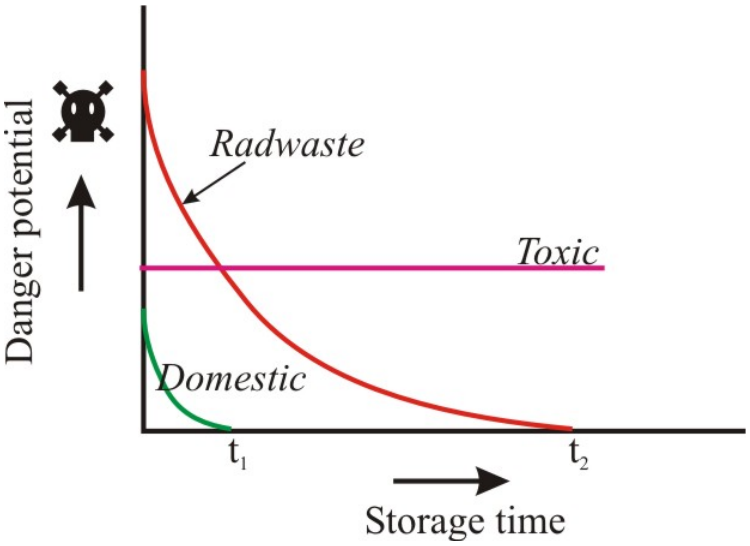

Figure: I-1

The potential danger of various types of waste, evolve differently with time.

Especially the danger potential of domestic landfill waste decreases fast (t_1 about 100 years[2]). The danger potential of radwaste decays much slower. Depending on the type of radwaste t_2 can be $1 \cdot 10^5$ to $1 \cdot 10^6$ years. The danger-potential of other toxic waste does not decay. The technical life of a clay barrier is limited. In the case of domestic waste the necessary technical life, about 100 years, is not unlike the requested technical life of other engineered structures like bridges and tunnels. These latter structures are, however, accessible during their life unlike the clay barrier, where no maintenance can take place. During the storage of radwaste the technical life of the clay barrier is shorter than the time needed for the waste to reduce its danger potential to near zero. In this case adequate geological barriers must take over the function of the engineered clay barrier (note that in $1 \cdot 10^6$ years regions like the Ardennes but also salt diapers will have risen by several 100 m, deep seated storage is not as deep anymore). In the case of other toxic waste without a decay time clay barriers can isolate the waste up to 1000 or 10000 years (Which type of civilisation will exist in 10000 years? What is the genetical decay time of its individuals? Will there still be engineers to solve the problems of society? Is the location and type of waste still known?) Is the only (unavoidable) solution the eventual dilution?

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[2] *In a period of hundred years after closure of the landfill most biological activity will have slowed down to a negligible rate (PC Rodriguez).*

Table: I-1

Geological times referred to in this thesis and the waste containment time next to the geological and bio-social time scale. Time in years before (-) or after (+) today.

Time (y) Life of earth		Sources of the clay species	How did civilisation look like	What did the Tournai, Soignies and Kruibeke clay do
$-4\cdot10^9$ Birth of planet Earth				
$-6.5\cdot10^7$	Tertiary Paleogene	start Palaeocene	The ancestors of humans are mouse-sized mammals.	
$-5.5\cdot10^7$		start Eocene (Ypresian from $-55\cdot10^6$ to $-50\cdot10^6$)		Soignies and Tournai clay deposited
$-3.4\cdot10^7$		start Oligocene (Rupelian from $-34\cdot10^6$ to $-29\cdot10^6$)		Kruibeke clay deposited
$-2.3\cdot10^7$	Tertiary Neogene	start Miocene		
$-5\cdot10^6$		start Pliocene	The ancestors of humans are without tools (except twigs).	
$-2.6\cdot10^6$		start Pleistocene	Homo erectus Homo Neandertalis Homo “Sapiens”	
$-1\cdot10^4$	Quaternary	Holocene	Start iron age; Start stone age; Start bronze age;	Sea level rose 120m
0 Mid-life earth			First city Ur; Siege of Troy; Classical Greece; End Roman Empire; Start steel age; Start Plastic & nuclear age; First nuclear waste	Loessic cover Leaching through loessic cover

Time (y) Life of earth	Sources of the clay species	How did civilisation look like	What did the Tournai, Soignies and Kruibeke clay do
$+1\cdot10^4$	Post-Holocene	Post Plastic & nuclear age? Even the most prudent deep disposal centre thinks it is possible to safeguard waste up to this time	New regression or transgression New ice age; Changes in volcanic activity
$+1\cdot10^5$		Up to this point the first high active radwaste produced (1000Curie/m³) must be isolated	Ardennes rise by 100m New regressions or transgressions Ice ages pass and come
$+1\cdot10^6$		Homo-sapiens?	Major and definite climatic changes start
$+1\cdot10^7$		Mammals?	Noticeable continent move
$+4\cdot10^9$ End of earth and indirect solution to all waste problems			

1.3 The set up of this thesis

In this introduction the main question (How can the suitability of a clay to act as barrier to the flow of a specified fluid be determined?) and the co-questions that needed to be answered first were introduced. The answer to this question, found after years of scientific literature, laboratory and numerical research, has been written down in this thesis and can be accessed and understood by reading the main text which is divided in three parts **A**, **B** and **C**:

In part **A** a literature overview is given on clay-leachate interaction. An introduction to part **A** is given in chapter **A 1**. In chapter **A 2** it will be explained how fluids influence the mechanical behaviour of clay. A new system to analyse clay - fluid interaction is proposed on the basis of the level (particle, interlayer and TOT/TO) on which these interactions occur. This three level approach will be followed throughout this thesis. In chapter **A 3** the different physical and chemical laws and processes used in literature to explain certain clay-fluid interactions are described and their value is examined. On the particle level the dis- and advantages of the diffuse double layer theory are explained. It is shown that in geomechanical literature confusion prevails in translating changes in diffuse double layer thickness to changes in geomechanical properties. The different schools of thought are reorganised into a new simple system. The overview given of clay - leachate interactions on the interlayer and TOT/TO level are new in geomechanical literature.
In chapter **A 4** the influence of the different physical and chemical models on geomechanical parameters as the particle size distribution, the Atterberg limits, the shear strength and the hydraulic conductivity is given. It is shown why it is comfortable to analyse possible interactions on three different levels: The particle, interlayer and TOT/TO level. In chapter **A 5** the conclusions are summarised.

New in geomechanical literature is the description of the life of clay from its sedimentation (birth) to its later use as barrier, to the end of the containment period (death) followed in part **B.** Three natural clays were selected for this analysis: Soignies and Tournai clay represent by their genesis, their availability (reserves and resources) and mineability, the potential clay-barrier source material in the Walloon-region. The third natural Belgian clay that was analysed is Kruibeke clay (large reserves and resources) from the Flemish region which is well characterised under the name Boom clay in geomechanical literature.
Each step, excavation, construction of the barrier, mechanical loading and permeation of landfill leachates stresses the clay barrier differently. In chapter **B 1**, part **B** is introduced. In **B 2** the depositional history of the clay is reviewed and it is explained why the sedimentological history plays an important geomechanical role in the later function of the clay as barrier used to seal waste. Then the changes *in situ* up to anthropogenic influence are discussed.
In chapter **B 3** a new sample preparation method for clay mineral analysis is introduced. Then the evolution of the clay during the Holocene is described. This includes the changes provoked by the exposure to the present day's atmosphere in the quarry, the treatment on the landfill construction site, the workability of the clay, the mechanical loading by infill of the waste, the contact with the young landfill leachate, the steady rise of the temperature and the final permeation of the mature landfill leachate through

the clay barrier. The changes in clay mineral alteration (new: recognition of clay mineral alteration pathways), geochemistry and geomechanical properties like the Atterberg limits, the shear strength and the hydraulic conductivity are discussed in detail. New results were produced concerning the evolution of the hydraulic conductivity upon leachate permeation. In chapter **B 4** the final stage in the life of the clay is presented in which the biological life of the landfill ends. The prediction of the long-term behaviour of the clay barrier is given by referring to natural analogues. In chapter **B 5** the conclusions concerning part **B** are given.

Part **C** represents the spin-off of this thesis. In chapter **C 1** part **C** is introduced. In chapter **C 2** the natural heterogeneity of the clays used in the experiments is discussed in relationship to the influence of different leachates. In chapter **C 3** the variations of the LL are analysed in a new approach, which consists in the implementation of the chemical composition of the fluids contained in the clay into the analysis of clay - leachate interactions. In chapter **C 4** correlations between Atterberg test parameters are sought. In the same chapter correlations between mineral phases of the clay exposed to landfill leachates are used to confirm mineral alteration pathways described in part **B 3**. In chapter **C5** it is explained how changes on the interlayer level *i.e.* changes in clay mineralogy can be related to geomechanical properties. Therefore the equivalent basal spacing (EBS) is defined as new tool in geomechanical engineering. In the remainder of the chapter it is shown how the EBS can be used to predict the behaviour of clay when heated, exposed to salts, mixed with other clays *etc.* In chapter **C 6** it is explained how a clay sample can be discretised as a homogenous assembly of discrete clay particles. With a new method it is shown how the dimensions of clay particles and their orientation can be deduced from geomechanical tests. It is shown that physical - chemical laws that describe clay - leachate interaction derived for pure Smectites are not necessarily applicable to natural clays. In chapter **C 7** the clay - leachate interaction on the particle level is analysed. A constitutive law relating the interparticle spacing to external stress and fluid chemistry is explained. Finally, it is shown how this constitutive law was introduced into the finite element code *LAGAMINE* to predict the evolution of the hydraulic conductivity during permeation of a clay barrier. A new extrapolation approach is given. In chapter **C 8** examples are shown how the information contained in **Parts A, B** and **C** can be used to assess clay - leachate interactions. In chapter **C 9** conclusions concerning part **C** are given.

In the Part: **Conclusion** the results found in part **A**, **B** and **C** have been classed separately for each co-questions raised in the introduction.

In the Part: **Synthesis**, a manual is given to access the data contained in this thesis in order to answer the main question raised in the introduction: "How can the suitability of a clay to act as barrier to the flow of a specified fluid be determined?"

A Literature review

A 1 Introduction

In part **A** a literature overview is given on clay[3,4]-leachate interaction. The existing literature is vast but at the same time confusing. Much confusion and contradiction arises from an incorrect description of the clays involved in the tests and the exact boundary conditions used.

In chapter **A 2** it will be explained how fluids influence the mechanical behaviour of clay. A new system to analyse clay - fluid interaction is proposed on the basis of the level (particle, interlayer and TOT/TO) on which these interactions occur. This three level approach will be followed throughout this thesis. In chapter **A 3** the different physical and chemical laws and processes used in literature to explain certain clay-fluid interactions are described and their value is examined. On the particle level the dis- and advantages of the diffuse double layer theory are explained. It is shown that in geomechanical literature confusion prevails in translating changes in diffuse double layer thickness to changes in geomechanical properties. The different schools of thought are reorganised into a new simple system. The overview given of clay - leachate interactions on the interlayer and TOT/TO level are new in geomechanical literature. In chapter **A 4** the influence of the different physical and chemical models on geomechanical parameters as the particle size distribution, the Atterberg limits, the

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[3] *Clay minerals can be defined differently according to their crystal structure or their grain size. All particles smaller than 2 micrometer are called clay. But a clay mineral, defined by its sheet-like structure of layered tetragonal and hexagonal units, can be larger than this threshold value, and can still possess the typical mechanical properties of a clay. Vice versa, particles of other minerals can be ground to a fraction smaller than 2 micrometer but they do not attain any of the clay characteristic mechanical features.*
The basics of clay mineralogy are not summarised here because many good books are available, e.g.: "Practical identification of clay minerals, a handbook for teachers and students in clay mineralogy" by J. Thorez, (1976). "Tonmineralogie und Tone" by K. Jasmund and G. Lagaly, 1993, "Origin and Mineralogy of Clays, Clays and the Environment" by B. Velde, 1995 or "Fundamentals of soil mechanics" by J.K. Mitchell, 1993.

[4] *The word "clay" has relatives in languages of the same language group: mediaeval Dutch (12-15th century) = clei; old Saxon (until 1100AD) = klei; new Dutch = klei; old Frisian (until 1600AD) klây; old English (until 1100AD) = clâêg; all these denominations are derived from the Germanic word klaija which means "sticky fluid". The Dutch word for "sticky" = kleven belongs to the same word group as "clay" = klei, like the Norwegian "kleima" which means smearing (Vries and Tollenaere 1983). Our forebears with their description of clay as a sticky material were very conscious about the physical phenomena, which would later be described as the plasticity of clays. In Romanic languages, the name for clay, argile (French), argilla (Italien) and arcilla (Spanish) originate from the Latin: argilla which has been borrowed from the Greek: αργιλ(λ)ος.*

shear strength and the hydraulic conductivity is given. Conclusions are drawn about the clay-fluid interactivity *e.g.* on which physical and chemical processes batch tests like Atterberg tests depend. It is shown why it is comfortable to analyse possible interactions on three different levels: The particle, interlayer and TOT/TO level. In chapter **A 5** the conclusion are summarised.

The information contained in chapter **A** formed the basis of the analyses described in part **B** and part **C**.

A 2 How can a fluid influence the mechanical behaviour of a clay?

A 2.1 Introduction

Atterberg showed in 1911 that the geomechanical properties of clays change when fluids (organic fluids and acids) are added to clay. Terzaghi (1925) recognised that a pure mechanical analysis of clays is not sufficient to describe its physical (geomechanical) properties because of the profound influences of even small amounts of adsorbed substances. Fluids carrying such substances can be added before the clay is used in an engineering application (Atterberg 1911, Terzaghi 1925) to enhance its properties. However, if such fluids interact with an engineered clay structure during its technical life, the assumption that the clay will retain the appropriate standard reached after construction, does not need to be valid (Arch *et al* 1996). As was summarised by Müller-Vonmoos and Kohler (1993) one and the same clay can change its mechanical properties due to cation exchange, changes in the electric potential at the edges of the silicate layers, changes in the concentration of the electrolyte and the pH. Mitchell (1993) agreed that the mechanical properties of clays are not fixed properties and stated that these properties are function of factors such as particle size, degree of crystallinity, type of adsorbed cations, pH, presence of organic matter, and type and amount of free electrolytes in the pore water. These literature results spanning nearly one century of geomechanical research of clays clearly show that clays are influenced by diverse components contained in fluids contacting clay. It is apparent that these reactions are complex by the heterogeneous nature of clays and the variety of fluids these clays will encounter during their engineering life. It is known that clay minerals[5] may become unstable in soils and may become decomposed after a change in environmental conditions (Brinkman 1979). But does this happen in the case fluids, like landfill leachates, penetrate engineered clay barriers? Clay mineral alteration occurs but the relevant question is if it is also an important factor that can change the engineering characteristics of clay? Literature about this aspect is rather contradictory. First of all a distinction needs to be made between the levels on which clay alteration occurs. Depending on the level, different clay alteration processes are important. Therefore a three-level approach is followed: On level 1 tetrahedral- and octahedral-layers are concerned, on level 2 the interlayers and on level 3 the clay particles.

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[5] *The word "Mine" for a mining shaft is of Celtic origin. It entered mediaeval Latin as "Mina" for shaft and "Minerare" for mining. "Mineralia" were mined ores and rocks (Museum of Mineralogy, University of Marburg).*

A 2.2 Modifications analysed per level

It is very convenient to analyse the reactions between chemicals and clays on different levels[6]. If one deals with clay three levels can be discerned (see **Table: A2-1**):

1) Particle level.
2) Interlayer level.
3) TOT/TO level.

In this chapter the reactions on the different levels are discussed separately.

A 2.2.1 Tetrahedral - octahedral level

This is the smallest level at which clay minerals are analysed. The general opinion found in literature dealing with clay barriers and landfill leachates is that the layer silicates remain intact (*e.g.* an Illite remains an Illite, and a Kaolinite remains a Kaolinite) see Kohler (1988) and the literature overview by Prinz (1997), and recently by the author (Schmitz *et al*. 2001, 2002a and 2003b). An example of a process in which layer silicate damage occurs concerns the ripping of a tetrahedral-sheet during Kaolinisation through transformation.

A 2.2.2 Interlayer level

In geomechanical terms the main difference between clay minerals is related to differences in interlayer space (Schmitz *et al*. 2004a). Clay mineralogists study this interlayer space in order to classify clay minerals by X-ray[7] diffraction analyses[8]. The appropriate way to introduce clay mineralogy to geomechanics is to analyse changes in EBS[9] (equivalent basal spacing introduced by the author: Schmitz *et al*. 2002b, 2003a and 2004a).

A 2.2.3 Particle level

Long-term tests have shown that the following processes take place (Prinz 1997): Dissolution of calcite, reduction of the swelling capacity of Smectites, decrease of plasticity and increase of size of clay particles due to aggregation. Chemicals can dissolve cementing agents between clay particles. As a result clay particles become free and the colloidal behaviour is changed (Komodromos and Göttner 1988).

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[6] *The analyses of interactions between clays and fluids and clay and chemicals contained in fluids on the three levels was first proposed in Schmitz (et al 2003d), extended in Schmitz (et al 2003e) and developed to the final form in Schmitz (et al 2004b).*

[7] *These rays were called X when they were discovered in 1895 in attendance of further analysis of their true nature. After their nature had been analysed, their temporary name was retained in Anglo-Saxon countries. In continental Europe they were called Röntgen rays after their discoverer W.C. Röntgen (Allmann 2003).*

[8] *The X-ray diffraction analysis started in 1912 when Friedrich, Knipping and von Laue discovered diffraction of X-rays on crystals (Allmann 2003).*

[9] *This variable will be defined in chapter C5.*

The following interactions between the particles are generally analysed as a function of fluid composition:
- The thickness of the double layer.
- The type and size of elementary particles.
- The inter-particle forces (di Maio and Fenelli 1994), including cementation.

Table: A2-1

The three different levels on which a nano-engineering geological analysis should be based.

	Level		
	TOT/TO	Interlayer	Particle
Time needed for alteration in nature	Several years to centuries	Diffusion (laboratory sample) months	Flow (laboratory sample) weeks
Scale	Ångströms[10]	Nanometers	Micrometers
Degree of modification of geomechanical properties	Large	Smaller	Smallest

A 3 Physical models and physico-chemical processes that explain the reactivity of clays exposed to leachates

A 3.1 Particle level

A 3.1.1 Bonds between particles

In geomaterials individual particles are linked to each other by:
- Cementation: calcite, silica and oxides. These cements are more or less stable at ambient pressure, temperature and/or pore fluid chemistry.
- Interlocking of particles, which occurs in metamorphosed or otherwise compressed clayey soils.
- Electrostatic forces: These forces depend strongly on the pore fluid chemistry and the charge at the particle surfaces.

Changes in these properties modify geomechanical properties like the shear strength, compressibility and liquid limit. Changes in hydraulic conductivity also depend on cementation (removal or formation during leaching), electrostatic forces (increasing or

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[10] *The unit Ångström, named after Anders Jöns Ångström, a Swedish Astronomer and physician (1814-1874) (WP 1977), is the only non-SI unit used throughout this thesis because even in 2004 all mineral literature pertains to this unit. Note that* $1Å = 1\cdot10^{-10}m = 0.1$ *nanometer.*

decreasing the flow channel diameter), and additionally on processes like erosion in flow channels and pore clogging.

Especially in clays the electrostatic forces between the particles determine the geomechanical behaviour. This aspect will be discussed in this chapter.

A 3.1.2 What is a double layer[11]?

Clay particles are negatively charged[12]. As a consequence of the negative charge at the surface of clay particles, electrostatic forces exist between the negative surface and exchangeable cations (see **Figure: A3-1**). The strength of these forces is a function of the charge, the position of the charge and the valence of the exchangeable cations (Hasenpatt 1988). If clay particles come into contact with fluid, an ionic counter charge (gegenions or counter-ions) accumulates at the surface of this particle in order to preserve electrical neutrality. The concentration of the cations decreases further from the surface of the clay minerals. This produces an electrostatic surface property known as the electrical or diffuse double layer of the clay particle. The nature and properties of such layers are highly dependent on the type of mineral and the chemistry of the pore water (Moore 1991).

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[11] *An overview of the double layer theory is given by van Olphen (1963) and Mitchell (1993).*

[12] *The negative charge of the clay minerals is caused by:*

- *diadochy or isomorphous substitution of the central cations by suitable cations with the same radius but differently charged. This results in a negative charge of the clay particle. In trioctahedral clay minerals Si^{4+} is often exchanged by Al^{3+} in the tetrahedral layer; Al^{3+} is often exchanged by Mg^{2+} or Fe^{2+} in the octahedral layer (PC Dohrmann)*
- *incomplete occupation of the positions available for metal ions (Lagaly and Köster 1993)*
- *release of protons from hydroxides (Lagaly and Köster 1993)*

About isomorphic substitution:

If in a mineral the kind of atoms changes but the atoms' arrangement remains the same e.g. M^{3+} replaces M^{4+} in T sheet and M^{2+} replaces a M^{3+} in O sheet in Smectites, this is called isomorphous substitution. Once the mineral has been formed the chemical constituents do not change until the mineral is weathered. Why isomorphous substitution occurs in the Smectite clay and not in the Kaolinite and why the Smectites are TOT clay minerals rather than TO clay minerals is still a matter of speculation. However, one explanation is that Smectites form under conditions in which twice as much Si^{4+} as Al^{3+} is present. Additionally other cations are present in large amounts. Kaolinites, on the other hand, form in soils in which the ratio of Si^{4+} to Al^{3+} is closer to 1:1, and fewer other cations are available to substitute in the clay structure or to balance the changes that would result from substituted ions (Singer and Munns 1996).

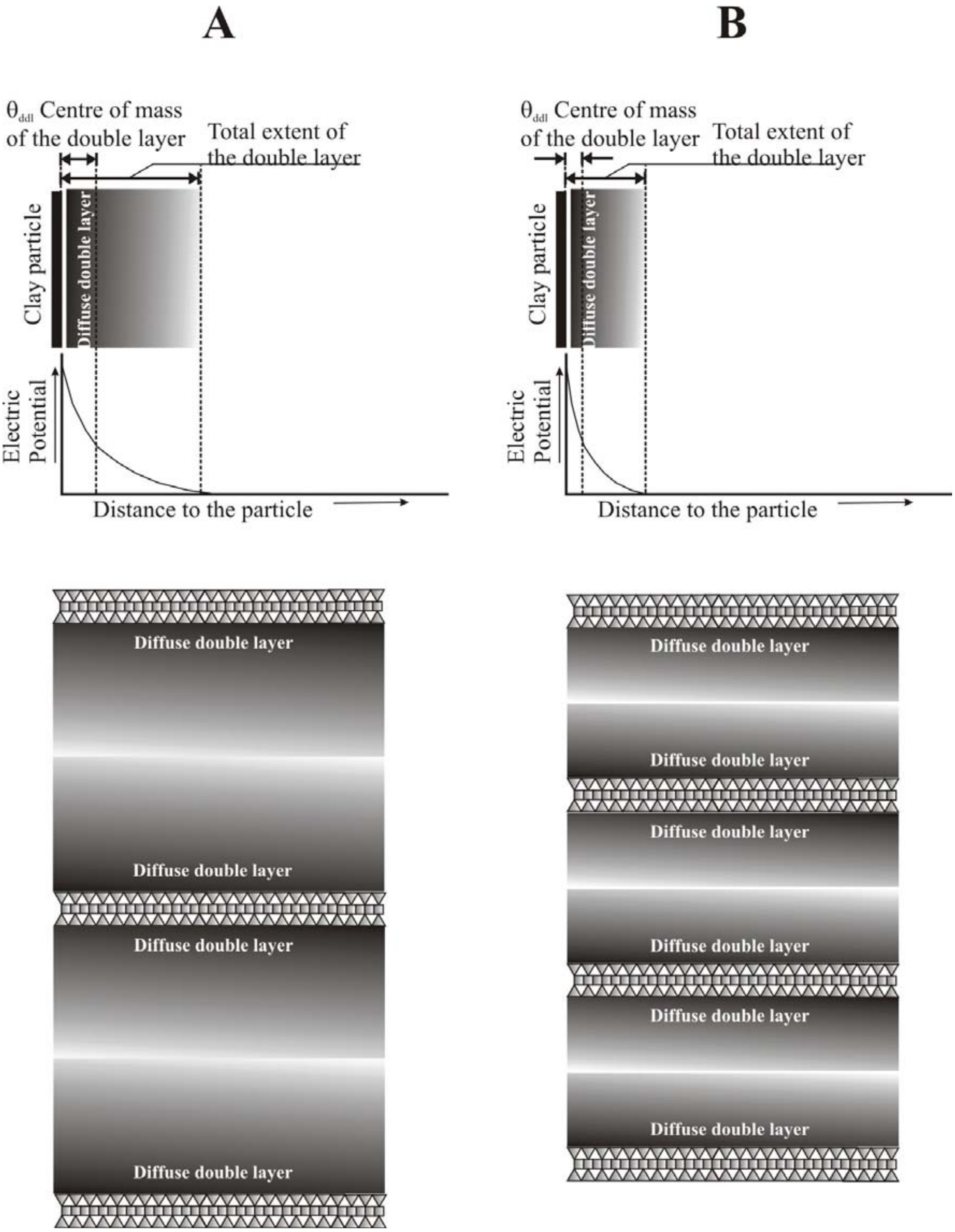

Figure: A3-1

A: Situation with a low concentration of gegenions. B: Situation with more gegenions. If the concentration of cations increases, the negative potential of the clay extents less far (the thickness of the double layer decreases) and the clay particles can approach each other. Explanation of the symbols is provided in ***Figure: A3-4****.*

A 3.1.3 Influence of double layer on engineering properties of clay

It is well-known that double layers influence clays in suspension. About the influence of double layers on the compacted clay or clay subjected to external stress one has not reached any consensus, as is shown by the following examples. The hypothesis relating double layer effects to dense clayey soils have been classed in three different groups.

A 3.1.3.1 Group I: The double layer influences the geomechanical properties of a compacted clay

Diffuse double layers bound to each clay mineral cause assemblages of clays to exhibit plasticity, cohesion and swelling. A second consequence of the presence of these double layers is a reduction of the frictional properties of the clay through the separation of mineral and particle contacts by double layers or through swelling (Moore 1991). All processes that change the electric properties of the double layer can change the macroscopic structure and the physical properties of clays (Wienberg 1990). Thus also the hydraulic conductivity is supposed to change if the thickness of double layer changes. Changes in hydraulic conductivity form an interesting source of examples. These have been grouped into 4 explanation types depending on specific assumptions that were made (see **Figure: A3-2**):

Explanation type 1 - Boundary conditions held unconsciously:

- No external stresses.
- Changes in double layer thickness change only the pore volume available for flow.

Example 1(Prinz 1997): If the thickness of the diffuse double layer (ddl) is decreased, the effective pore space and the space available for advective transport is increased (in the case of liquid hydrocarbons in dense soils).

Example 2 (Fernandez and Quigley 1985): “The double layer theory predicts a decrease (if the specified compacted natural clay is permeated by ethanol and benzene) in double layer size and by inference (Note: Would be nice to know what they had in mind) … an increase in ... hydraulic conductivity”.

This explanation can be summarised as follows:
< ddl (> effective pore space) > K_{hc}
From the point of view of the authors there is no reason for irreversibility thus:
> ddl (< effective pore space: Either by swelling or by individual (peptisation, deflocculation) clay particles filling up the pore space) < K_{hc}

Explanation type 2 - Boundary conditions held unconsciously:

- No external stresses.
- Changes in double layer thickness change the erodability of clay layers which can lead to pore clogging.

Example 1 (Van Olphen 1963): “.. when salt water flows through..a porous rock which contains a certain amount of clay..the clays is in a flocculated condition … hence the permeability… will not be greatly affected by the presence of clays.. When fresh water

flows through..a porous rock which contains a certain amount of clay..the clays will be in a peptised[13] condition. The individual peptised particles will be entrained by the fluid and will be deposited as microscopic filter cakes on narrow pore openings. Such filter cakes will reduce the permeability of the rock considerably."
Example 2: The first part: < concentration of cations > ddl (deflocculation) > erosion, has been experimentally observed by Quirk and Schofield (1955) but they did not interpret the erosion as a prove of clay transport that could lead to pore clogging but as a reduction in space available for flow as in explanation type 1.

This explanation can be summarised as follows:
>ddl > peptised condition > erosion > pore clogging < K_{hc}
This process is largely irreversible:
< ddl → no effect

Explanation type 3 - Boundary conditions:

- No external stresses or external stresses which are too small to prevent particle increase or rearrangement.
- Changes in double layer thickness cause an increase in particle size (N_{int} reduces, N_{layers} increases) with no loose particles in suspension (flocculation) or decrease with loose particles in suspension (peptised).

Example 1: If the clay is mixed with the fluid before consolidation (*BOAC*[14] concept; chapter **C 6.4** or Schmitz *et al*. 2004b) the particle size can increase (aggregation, flocculation) or decrease (peptisation, dispersion) in this slurry and these properties are retained in the consolidated sample obtained from this slurry.
Example 2 (Wienberg 1990):
< ddl → collapse ddl → flocculation, aggregation > larger particles (more silt-than clay-like) > K_{hc}
This process can be, depending on the clay type, reversible:
> ddl → increase ddl → peptisation, dispersion (more clay- than silt-like) < K_{hc}

Example 3: Another example of the third type can be found by reinterpretation of the data by Mesri and Olson (1971).
> EBS < particles < diameter flow channels (cubic law) < K_{hc}

The explanation type 3 is very popular especially when working with slurries or muds or for educational purposes because the effects are rather dramatic (but as will be shown

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[13] *Flocculated, coagulated, aggregated, peptised and dispersed are terms often used but seldom defined. Attempts to define these terms are given by van Olphen (1963) and Mitchell (1993). In this thesis the terms are defined as follows:*

- *Peptised = dispersed = deflocculated; clay particles occur individually. Clay particles are well separated from each other by electrostatic repulsion. The double layers are thick.*
- *Flocculated = coagulated = aggregated; occurs when the double layer diminishes; clay particles are not hindered to approach each other by electrostatic repulsion. These terms indicate a destruction of the double layer.*

[14] *First published in Schmitz et al 2004b.*

not representative of the natural clayey soils an engineer will encounter under normal circumstances). If one is working with soils in geomechanical terms the soils are denser and the external stresses are higher, the rearrangement of particles is largely inhibited or (Terzaghi *et al* 1996) ".. in the range of void ratio encountered the clay particles did not have sufficient space and freedom to reorganise into larger units..". There is apparently an upper bound of exterior stress that leads to a reduction of relative particle movement driven by *e.g.* a change in double layer thickness. This observation leads automatically to explanation type 4.

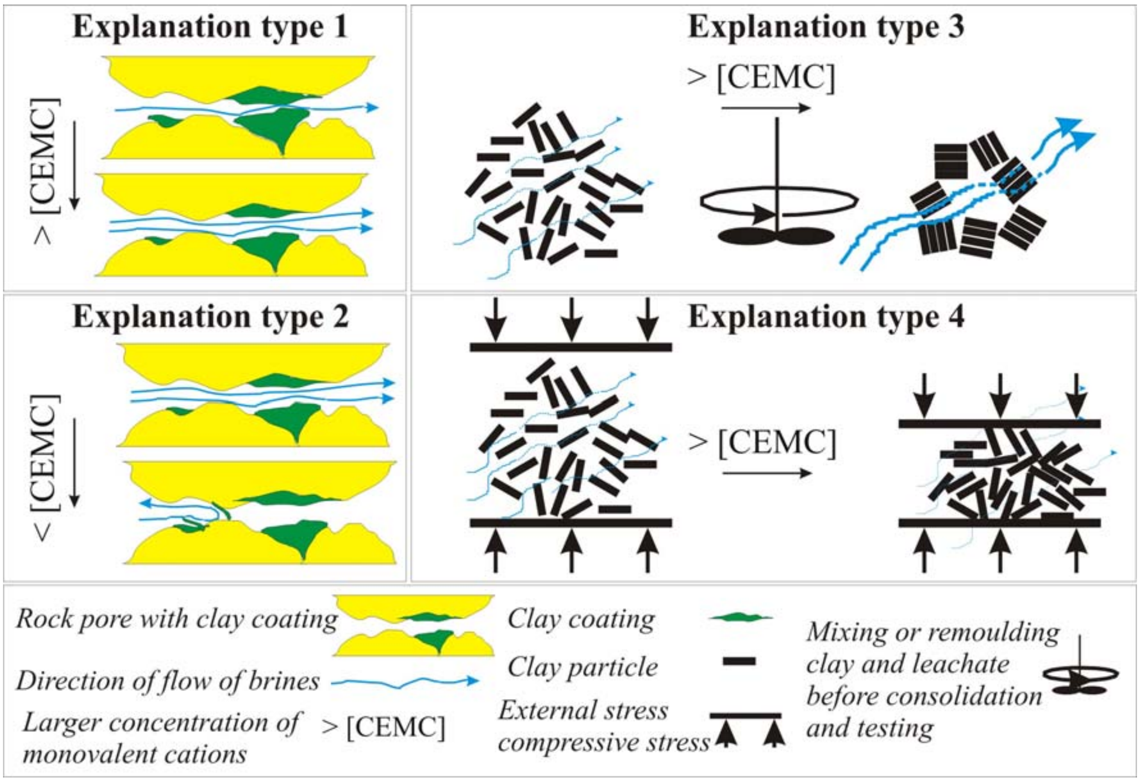

Figure: A3-2

The effect of certain fluids (e.g. brines) on the geomechanical properties of clays can be attributed to changes in double layer thickness, depending on the boundary conditions chosen.

Explanation type 4 - Boundary condition:

- External stresses are taken into account (interlayer accessibility may be reduced).
- If the diffuse double layer thickness decreases the particles will approach each other if driven by the external stresses. The medium densifies and the hydraulic conductivity decreases.

Example: See chapter **C 6** & **C 7**.
$<$ ddl $<$ diameter flow path $<$ K_{hc}
This process is largely reversible (if interlayers are not accessible):
$>$ ddl $>$ diameter flow path $>$ K_{hc}

Summary:

A summary of the hypothesis and theories presented in group 1 shows that the only thing the cited authors have in common is that they suppose that there is an influence of the double layer on the geomechanical properties of clays, even in (more or less) compacted samples. The different explanations show that the authors have unconsciously held ideas about the boundary conditions and the clay particle orientation. If these boundary conditions and the clay particle orientation are mentioned some seemingly contradictory results can be interpreted correctly.

A 3.1.3.2 Group II: The double layer does not influence the geomechanical properties of compacted clay

The unbalanced electrical forces are significant to the weight of a molecule but not with respect to a soil particle. Therefore it might be supposed that surface forces could have a significant influence on the behaviour of clay soils. At low stresses this is indeed the case and many clays behave as colloids in these circumstances. But in most geomechanical applications the surface forces between clay particles are generally not important (Powrie 1997). Contrary to Moore (1991) Powrie states that the macroscopic cohesion is not a consequence of the diffuse double layer[15].

A 3.1.3.3 Group III: The double layer partly influences the geomechanical properties of compacted clay

Bloomer and Coupe (1994) observed that the behaviour of clay soils does not only depend on the long range electrical forces but also on the shear resistance at or near the contact points within the soil mass and the elastic bending of the clay plates. Guimaraes (*et al.* 2001) reported in a literature review that in the case of highly compacted clays (as used in radioactive waste repositories) the effect of the diffuse double layer is limited because the particles are compacted too close together for the double layer to form correctly. Further these authors state that nevertheless the limitations of the diffuse double layer theory, it will provide an useful reference. This was recognised by Mitchell (1993): ".. there remains considerable uncertainty about how well the classical (Note: Gouy-Chapman) double layer theory represents the actual system, nonetheless … the influence of pore fluid composition on structure and swelling properties that are deduced from it are generally valid".

Why the author favoured the last standpoint of the third group: The double layer theory can be useful to explain some phenomena related to clay behaviour in the presence of percolating fluids with a diverse chemical composition, even in geomechanical engineering (see **Figure: A3-3**) is discussed in the remainder of **part A** and in **part C**.

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[15] *Moore (1991) states that: "...diffuse double layers bonded to each clay mineral cause assemblages of clays to exhibit... cohesion... ". Thereby the macroscopic cohesion is linked to the presence of double layers. It is apparent that there is no consensus because even in the same article Moore (1991) states that: "...when double layers develop...(there is a)...reduction in cohesion...".*

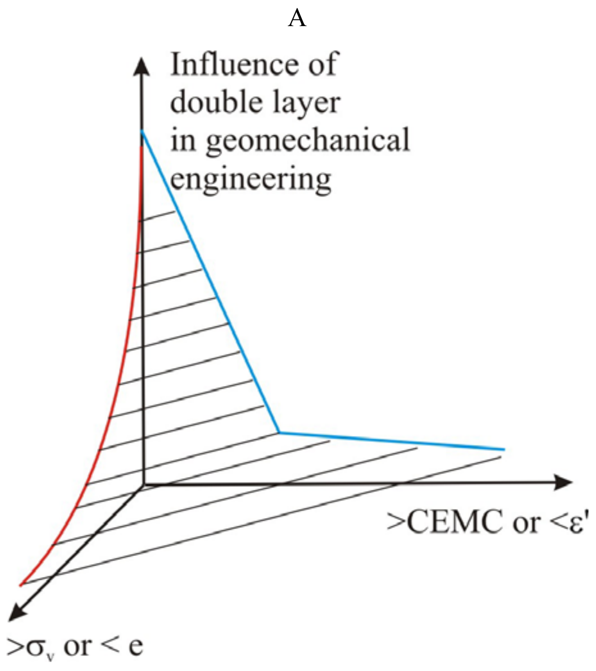

Figure: A3-3.

The double layer theory can explain processes related to variation of the concentrations of cations in the percolating fluid but the double layer effects decrease with: the density of the clay (<e) (literature) ; increasing exterior compressive stress perpendicular to the double layers (>σ_v*) ; increasing concentration of cations (>CEMC) in the percolating fluid ; decreasing relative dielectric constant of the percolating fluid.*

A 3.1.4 How thick is this double layer?[16]

A 3.1.4.1 Influence of the concentration of cations

What is commonly called the thickness of the double layer corresponds in fact to the distance from the centre of mass of the double layer to the clay particle surface. According to the classical diffuse double layer theory (Gouy-Chapman model), the thickness of the double layer decreases as the salt concentration in the bulk solution increases (see **Figure: A3-1**). The thickness of the double layer decreases also with increasing gegenion charge; thus the thickness of the double layer of Ca-Montmorillonite is smaller than that of Na-Montmorillonite (di Maio 1996). The increase of the salt concentration in solution decreases the net likelihood of cations to diffuse outwards from the clay surface, thereby the double layer is compressed.

A 3.1.4.2 Not only the cation concentration counts

Influence of the valence of the cations:

Compression of the diffuse layer will require little salinity if the predominant cations are held tightly (Mg^{2+}, Ca^{2+}, Al^{3+}) but it will require high salinity if the predominant

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[16] *The author suggests the inquisitive reader who is interested in colloid chemistry to consult the standard work dealing with the double layer theory by van Olphen (1963): "An Introduction to Clay Colloid Chemistry".*

cations are held loosely (Na^+, K^+, NH_4^+) (Singer and Munns 1996). Note that Smectites prefer 1 gegenion (counter ion) layer above two repulsive layers (Lagaly 1993). If enough Ca^{2+} cations are present to counter the negative charge of the particle no diffuse double layer is formed. This effect can be used to stabilise dispersed (Note: Individual particles with thick double layers) soils: If Ca^{2+} (*e.g.* in the form of CaO) is added, the double layers are destroyed, the attraction between clay particles outweighs (the repulsion) (Müller-Vonmoos and Kohler 1993).

Influence of the radius of the hydrated ions:
The Gouy-Chapman model cannot be used to explain the differences in double layer thickness in the presence of Na^+ or K^+ cations because this model considers ions as point charges. The Stern model takes this into account: The thickness of the diffuse double layer also decreases with decreasing hydrated ion radius. Since the radius of hydrated K^+ cations is smaller than that one of hydrated Na^+ cations, the thickness of the double layer of a K-Montmorillonite is also smaller than that one of Na-Montmorillonite.

To summarise the statements made above, the double layer is smaller if the fluid in contact with the clay:
- Has a smaller relative dielectric constant.
- Has a larger cation concentration.
- Contains cations with a larger valence (Hasenpatt 1988).
- Contains cations with a smaller hydrated ion radius (di Maio 1996).

A 3.1.4.3 Example calculation of the diffuse double layer

Example by van Olphen (1963: Gouy-Chapman double layer model):

The double layer thickness is given by:

$$\theta_{ddl} = \sqrt{\frac{R \cdot T \cdot \varepsilon_0 \cdot \varepsilon'}{2 \cdot F^2 \cdot C \cdot val^2}} \qquad \textbf{(A3 - 1)}$$

In which:

R = Gas constant (J/mol/K)
T = Temperature (K)
ε_0 = Permittivity of vacuum (F/m)
ε' = Relative permittivity (-)
F = Faraday's constant (C/mol)
C = Concentration of cations (mol/m^3)
val = Valence cations (-)

If clay particles are in contact with a 0.001M NaCl solution in water (ε_m=80) the thickness of the double layer is:

$$\theta_{ddl} = \sqrt{\frac{8.3145 \cdot 298 \cdot 8.85419E-12 \cdot 80}{2 \cdot (9.64853E4)^2 \cdot 1 \cdot 1^2}} = 1 \cdot 10^{-9}\, m = 100\, Å \qquad \textbf{(A3 - 2)}$$

A 3.1.4.4 Special case: thin double layers

Repulsion and separation arise from the tendency of the:
- Cations to hydrate, drawing water in between the colloid particles.
- Double layer repulsion.

If the diffuse layers remain compressed and dehydrated, short-range forces (hydrogen bonds, Coulomb forces, interlayer cation attraction) can keep colloid particles together and stable soil structures remain possible. These short ranged attractive forces are largely independent of pore fluid chemistry (Wienberg 1990). But if the salt concentration in a sodic soil is lowered, the diffuse layer hydration and repulsion push the colloid particle apart (Singer and Munns 1996). These short ranged forces are:
1) Van der Waals forces which are based on the attraction between the electron cloud of an atom and the core of another atom. The van der Waals forces decrease with increasing distance (of molecules) (Hasenpatt 1988). Particles stick together (Müller-Vonmoos and Kohler 1993) or cohere because of van der Waals forces (Singer and Munns 1996). The shear strength in undisturbed clay is a function of attracted van der Waals forces between the adsorbed cations of one mineral and the ions of adjacent minerals (Moum and Rosenqvist 1961). Just a little separation weakens the cohesion. This separation can be the result of the presence of repulsive forces.
2) Coulomb forces, between *e.g.* positively charged clay particle edges and negatively charged faces.
3) Hydrogen bonds.
4) Interlayer cations.
The latter are associated with the interlayer level and come into action when the particle-particle spacing becomes an interlayer within the new larger particle.

A 3.2 Interlayer level

A 3.2.1 Clay species and interlayer reactivity

In the previous paragraph it was discussed how the double layer theory is used to describe the processes between clay particles. In this paragraph the focus will be on processes within clay particles, more precisely on processes between the TOT- or TO-layers of clay minerals. Between these layers there is space for physico-chemical reactions to occur. This is called the interlayer (see **Figure: A3-4**).

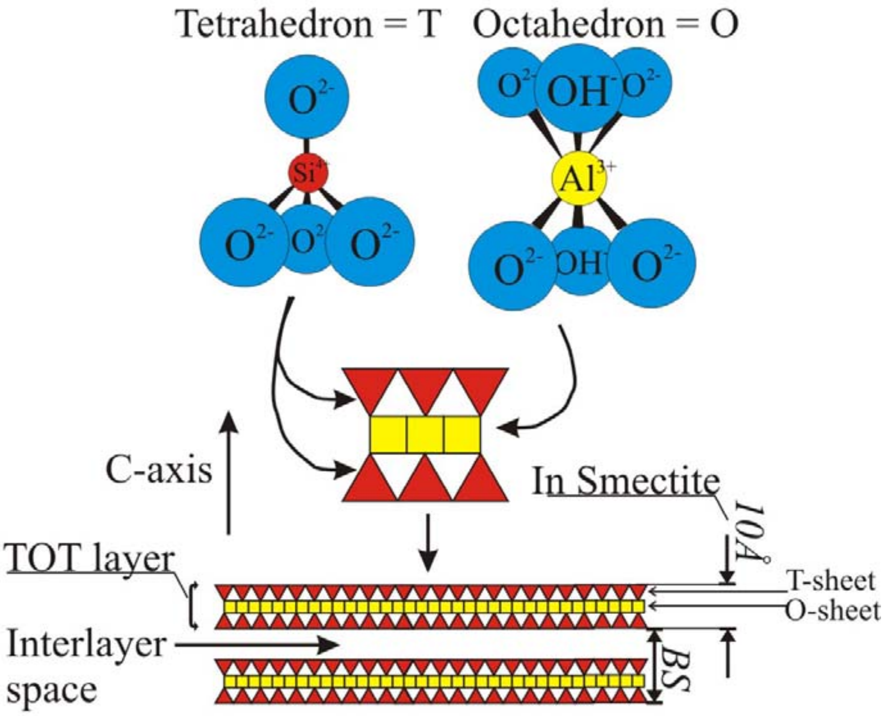

Figure: A3-4

Definition of the interlayer space. BS = Basal spacing.

In contrast to changes in double layer thickness, changes within the interlayer space are not always reversible.

The main difference between clay minerals in terms of geomechanical properties is related to the difference in interlayer space whatever its origin is. Fortunately clay mineralogists are as well interested in this interlayer space to identify and classify clay minerals. Clay mineralogists have a tool to measure this interlayer space: XRD analysis. Thus, information about the interlayers of clay minerals can be accessed using clay mineralogy. Clay mineralogy is largely based on the determination of interlayer distances. The appropriate way to introduce clay mineralogy to geomechanics (with the equivalent basal spacing) will be solved in **Part: C**.

A 3.2.2 Interlayer accessibility part I

The surface of clay particles (the space between clay particles) (see **Figure: A3-8** or **Figure: A3-5**) interacts more frequently with charged substances than the interlayer space itself. In some clay types the interlayer space is hardly accessible (Kaolinite) in contrast to others (*e.g.* Smectite). But if the interlayers are accessible cations can enter them only with some difficulty. Note *e.g.* van Olphen (1963): “Interlayer swelling is not affected by the presence of salt unless the salt concentration is very high, *i.e.* of the order of 1N (Note: 1mol/l Na^+ cations for *e.g.* NaCl) and above”. For the same clay, the accessibility of the interlayer space depends on the boundary conditions as shown in the following example when ethylene glycol (EG) intervenes:

Ethylene glycol (EG) is used in X-ray diffraction analyses (XRD) to identify in particular Smectites *sensu lato*. If interlayers are accessible (as in Smectites in suspension) EG is adsorbed in two layers in the interlayers. This causes an increase of the basal spacing (BS) from 14 Å to 17 Å. Because the equivalent basal spacing (EBS) increases by this adsorption (see chapter **C 5**) the liquid limit (LL) will increase as well. Tests in the Liège laboratories have shown that the liquid limit increases in this case to such an extent that the particles do not interact anymore with each other and a liquid limit determination is not possible anymore.
In contrast however, if EG is leached through compacted clay, the hydraulic conductivity is reduced slightly and the sample consolidates slightly. This phenomenon can be explained (explanation type IV, see **Figure: A3-2**) qualitatively and quantitatively by a decrease of the diffuse double layer thickness acting in the interparticle space (between different clay particles). This behaviour is not different from permeations with other alcohols and can be related to the value of the relative dielectric constant of EG which is smaller than that of the original fluid contained in the clay. Instead of generating a swelling of the sample the sample consolidated thus during permeation of a sample under an exterior compressive stress, EG was not able to enter the interlayer space.

Interlayer reactivity or accessibility or availability can be found in literature (although it has never been attributed to this) when it is stated that expected damage (of soils by landfill leachates) can be represented as follows (starting with the mineral that is most likely damaged):

- Smectite (Na, K) > Smectite (Ca) > Illite > Kaolinite > quartz (Entenmann 1998).
- Smectite > hydrous mica (Illite) > Kaolinite (Mitchell 1993).

Note that these series follow the same order given for the basal spacing (*e.g.* Mitchell 1993) of the different minerals: Smectite: 14 Å, Illite: 10 Å, Kaolinite: 7 Å, quartz: 3 Å (characteristic line).

In paragraph **C 6.4** the interlayer accessibility discussion will continue.

A 3.2.3 Processes on interlayer level:

Now it will be discussed what kind of processes can occur in the interlayer space.

Not all imaginable clay alteration processes occur in nature or under geomechanical engineering conditions because the reactivity of the interlayer space depends on the type of clay present. In Kaolinites (TO-layer minerals) the interlayer reactivity is limited to intercalation[17] and to the exchange of host molecules. In Smectite and Illite (TOT-layer clay minerals) the interlayer reactivity includes *e.g.*:
- Exchange of interlayer cations by organic or inorganic cations.
- Absorption from organic substances in-between the layers (Lagaly and Köster 1993).

Some transformation processes induced in the laboratory on the interlayer level have been listed in **Table: A3-1**.

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[17] *Intercalation involves the entry of organic molecules between silicate layers and is particularly important if dealing with Kaolinite minerals (Mitchell 1993).*

Table: A3-1

This table presents an overview of modifications on the interlayer level as these can be obtained in the laboratory. The initial material was a Belgian Pleistocene natural clay containing: (I), (10-14m), Illite-Vermiculite mixed-layers, V, Kaolinite, Chlorite-Vermiculite mixed-layers, Intergrade Smectite-Vermiculite. After Thorez (1983) modified.

What happens to the interlayer space?	Chemical treatment provoking the change:
Extraction of interlayered material	NaOH (boiling) (1); Na_2CO_3 (boiling) (1); Na-citrate
Destruction of mixed-layers	NaOH (boiling) (4); Na-citrate; Na_2CO_3 (boiling) (4); Na_2CO_3 + dithionite + citrate; oxalic acid (5); dithionite + citrate (4)
Smectitisation	KOH; NaOH (boiling); Na-dithionite (7); Na_2CO_3 (boiling); Na-citrate (3); Na_2CO_3 + dithionite; Na_2CO_3 + dithionite + citrate; H_2O + HCl + NaBrO; H_2O (3); dithionite + citrate (8); calgone + dithionite
Vermiculitisation	KOH (8); NaOH; NaOH (boiling); Na_2CO_3 (boiling); Na-citrate (3); Na-oxalate; Na-dithionite (6); Na-EDTA; Na_2CO_3 + dithionite; Na_2CO_3 + dithionite + citrate; H_2O (3); H_2O + HCl + NaBrO (2); oxalic acid; dithionite + citrate
Chloritisation	H_2O; dithionite + citrate (9)
Destruction of Chlorite	oxalic acid; dithionite + citrate
Opening of some interlayers	HCl (boiling)
Important weathering of clay minerals	H_2O + HCl + NaBrO
Exfoliation of mica (potential source of Illite)	H_2O + HCl + NaBrO

(1) from intact or degraded clay minerals; (2) of slightly weathered micas;(3) of Chlorite; (4) destruction of labile or fragile mixed-layer material; (5) destruction of some mixed-layers; (6) Vermiculitisation of Biotite; (7) partial Smectitisation; (8)Vermiculitisation of Chlorite and/or micas; (9) increasing secondary Chloritisation

The possible transformation processes that can take place in open systems *in situ* (geomechanical engineering conditions), at low pressure and low temperature and short time spans (engineering time scale, not geological time scale) are given in **Table: A3-2**.

Table: A3-2

Clay mineral alteration processes that can take place in open systems under geomechanical engineering conditions (PC Thorez)

If the amount of (10-14m) decreased, what was produced?:	Irreversibility of the clay alteration process:	Name of clay alteration process:
(10-14m) + K^+ ↔ "I"	partly reversible	Illitisation/Smectitisation
(10-14m) + Al hydroxides → Sm$_{Al}$	irreversible	Chloritisation
(10-14m) + organic matter → 14(500) = Sm$_{org}$	potentially reversible if acids are added	Chloritisation
Sources of (10-14m):		
(10-14m)$_{\text{, inherited}}$ → (10-14m)	inherited	
"I" ↔ (10-14m) + K^+	partly reversible	Smectitisation/Illitisation
14(500)[Sm$_{org.}$] + acid ↔ (10-14m)	reversible	Smectitisation
If the amount of mixed-layers I decreased, what was produced?		
"I" ↔ (10-14m) + K^+	reversible	Smectitisation
"I"+ Al-hydroxides → (10-14c)	irreversible	Secondary Chloritisation
Sources of I?		
I → I	inherited	
(10-14m) + K^+ ↔ "I"	partly reversible	Illitisation
Sm$_{org.}$ + acid → "I"	irreversible	Illitisation
If the amount of 14(500), either Sm$_{Al}$ or Sm$_{org.}$ decreased, what was produced?:		
Sm$_{Al}$ = stable		
Sm$_{org.}$ + acid ↔ (10-14m)	reversible	Smectitisation
Sm$_{org.}$ + acid → "I"	irreversible	Illitisation
Sources of 14(500):		
14(500) ↔ 14(500)	inherited	
(10-14m) + Al hydroxides → Sm$_{Al}$	irreversible	Chloritisation
(10-14m) + organic matter → Sm$_{org.}$	potentially reversible if acids are added	Chloritisation
If the amount of Kao decreased, what was produced?:		
Kao = stable		
Sources of Kao:		
K$_{inherited}$ → Kao	inherited	Kaolinisation
feldspar → Kao	irreversible	Kaolinisation
Chlo + acid → Kao	irreversible	Kaolinisation
If the amount of mixed-layers (10-14c) decreased, what was produced?		
(10-14c) is stable		
Sources of (10-14c)?		
(10-14m) + Al-hydroxides → (10-14c)	irreversible	Secondary Chloritisation
If the amount of Chlo is decreased, what was produced?		
Chlo is stable		
Sources of Chlo?		
Chlo + acid → Kao	irreversible	Kaolinisation

One of the processes listed in **Table: A3-2** that provokes a major shift in clay mineral and geomechanical properties is the Illitisation of a Smectite. This transformation causes (see **Figure: A3-5**) a decrease in the number of interlayers, thus a smaller activity towards fluids in general, thus a decrease of the swelling potential, and thus an increase of the liquid limit *etc.* These processes will be explained in more detail in **Part: C**.

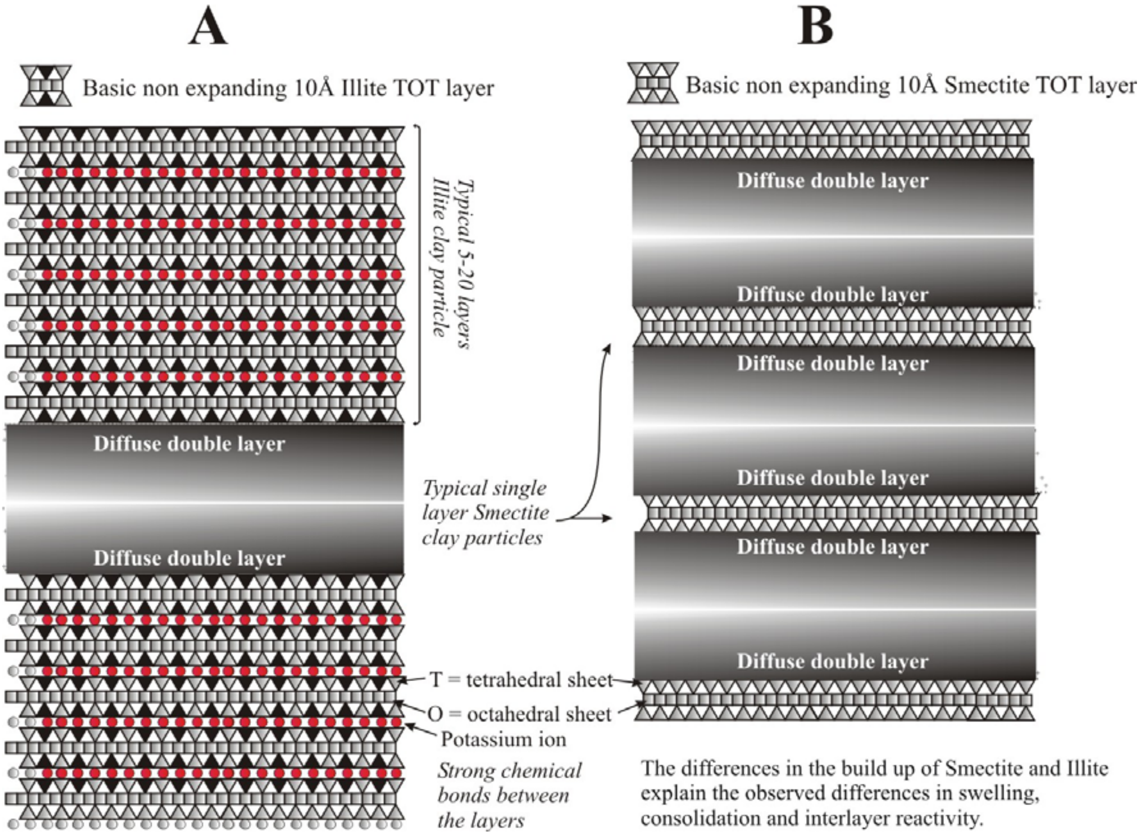

Figure: A3-5.

This example shows why the interlayer is an important factor changing mineralogical and geomechanical properties of clays. In A, a clay mineral is shown in which the interlayers are stuck together by suitable interlayer cations (large N_{layers}, small N_{int}). Diffuse double layers are only formed between the two large particles. The relative reactive "surface" is small. This situation is representative of an Illite. In B, a clay mineral is shown in which diffuse double layers separate the individual TOT-layers from each other (small N_{layers}, large N_{int}). The particles are small and the relative reactivity "surface" versus fluids is large. This clay mineral is representative of a Smectite.

In **Figure: A3-5** it was shown that there is a large difference between the build-up of Illite and Smectite clay minerals. The special properties of these two minerals are therefore discussed in the next paragraph.

A 3.2.4 Differences on interlayer level: Illite and Smectite

- Illite

Illite contains K^+ cations in the interlayers like mica. The interlayer K^+ cations contribute to the stability and non-expanding nature of Illite (Singer and Munns 1996). Illite like Montmorillonite has a TOT-structure but in contrast to Montmorillonite the TOT-layers in Illite are highly charged. The charge is concentrated in the T-sheet (due to isomorphous substitution of Si^{4+} for Al^{3+} atoms) and is thus more effective with respect to charged particles in the fluid contained in the clay than a charge concentrated in the O-sheet. The charge is countered by K^+ ions.

K^+ ions cannot easily be removed because of their:
- Low hydration energy (they "loose" their -OH group easily).
- Ion size (fits exactly in the pseudohexagonal void).
- Position in the pseudohexagonal voids of the silicate sheet.

The electrostatic attraction of the K^+ cations is large. Therefore no water can enter the interlayer space in Illites. Only at the crystal surface and at the edges of the layers hydrated and exchangeable ions can be found (Hasenpatt 1988).

Therefore the interlayer spacing of Illite is fixed and:
- The layer spacing of Illite is constant and equal to or near 10 Å, even upon heating or after addition of ethylene glycol (EG).
- Illite does not swell.
- The interlayer is not influenced by ions in the pore space.

- Smectite

In contrast to Illites, the negative charge at the surface of Smectite TOT-layers is not very effective because it is located in the O-sheet and is shielded on both sides by T-layers (Hasenpatt 1988). Therefore the surface charge density is low, and the (electrostatic) bond between the different layers is weak and cations located in the interlayer spaces can hydrate. As a result of the hydration capacity of the cations in the interlayer spaces, water invades these interlayers, resulting in layer separation and expansion (Mitchell 1993). The basal spacing of the layers ranges from 12 - 18 Å and is variable with:
- The exchangeable cation species and the degree of interlayer solvation (complete drying at 500°C yields a basal spacing of 9.7 - 10 Å).
- The presence of positive Al-hydroxides (called pillars, or islands) in the interlayer (*c.f.* Sm_{Al}).

- Reversibility and irreversibility of Illitisation and Smectitisation

Like the process in which the non-expandable Illite changes its properties and shows an interlayer to interparticle-void transition (N_{layers} decreases, N_{int} increases) that allows swelling, Smectite can change its properties as well and loose its reactivity by the process of Illitisation (N_{layers} increases, N_{int} decreases): If Illite is formed by the insertion of K^+ cations into a neoformed volcanogenic Smectite, this process represents a reversible[18] form of Illitisation (PC Thorez).

Expressed in terms of changes in basal spacing as these are measured by X-ray diffraction analyses this can be expressed as follows. If Illite is formed by the insertion of K^+ cations into a neoformed volcanogenic Smectite there is a measurable collapse, not to 10 Å (value of an Illite) but to 11 - 12 Å. If the EG is added there is, like in untreated Smectites, a swelling to 17 Å. The normal untreated clay has a BS = 14 Å, after treatment with EG the BS = 17 Å, after treatment with K^+ cations the BS = 11 - 12 Å and after renewed treatment with EG the BS = 17 Å.

However in degraded Illite (this is an open Illite because there is less K^+ cations in the pseudohexagonal voids), K^+ cations have been lost but the clay has a ”memory” if it encounters K^+ cations once again; it will close and will not swell if EG is added. This behaviour is measurable in the laboratory as:
The normal untreated sample has a BS = 14 Å, after treatment with EG the BS = 17 Å, after treatment with K^+ cations the BS = 10 Å and after renewed treatment with EG the BS remains at 10 Å.
If this occurs it is the proof that one is dealing with a transformed Smectite originating from a completely degraded original or primary Illite.

Di Maio's (1996) well-known and frequently cited results showed an excellent example of the interlayer reactivity of a pure Bentonite towards the addition of KCl, NaCl and $CaCl_2$ solutions: She showed that salts affect the liquid limit, shear properties and consolidation properties in a similar way, except, and this is important, that the effect provoked by *e.g.* K^+ salts are (partly) irreversible and those by Na^+ salts not, but she did not attribute this to/or call it “Illitisation”[19].
In **Figure: A3-6** it is shown how one can discern, with the help of different special tests (combined cation saturation with Li^+ and K^+) using X-ray diffractometry, between a:
- Neoformed or a transformed Smectite (important for potential irreversibility of Illitisation).
- Beidellite or a Montmorillonite.

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[18] *Illitisation by the insertion of potassium ions in the interlayer space of Montmorillonites (a Smectite in which the negative charge is predominantly located in the octahedral sheet) is partly reversible because the negative charge “holding” the potassium is located in the octahedral sheet like in Smectites and not in the tetrahedral sheet like in Illites. Therefore the potassium ions are not as tightly held as in Illites originating from the weathering of mica which lost some potassium ions or Illites originating from the insertion of potassium ions in the interlayer space of Beidellites (a Smectite in which the negative charge is predominantly located in the tetrahedral layer).*

[19] *A literature overview of Illitisation-Smectitisation is given by Lagaly (1993), pages 168-192*

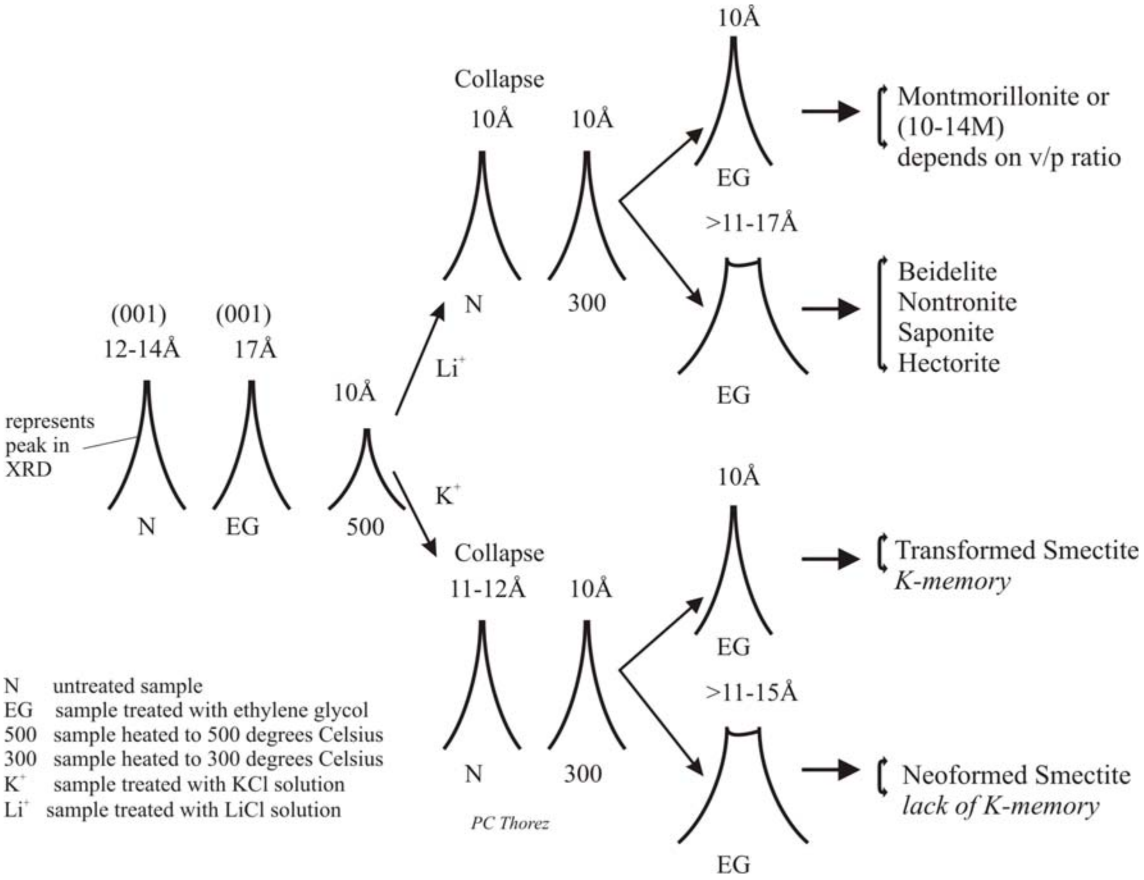

Figure: A3-6.

This figure shows how one can differentiate between the different species of the Smectite family and their origin (transformed or neoformed) during XRD analyses. This identification is important because Illitisation which plays an important geomechanical role, is irreversible in transformed but partly reversible in neoformed Smectite.

Due to weathering (loss of K^+ ions) however the behaviour of Illite can change and starts to resemble that of a Smectite (shows signs of swelling *etc.*). This transformation is called Smectitisation. Under ordinary weathering conditions any given mica interlayer tends to remain completely filled with K^+ ions or else, to become completely affected by interlayer swelling (Jackson 1964). Smectitisation of an Illite is reversible if K^+ ions are added to the interlayer.

Al-Pillars

Smectites do not only loose reactivity (N_{layers} increases, N_{int} decreases) by Illitisation. Another example that shows how the reactivity of Smectites can be reduced is the formation of Al-pillars (Al-hydroxides or islands or hydroxy layers) in the interlayer space (see **Figure: A3-7**). By the formation of these pillars in the interlayer space, the original swelling clay minerals are brought to a fixed 14 Å spacing (Brinkman 1979).

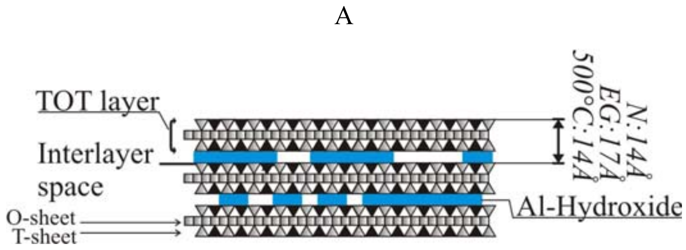

Figure: A3-7

This figure shows were one can find Al-hydroxide pillars on clays.

Upon heating the clay will not collapse to 10 Å due to the presence of the pillars which prevent total collapse. In most laboratories the Al-pillars are washed out during preparation (PC Thorez) and the interlayer activity of Smectites is overestimated if the Al-pillars remain in the interlayer space under the boundary conditions of the clay used as a barrier.

A 3.3 TOT/TO level

Changes on the TOT/TO level cause the most severe changes of the geomechanical properties of clay minerals because these changes modify the building stones of clay minerals: The tetrahedral- and octahedral-layers and thereby the interlayers and particles. Different degrees of alteration can be discerned on this level:

- Neoformation of clay minerals: This involves the new formation of *e.g.* clay minerals from individual atoms. These processes are only of concern if the initial material was the clay mineral that was subject of study (*e.g.* clay mineral in engineered barrier). An example is Kaolinite that can be neoformed from the residual matter of an initial TOT parent clay mineral.

Destruction of TO- or TOT-layers in the laboratory can be produced by:
- The addition of H^+ protons, which free aluminium from TOT-layer (Lagaly and Köster 1993); this is an example leading to the destruction of a TOT clay mineral into its individual atoms.
- The percolation of 5% acetic acid + propionic acid through natural soils containing Smectite, Kaolinite and Illite under oedometer conditions. In 300 days 0.2% of the Al atoms and 0.8% of the Si atoms were dissolved from the TOT- and TO-layers (Wienberg 1990).

- Transformation of clay minerals: During transformation, the T- and O-layers are not dissected into their atoms but entire parts of T- and O-layers are recycled, *e.g.* Kaolinite can be formed by the ripping (weathering) of a tetrahedral layer from an original TOT clay mineral.

In nature alterations on the TOT/TO level take a long time:
- Podzolisation of the original soil[20] to form a soil enriched in Kaolinite: $1 \cdot 10^3$ - $1 \cdot 10^4$ years.

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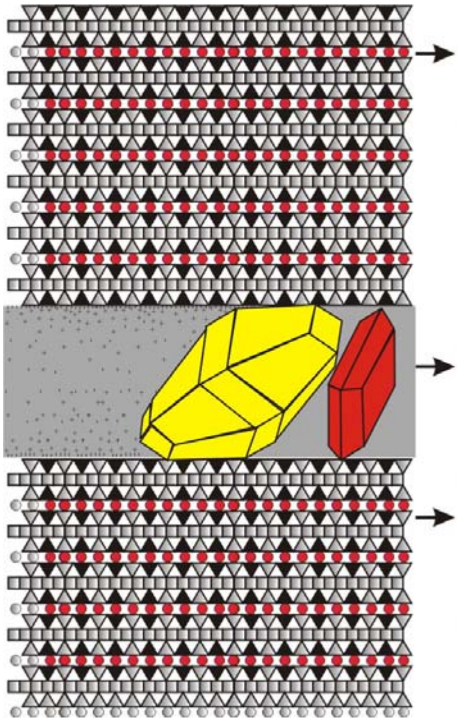
[20] *The original soil can be any clayey soil. If the parent material is more sandy or silty, Podzolisation will progress more easily (PC Thorez).*

- Illitisation from an original Smectite during shale diagenesis: $1 \cdot 10^6$ years (PC Velde). Because up to now no one has succeeded to reproduce these processes in the laboratory, it is not clear if one should talk about a long time or a long history of subsequent physico-chemical processes needed in these formation processes.

A 3.4 Application

With the differentiation of processes related to the three levels: TOT- and TO-layer levels, interlayer level and clay particle level, one can assess the influence of various fluids on the geomechanical properties of clays by analysing the various fluid-clay interaction processes at each level separately (see **Figure: A3-8**). This is called the three-level approach.



Changes in interlayer distance
modify:
- LL
and all related properties like
- C_c; ϕ'; C_v
e.g. change of Smectite into Illite

Changes in distance between particles
or particle erosion modifies:
- hydraulic conductivity
- cohesion
e.g.by dissolution of calcitic cement in
Smectitic clays

Changes in TO/TOT-layers modify:
-surface potential; cation exchange capacity
e.g. transformation of Smectite into
Kaolinite

Figure: A3-8.

The three-level model. The influence of various fluids on the geomechanical properties of clays can be studied by differentiating the effect of these fluids at the different levels of a clay material.

With the three level approach an engineering geological assessment can be made (a kind of nano-RMR). Even if the clay has not been in contact with the fluid during laboratory tests, the behaviour of the clay-leachate combination can be predicted. Examples are discussed in chapter **C 9**.

A 4 Modification of the mechanical characteristics

A 4.1 Modification of the particle size

A 4.1.1 The particle size

Each clay mineral has, driven by differences in its mineralogy, a specific particle size. This particle[21] size must not be confused with the particle size of oven-dried samples. A literature overview is given in **Table: A4-1**. Although the values given in **Table: A4-1** differ largely, Montmorillonites are the only clays with a particle thickness close to 1 TOT-layer. The given maximum thickness is fairly identical for all the three clay minerals. If only the minima are regarded, the particle size increases in the following order: Montmorillonite < Illite < Kaolinite.

Table: A4-1

Some general properties of clays on the particle level.

	Particle diameter (micrometer)	Particle thickness [number of TOT- or TO-layers]	Clay minerals can be found in the fraction (micrometer)
Kaolinite	0.1-5 [1] 0.1-4 [2] 0.5-4 [8]	25-80 [1]; 70-3000 [2]%; 3000-4000 [4]; several 100 [6]	2-63 [3] < 1.5 [1]$
Illite	0.1-5 [1] 0.1-few micrometer [2] < 0.6 [8]	5-80 [1]; >3 [2]% ; 3-10000 [4]%; 5-20 [5]; several 100 [6]; 10 [8]	< 8 [1]$
Smectite	0.03-0.3 [1] 1-2 [2] <0.2 [8]	5-12 [1]; 1 [5]; 1-20 [8]; 1-1/100 times particle diameter [2]; 1-10000 [4]% 6-7 if Ca^{2+}; 4-6 if Mg^{2+}; 2-3 if K^+; 1-2 if Na^+; 1 if Li^+[7]	<2 [3] < 1.5 [1]$

[1] Müller-Vonmoos and Kohler (1993) crystal size; [2] Powrie (1997); [3] GDA (1997); [4] Mitchell (1993) size of clay minerals, electron microscope; [5] Bolt (1956) particle size; [6] Mitchell (199: lit rev.) quasicrystal size, light scattering and neutron scattering; [7] light scattering; [8]Köster and Schwertmann (1993) Kao: phase contrast microscope, I and Sm: SEM; [8]Köster and Schwertmann (1993).

% indicates that the thickness was expressed in micrometer in the original publication

$ 90% (mass) of the oven dried (105°C) fraction

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[21] *Some authors call particles: aggregate domains, crystals or quasicrystals, in decreasing order of size. Their thickness in **Table: A4-1** is expressed in the numbers of combined TOT/TO layers. These TOT/TO layers are called platelets, sheets, layers or stacks in literature.*

A 4.1.2 Modification of the particle size

As a results of the insertion and attachment of chemicals onto a *e.g.* Smectite, stable particles can be formed (N_{layers} increases, N_{int} decreases). The grain size increases (Hasenpatt 1988). Due to this process:

- The capacity to swell will reduce.
- Shrinkage will occur.
- The hydraulic conductivity will increase.
- Atterberg limits will approach those of a silt.
- Values of the frictional shear strength of *e.g.* a Smectite will approximate to those of a fine-grained quartz, but there will be a strong decrease to the residual shear strength (Note: particle reorientation) (Hasenpatt 1988).

A 4.2 Modification of the Atterberg limits

A 4.2.1 General information about Atterberg tests

A 4.2.1.1 Why should one use Atterberg limits?

The Atterberg limits have been widely used in soil mechanics since their potential value was first indicated by Karl Terzaghi in 1926. Terzaghi wrote about this subject: "... the result of the simplified soil tests (Note: Atterberg limits) depends precisely on the same physical factors which determine the resistance and the permeability of soils (shape of particles, effective size, uniformity) only in a far more complex manner... in spite of these complications one is safe in making the following statement: If several soils with similar geologic origin have fairly identical limits, their physical properties too will be fairly identical and it will be sufficient to investigate a single one of them more thoroughly. Hence the limits represent an excellent means for preliminary soil classification... If we know the three limits (Note: Liquid limit, plastic limit and shrinkage limit) of the soil, we are already in a position to compare this soil with others and can at least anticipate what its properties may be. If we know in addition the results of physical tests performed on another soil with fairly identical limits, we can say the soil is known." (Terzaghi 1926 used the extract selected by Seed *et al*. 1964).

A 4.2.1.2 Atterberg tests, remoulded tests

"Since the liquid and plastic limit tests can be performed only after the natural structure of the clay is destroyed by remoulding (like during the XRD tests), they are incapable of reflecting any mechanical properties of the clay in undisturbed state" (Casagrande 1932). Thus it was recognised that the Atterberg limits provided a means of identifying the nature of the constituent particles of a soil and not properties related to the arrangement of particles. Additionally the liquid limit can be used for the genetic distinction, the identification of layers and for estimating the expected values of the physical characteristics (Rétháti 1988). Following this thesis from Part: **A** to Part: **C** the real nature of the liquid limit will be revealed step by step.

A 4.2.1.3 History of the Atterberg limits

1911: Paper by A. Atterberg.
1922: Swedish railway engineers experimented with a cone located just above the soil

surface which when released freely penetrated the soil and the depth of penetration was observed. Their experimental procedure is the basis of the current cone penetrometer test (Littleton and Farmilos 1977).

1926: Terzaghi indicates the potential values of the Atterberg limits (Seed *et al*. 1964).
1932: Development of a mechanical device for making the liquid limit test (Casagrande 1932) later called the Casagrande cup.
1947: Casagrande introduces the plasticity chart for the classification of cohesive soils.
1950: Skempton (see his 1953 publication) introduces the: colloidal activity of clays.
2002: Correlation between clay mineralogy and the liquid limit (see **Part: C** of this thesis).

A 4.2.2 Application of Atterberg tests: Clays at different fluid contents with respect to their liquid limit

Clays at different fluid contents with respect to their liquid limit behave in a different way. At a high fluid content the clay is liquid. Upon loosing water the clay becomes semi-liquid, sticky, good mouldable, stiff and hard. The various clay types do not show exactly the same behaviour. One clay is longer sticky, another clay is less sticky and can be better moulded. To express this behaviour in numbers the boundaries have to be found where these properties change (Atterberg 1911). Nowadays four states (depending on their fluid content) are recognised. These four states are in order of increasing fluid content:

- Solid: boundary shrinkage limit.
- Semi-solid: boundary plastic limit.
- Plastic: boundary liquid limit.
- Liquid (Bell 1998).

Clays remain at one consistency as long as the density is not influenced by external forces (Keverling-Buisman 1940). The plastic and liquid limits are called the Atterberg limits. The change from one stage to another can be found in nature as well during the gradual deposition of solid particles from suspension in water. In the process of settlement, consolidation and drying out, the material passes through several well-defined stages: Suspension in liquid, viscous liquid, plastic solid, semi-plastic solid. The changes from one state to another are accompanied by important changes in physical properties (Capper and Cassie 1963).

A 4.2.3 Methods to determine the Atterberg limits

The liquid limit can be determined in at least two different ways, with the:

- Casagrande cup (*e.g.* DIN18122, NF P94-051).
- Falling cone test (*e.g.* BS 1377).

Muir-Wood (1990) states about these two methods: “Even though the.. cone parameters.. give liquid limits which correspond reasonably with Casagrande liquid limits, the very different procedures.. must lead to different values of liquid limit for extreme soil types”. Head (1992) presented a diagram in which was indeed shown that the falling cone test and the Casagrande cup give comparable results up to 100% liquid

limit but that at higher liquid limits the two tests give different values. Which method is right? Which method is wrong?
On theoretical considerations, the cone test is preferred above the Casagrande cup. Muir-Wood (1990) showed with dimension analysis that the falling cone test can be related to physical properties and that there is no reason why this should change at liquid limits larger than 100%. The deviation in the determination of the liquid limit at high liquid limit values must thus be related to changing processes in the Casagrande test.

Nevertheless the Casagrande cup is still a widespread method (**Table: A4-2**).

Table: A4-2

Methods currently used to determine the liquid limit at Belgian and neighbouring Universities.

University	Tool for Atterberg test	Standard
VU-Brussel	Casagrande cup	ASTM D4318
UL-Brussels	Casagrande cup	ASTM
FA-Gembloux	Casagrande cup	LCPC M.O. S.I.-4-1963
RU-Gent	Casagrande cup	
	Cone penetrometer*(1)*	BS 1377
U-Liège	Casagrande cup	NF P94-051 ASTM D4318
U-Louvain la Neuve	Casagrande cup	BS 1377 NF P94-051
RWTH-Aachen	Casagrande cup	DIN18122
TU-Delft	Cone penetrometer	BS 1377

(1) A cone penetrometer is present but used only if explicitly demanded by client

Head (1992) showed that the falling cone test results are lower than the Casagrande cup results at liquid limits larger than 100%. It would be practical if this difference between the two methods could be quantified. Littleton and Farmilos (1977) concluded that the cone to BS1377 (1975) gives the best correlation (compared to other cones) with the Casagrande cup over the range examined (sandy loams of low plasticity, to clays consisting predominantly of Illite, Kaolinite and Montmorillonite with a range 20%<liquid limit<450%):

For values 20%<liquid limit<100%:

$$LL_{cone} = 1.6 + 0.97 \cdot LL_{casa} \qquad \textbf{(A4 - 1i)}$$

The small variations between the two tests (Casagrande and cone) are within the accuracies associated with the determination of the liquid limit in general.
Above a liquid limit of 100%:

$$LL_{cone} = 1.24 \cdot LL - 4.8 - 2.6 \cdot 10^{-3} \cdot LL_{casa}{}^{2} + 33 \cdot 10^{-7} \cdot LL_{casa}{}^{3} \qquad \textbf{(A4 - 1ii)}$$

More tests might alter the equation in the upper range (Littleton and Farmilos 1977). It would be practical to have an empirical formulation for the whole range of liquid limit values. For this reason the results collected by Head (1992), the results of the reference Smectite obtained by van Paassen (2002) according to the cone test (BS1377: 1990) and

Liège results using the Casagrande cup according to NF P94-051, were plotted in **Figure: A4-0**.

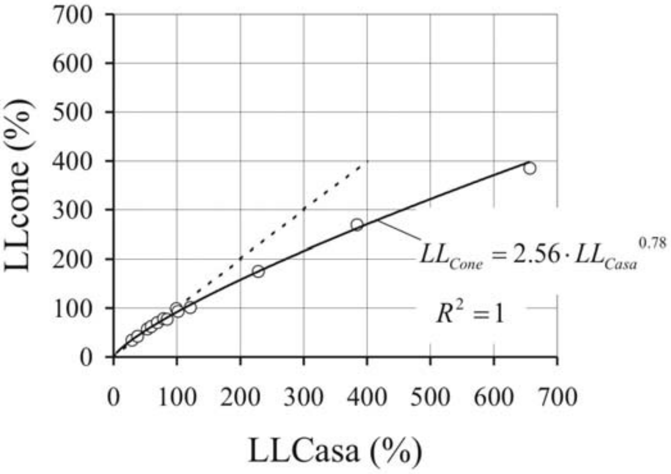

Figure: A4-0.

In this figure the liquid limit determined with the cone test and the Casagrande cup are compared.

The new empirical formulation correlating the LL_{cone} to the LL_{casa} for LL>20% is:

$$LL_{cone}^{*} = 2.56 \cdot LL_{casa}^{0.78} \qquad \textbf{(A4 - 2)}$$

This relationship will be used in chapter C **5** to access cone test databases.

A 4.2.4 How the liquid limit can be interpreted

A 4.2.4.1 Qualitative interpretation of the liquid limit

The meaning of the liquid limit can be interpreted in different ways. As was discussed above Muir-Wood (1990) showed with dimension analysis that the LL can be related to the undrained shear strength (which itself is a function of the fluid content thus the liquid limit) of the clay but other interpretations are possible:

- The liquid limit is empirically understood to be the fluid content at which the shear strength approaches the shear strength of a liquid (Fam and Dusseault 1999).
- The liquid limit of a clay is the fluid content at which, in the remoulded state, it passes from the plastic to an almost liquid condition (Skempton 1970).
- The liquid limit test is essentially a test, which measures the moisture content at which the soil has a particular strength (Bloomer and Coupe 1994 lit review).
- “The liquid limit means the fluid content at which the soil grains still have a certain degree of liberty to readjust themselves... without changing partners freely”. “At the liquid limit the pressure exerted by the surface tension of water or by the capillary pressure... is practically equal to zero” (Terzaghi 1926).

A 4.2.4.2 Quantitative interpretation of the liquid limit

The liquid limit can be related to physical parameters of the clay and the fluid contained in the clay by the following relations. The derivations are presented here because they were among the first attempts to relate the liquid limit theoretically to other physical properties (unfortunately restricted to the particle level as will be shown):

Step I: The interparticle void ratio (or void ratio of Smectites):

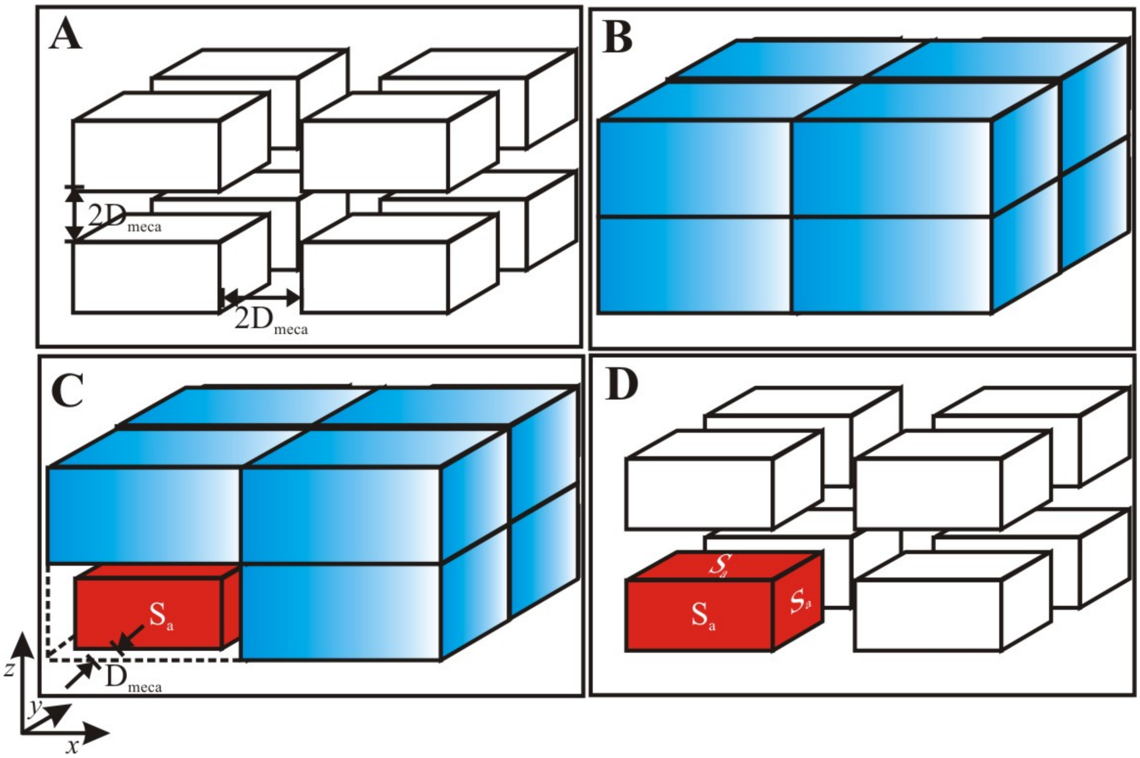

Figure: A4-1.

If a simple assembly of clay particles is considered the interparticle void ratio of parallel clay particles (e_d) can be expressed as a function of the specific surface (S_a), the distance between the clay particles ($2D_{meca}$) and the density of the clay particles (ρ_s).

In **Figure: A4-1-A** an assembly of clay blocks is shown which are separated by interparticle voids. The distance between the clay particles is called $2D_{meca}$. Once the clay block matrix is saturated (**Figure: A4-1-B**) one could imagine that each clay block “possesses” a fluid hull which extents up to a distance equal to D_{meca} from each clay block (**Figure: A4-1-C**). Because the actual clay block size is not known, it has to be calculated differently. In **Figure: A4-1-D** it is shown what is understood as the specific surface.

Step I

If $M_{clay\ block}$ stands for mass, $V_{clay\ block}$ for volume and $A_{clay\ block}$ for surface, ρ_s for density of the clay block, then the specific surface (S_a) of a clay block can be expressed as:

$$\rho_s = \frac{M_{clay\ block}}{V_{clay\ block}} \qquad \textbf{(A4 - 3)}$$

$$S_a = \frac{A_{clay\ block}}{M_{clay\ block}}$$ **(A4 - 4)**

If expression **(A4 - 3)** is inserted in **(A4 - 4)**:

$$S_a = \frac{A_{clay\ block}}{\rho_s \cdot V_{clay\ block}}$$ **(A4 - 5)**

The volume of fluid around a clay block (V_{fluid}) can be expressed as a function of the surface of a clay block ($A_{clay\ block}$) and the half distance between different clay blocks (D_{meca}):

$$V_{fluid} \approx A_{clay\ block} \cdot D_{meca}$$ **(A4 - 6)**

The void ratio (e_d) is defined as ratio between the volume of fluids (V_{fluid}) and solids (V_{solids}):

$$e_d = \frac{V_{fluid}}{V_{solids}}$$ **(A4 - 7)**

Inserting expression **(A4 - 5)** and **(A4 - 6)** into **(A4 - 7)**:

$$e_d = D_{meca} \cdot \rho_s \cdot S_a$$ **(A4 - 8)**

The specific gravity (G_s) is defined as ratio between the density of fluid (ρ_f) and solid (ρ_s):

$$G_s = \frac{\rho_s}{\rho_f}$$ **(A4 - 9)**

Insert **(A4 - 9)** into **(A4 - 8)** the void ratio can be expressed as:

$$e_d = S_a \cdot \rho_f \cdot G_s \cdot D_{meca}$$ **(A4 - 10)**

The distance between two particles is $2D_{meca}$

$$e_d = \frac{1}{2} \cdot S_a \cdot \rho_f \cdot G_s \cdot 2D_{meca}$$ **(A4 - 11)**

Introducing the expression for the double layer thickness this can be written as:

$$e_d = \frac{S_a \cdot \rho_f \cdot G_s \cdot \theta_{ddl} \cdot 2D_{meca}}{2 \cdot \theta_{ddl}}$$ **(A4 - 12)**

The reactivity of the fluid contained in the clay can be defined as:

$$\lambda_{ddl} = S_a \cdot \rho_f \cdot G_s \cdot \theta_{ddl}$$ **(A4 - 13)**

The void ratio can finally be expressed as:

$$e_d = \frac{\lambda_{ddl} \cdot 2D_{meca}}{2 \cdot \theta_{ddl}}$$ **(A4 - 14)**

This expression is identical to the expression given by Fam and Dusseault (1999). The void ratio e_d is the void ratio of *e.g.* Smectites because it is based on the assumption that the height (z direction in **Figure: A4-1**) of a particle is identical to the basal spacing of the clay *i.e.* a clay with only interparticle voids and no interlayer voids ($N_{layers} = 1$).

Step II
Background information about the expression used to describe the distance between the centre of mass θ_{ddl} of the diffuse double layer to the clay particle has been given in paragraph **A 3.1**.

Step III
At equilibrium the double layer repulsion is balanced by the applied effective stress (see as well paragraph **C 7.2.1.1**).

$$\sigma_s' = \frac{\pi^2 \cdot \lambda_{ddl}^{\ 2} \cdot R \cdot T \cdot CEMC}{e_d^{\ 2}} - 2 \cdot R \cdot T \cdot CEMC \qquad \textbf{(A4 - 15)}$$

if $\frac{2 \cdot D_{meca}}{2 \cdot \theta_{dll}} < 2$ for small interparticle spacing .

$$\sigma_l' = 64 \cdot R \cdot T \cdot CEMC \cdot e^{-\frac{2 \cdot e_d}{\lambda_{ddl}}} \qquad \textbf{(A4 - 16)}$$

if $\frac{2 \cdot D_{meca}}{2 \cdot \theta_{dll}} > 3$ for large interparticle spacing.

$$e_d = \frac{\lambda_{ddl}}{2} \ln\left(\frac{64 \cdot R \cdot T \cdot CEMC}{\sigma_l'} \right) \qquad \textbf{(A4 - 17)}$$

Step IV
According to different literature sources the undrained shear strength (S_u) of various clays at the liquid limit varies between:
- 1.3 to 2.4kPa (Bloomer and Coupe 1994).
- 2 - 3kPa (ASTM) (Casagrande 1958).
- 1kPa (BS) (Casagrande 1958).
- 3kPa (for soils close to their liquid state) (Bardet 1997).

With the assumption that the possible range in the effective angle of shearing resistance of clays varies between 10° and 20° (Fam and Dusseault 1999) the range of undrained shear strength (S_u) values given above (vary between 2 kPa and 3 kPa) will be attained for soils at a mean effective pressure at failure (Bardet 1997):

$$p_f' = \frac{S_u \cdot (3 - \sin \phi')}{3 \cdot \sin \phi'} = 10\ kPa \qquad \textbf{(A4 - 18)}$$

If $\sigma' = 10$kPa, R = 8.3 J/mol/K and T = 293 K, the expression for the void ratio can be simplified to:

$$e_d = \frac{\lambda_{ddl}}{2} \ln\left(\frac{16 \cdot CEMC}{C_{st}} \right) \qquad \textbf{(A4 - 19)}$$

Step V
If the liquid limit is expressed as the fluid content in % at an effective pressure equal to 10 kPa this can be expressed as (if $V_{void} = V_{fluid}$):

$$LL = \frac{M_f}{M_s} \cdot 100 = \frac{(V_{fluid} \cdot \rho_f)}{(V_{solids} \cdot \rho_s)} \cdot 100 = \frac{e}{G_s} \cdot 100 \qquad \textbf{(A4 - 20)}$$

With the expression **(A4 - 19)** for the void ratio e_d found above:

A

$$LL = \frac{50 \cdot \lambda_{ddl}}{G_S} \ln\left(\frac{16 \cdot CEMC}{C_{st}}\right) = 50 \cdot \rho_w \cdot S_a \cdot \sqrt{\frac{R \cdot T \cdot \varepsilon_0 \cdot \varepsilon_m}{2 \cdot F^2 \cdot val^2 \cdot CEMC}} \cdot \ln\left(\frac{16 \cdot CEMC}{C_{st}}\right) (\%) \quad \textbf{(A4 - 21)}$$

$$\frac{kg}{m^3} \cdot \frac{m^2}{kg} \cdot \left(\frac{\frac{J}{mol \cdot K} \cdot K \cdot \frac{F}{m}}{\frac{C^2}{mol^2} \cdot (-)} \right) \cdot \frac{m^{1.5}}{mol^{0.5}} \cdot \ln\left(\frac{\frac{mol}{m^3}}{\frac{mol}{m^3}} \right) = \left\{ F = \frac{C}{V}, V = \frac{J}{A \cdot S}, C = A \cdot S, J = N \cdot m \right\} (-)$$

The practical value of this expression is discussed with several examples in chapter **C 3**.

Based on the derivation above one can conclude that the liquid limit depends on the:
- Specific surface of the mineral phase (Fam and Dusseault 1999).
- Physical and chemical characteristics of the fluid contained in the clay (Fam and Dusseault 1999).

From literature (*e.g.* Hasenpatt 1988) it is indeed known that the plasticity depends on the:
- The polarity of the fluid.
- Attractive and repulsive forces between the clay particles.
- Charge of the clay minerals.
- Valence of the exchangeable ions.
- Relative permittivity of the fluid contained in the clay.
- Electrolyte concentration.
- Grain size.
- Form and surface roughness.
- Adsorption characteristics.

A comprehensive literature overview of the modification of the liquid limit due to various clay-fluid interactions is given in **Table: A4-3** and **Table: A4-4**.

Table: A4-3

Literature overview of the qualitative changes in liquid limit, plastic limit etc. of clays, upon addition of chemicals or other treatments.

	Sm	*exp. clay*	**Kao**	*non-exp. clay*	*inorg. clay*	*f.gr.org soil*	*Lond on clay*	Ref.
> [Ca^{2+}]	<LL		>LL and <LL*(8)*					[1]
> [Cl^- salt]	<LL <PL		>LL >PL				<LL <PL	[2]
> Cation valence		<LL		>LL				[3]
> CEMC	<LL		<LL		<LL			[4] [12]
Addition of small amount of organic matter					>LL =PI			[5]
Ca^{2+} replaced by Na^+	>pla							[6]
		>LL		<LL				[7]
Na^+ replaced by Ca^{2+}		<LL		>LL				[7]
After oven drying					=pla	<pla		[8]
Highly charged ions	<LL >PL		>LL >PL					[7]
< Specific surface	<LL*(1)*							[9]
< Double layer thickness	<LL*(1)*							[9]
> Ion concentration	<LL*(1)*							[9]
> Temperature	<LL*(1)*							[9]
Polluted water, urine, bacteria, fungi			<PI					[10]
> Temperature (7°C to 24°C)	=LL,=PI,=PL*(2)*							[10]
< Double layer	<LL*(3)*							[11]
Collapse interlayer space	<LL*(4)*							[7]
> Amount charged ions on surface	>PL(5)		>LL*(4)* >PL	>LL *(4)* >PL				[7]
Marine clays in contact fresh water	>LL*(6)*							[9]
Clays from same deposit	// to A-line*(7)*							[8]
Parallel alignment particles	<pla							[6]

Legend to **Table: A4-3**:

- Abbreviations:

exp. clay = expansive clays in general

non-exp.clay = non-expansive clays

inorg. clay = inorganic clays

f.gr.org soil = fine-grained organic soils

pla = changes in plasticity, without further specification of the cited author

- Comments:

(1) Mathematical model

(2) On TL, TM and TA class (DIN 18196) clay; LL of the TL, TM clay were higher at lower temperatures, in general the effect is negligible.

(3) LL $_{Smectite}$ *=f(double layer); double layer=f(presence of multivalent exchangeable cations, exchangeable cations with small hydrated size, like* K^+ *cations, or a high pore salt concentration); <double layer → <LL*

(4) If highly charged ions ($CoEDA^{6+}$*: cobalt-ethylene-diamine-complex) are entering the interlayer of a Smectite (tested on Montigel ETH-Zürich - Hasenpatt 1988) the interlayer space is closed by these ions. Water is not able to enter and the LL decreases. Because these ions cannot enter the interlayer space of Illite and Kaolinite they are only present on the surface of these particles. In this case the LL rises. If more water is added the effect of the ions decreases (Hasenpatt 1988).*

(5) The presence of highly charged ions on the surface of the Smectite, Illite and Kaolinite causes a flocculated structure. Water is enclosed in this structure: the PL increases (Hasenpatt 1988).

(6) Clays deposited in marine environments (if they retain their fluid phase) will display lower LL compared to freshwater clays. If the saline fluid contained in the clay is gradually replaced by freshwater a dramatic increase in the clay-fluid system sensitivity will occur (Fam and Dusseault 1999).

(7) After plotting the results of Atterberg limit tests on a number of samples from the same fine-grained deposit in a LL-PI plot, the LL-PI points lie generally on a straight line approximately parallel to the A-line (Casagrande 1947).

(8) With increasing concentration first slight increase is followed by slight decrease.

- References:

[1] Anson and Hawkins 1998;
[2] Moore 1991 & 1992;
[3] Mitchell 1993;
[4] Van Paassen 2002;
[5] Casagrande 1947;
[6] Müller-Vonmoos and Kohler 1993;
[7] Hasenpatt 1988;
[8] Casagrande 1947;
[9] Fam and Dusseault 1999;
[10]Atterberg 1911;
[11]Moore 1991 literature review
[12] Schmitz and van Paassen 2003.

Table: A4-4

*A more complex cations-clay interaction than shown in **Table: A4-3**.*

Clay type:	Cations present in the interlayer space:	Reaction:	Result:	Ref
small N_{layers} large N_{int}	Na^+	Interlayer is enlarged by invading water	>LL	[7]
	Ca^{2+}	Interlayer is compressed by Ca^{2+}	<LL	[7]
large N_{layers} small N_{int}	Na^+	Large double layer; Clay deflocculates	<LL	[7]
	Ca^{2+}	Small double layer; Clay flocculates and encloses a lot of water in its structure	>LL	[7]
Tournai, Kruibeke, Soignies, Kao_{ref} and Sm_{ref}	with increasing concentration of Ca^{2+} or Na^+		<LL	[12]

[7] Hasenpatt 1988; [12] Schmitz and van Paassen 2003.

A 4.2.5 Reproducibility of the liquid limit and plastic limit determination

A 4.2.5.1 Why is the reproducibility a major question of the Atterberg tests

As shown in the previous paragraph the liquid limit depends on many parameters, amongst others on the composition of the fluid contained in the clay. To interpret small variations that are produced by different fluids correctly, one must know the degree of accuracy of a liquid limit determination. One source of liquid limit scatter is caused by the between-operator variance of the Atterberg limit determination. In spite of carefully standardised instructions a certain personal element inevitably adheres to every limit determination (Terzaghi 1926) which is fairly large (Kooistra 1996) but can be quantified with the method presented below.

A 4.2.5.2 Reproducibility of the liquid limit

Borus and Rév (1968) have shown that the standard deviation increases linearly with liquid limit:

$$S_{rp} = 0.0365 \cdot LL + 0.175 \qquad \textbf{(A4 - 22)}$$

The same Casagrande cup, same testing method were used by different technicians, 8 different clay soils, liquid limit varying between 34 and $2.5 \cdot 10^2$ %, > 200 tests.

If the Casagrande cups, testing methods and technicians differ (6 different clay soils, liquid limit varying between 28 and $1.0 \cdot 10^2$ %, > 458 tests) the standard deviation still increases linearly with liquid limit but is larger than in the previous case:

$$S_{rp} = 0.092 \cdot LL + 0.5 \tag{A4 - 23}$$

The test results presented in this thesis (**Part: B** and **C**) were performed by different technicians with the same testing device and under the same test conditions. Therefore the standard deviation is given by (expression (**A - 22**)): 0.0365·LL+0.175. If the average liquid limit of a soil is 100%, assuming a normal distribution, 95% of all results will fall within an interval defined by the mean + or - 2 standard deviations, thus: 92%<liquid limit<108%. If the same clay has a liquid limit outside this range upon addition of a leachate, this is a clear indication that the added fluid changed the properties of the considered clay.

Table: A4-5

Borus and Rév 1968: $7 \cdot 10^2$ *LL tests on 8 different clay samples varying between: 34.1<LL<251%. Samples were sent to different laboratories without requesting special specifications.*

	COV LL (%)	COV PL (%)
Casagrande cup might be different brand Test conditions might be different Different technicians	7.9 (1)	12 (1)
Same Casagrande cup Same test conditions Different Technicians	3.9 (2)	6.2 (2)
Same Casagrande cup Same test conditions Same Technician	3.6 and 4.2 (3)	3.8 and 8.0 (3)

Deduced from Borus and Rév (1968): (1) table IV and VI (2) table V and II row 1 and 2 together (3) table V and II either row 1 or row 2

The coefficient of variation[22] of the liquid limit (COV_{LL}) can thus be reduced by using the same Casagrande apparatus and the same testing method to a $COV_{LL} = 0.04$ (see **Table: A4-5** or expression (**A4 - 22**)). Additionally the aforementioned relationships (**A4 - 22**) show that the COV_{LL} is thus practically independent of the height of the liquid limit value (Réthári 1988 based on the data presented by Borus and Rév 1968). The reliability (*e.g.* by the coefficient of variation) increases with increasing liquid limit and can be increased by a rigorous standardisation of the testing device and the testing

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[22] *The coefficient of variation (COV) is the quotient of the empirical standard deviation and the expected value. Hoek (et al. 2000) states that (for geomaterials) a small uncertainty in the determination of the mean would typically be represented by a COV = 0.05 while considerable uncertainty would be indicated by a COV = 0.25 (assuming a normal distribution, in the first case ~90% of all data points lie within the range: mean value +/- 8% in the second ~90% of all data points lie within the range: mean value +/- 41%).*

method. If all the other parameters that were analysed by Borus and Rév (1968) are constant the influence of the technician on the outcome is small as long as the Casagrande cup used is the same.

A 4.2.5.3 Reproducibility of the plastic limit

From **Table: A4-5** one concludes that the coefficient of variation of the plastic limit is 12%, for one and the same technician the coefficient of variation is 6% based on the data by Borus and Rév (1968). Although the operator-dependency of the plastic limit test is larger than in the liquid limit test, it is less than the dependency of the liquid limit on different test conditions or Casagrande cup brands.

A 4.2.5.4 Reproducibility of the plasticity index

As the plasticity index is not a directly measured, but derived quantity, its standard deviation is, according to the law of error propagation (Rétháti 1988):

$$s_{PI} = \sqrt{s_{LL}^{2} + s_{PL}^{2}} \qquad \textbf{(A4 - 24)}$$

In which:

S_{LL}	*The standard deviation of the LL*	*(% fluid content)*
S_{PI}	*The standard deviation of the PI*	*(% fluid content)*
S_{PL}	*The standard deviation of the PL*	*(% fluid content)*

A 4.2.5.5 Determination of the natural heterogeneity of the soil

Like other geomechanical tests the apparent accuracy of the determination of the liquid limit includes the natural heterogeneity of natural soils, which reflects the depositional history (see **Part: B**). The standard deviation (S) of any physical characteristic of a given soil layer is composed of two main parts: The component S_{rp} (the standard deviation characterising the reproducibility) and S_h characterising the natural heterogeneity. The latter can be estimated according to the law of error propagation as:

$$s_h = \sqrt{s^{2} - s_{rp}^{2}} \qquad \textbf{(A4 - 25)}$$

The value of S_h calculated in this way is somewhat higher than its field value, because the standard deviation appearing in the final result of the test has also other components, whose majority is due to the fact that changes in the state of the samples are different caused by the sampling itself, as well as the subsequent transport and storage. Nevertheless the expression can be used as a first approximation (Réthási 1988). If the ratio S_h/S is rather large this means (following Réthási) that the overwhelming part of the standard deviation is not due to objective and subjective faults of the tests but to the natural heterogeneity (including homogenisation due to sample preparation) of the soil. This information is used in paragraph **B 3.4.2** and **C 2.2** to determine the natural heterogeneity of the Tertiary clays.

A 4.2.5.6 Concluding remarks

The uncertainty of liquid limit determination is small as long as test conditions and apparatus are identical. The uncertainty of plastic limit determination is larger than the uncertainty of the liquid limit determination. The determination of the PI includes the uncertainty of the liquid limit and plastic limit determination. Therefore its uncertainty is the highest.

A 4.3 Modification of the shear strength

A 4.3.1 Introduction

Depending on the clay mineralogy and the related morphology the shear properties are known to vary as was discussed previously by the author (see *e.g.* Schmitz 2000). The geomechanical structure on the level of clay particle determines the mechanical behaviour of the clay. This structure is related to the mineralogy but also to other factors as *e.g.*: Electrostatics, stress history and pH. This causes an elementary difference between XRD measurements of the mineralogy and the geomechanical measurements of the same soil (see **Figure: A4-2**). An example of how interlayer reactivity (particle to interlayer level) can change the shear strength: Because the (non-hydrated) K^+ ion is larger than the Na^+ ion, the attraction of highly charged clay particles will overrule the double layer repulsion. The particles start to attract each other. This will result in a higher shear strength (Müller-Vonmoos and Kohler 1993).

A 4.3.2 Shear strength of different clays

A 4.3.2.1 Kaolinite

The influence of colloidal forces on the shear strength of Kaolins (like Kaolinite) is slight (Skempton 1948). Direct shear tests on Kaolinite have shown that the behaviour of Kaolinite (determined by analysing the residual shear strength) is not influenced by the exposure to (1M) NaCl solution (di Maio and Fenelli 1994).

But van Paassen (2002) showed that the liquid limit of Kaolinite is affected by the addition of brines in qualitatively the same way as *e.g.* Smectites. Mitchell (1993) showed that the liquid limit and the effective friction angle are correlated. Thus, even for Kaolinites the shear strength will be influenced by changes in fluid contained by the clay. Hasenpatt (1988) confirmed this: Measurable differences (an increase of the shear strength) were obtained if Kaolinite was exposed to cations with a valence of 6, the effect was negligible with cations of lower valence: 2 or 1.

A 4.3.2.2 Illite

The shear strength of Illitic clays depends to a great extent on the cations present in the electrolyte (Müller-Vonmoos and Kohler 1993). This is due to the fact that the layer charge of the Illitic clay is concentrated in the tetrahedral layer. If for example the concentration of NaCl in the pore water is increased, the double layers of an Illite will decrease and the shear strength will increase.

A 4.3.2.3 Smectite

Numerous frictional sliding studies of Montmorillonite yielded a wide range of reported (residual shear) strengths, largely because of the strong influence of fluids or system chemistry (that is, composition of the fluid contained in the clay and type of ions adsorbed on the mineral particles) on this highly expandable clay (Kenney 1967 and Morrow *et al* 1992). The substitution of sodium by potassium (Note: Related to its alteration into open Illite) produced a systematic increase in shear strength and sensitivity of the Montmorillonites in their undisturbed state (Moum and Rosenqvist 1961).

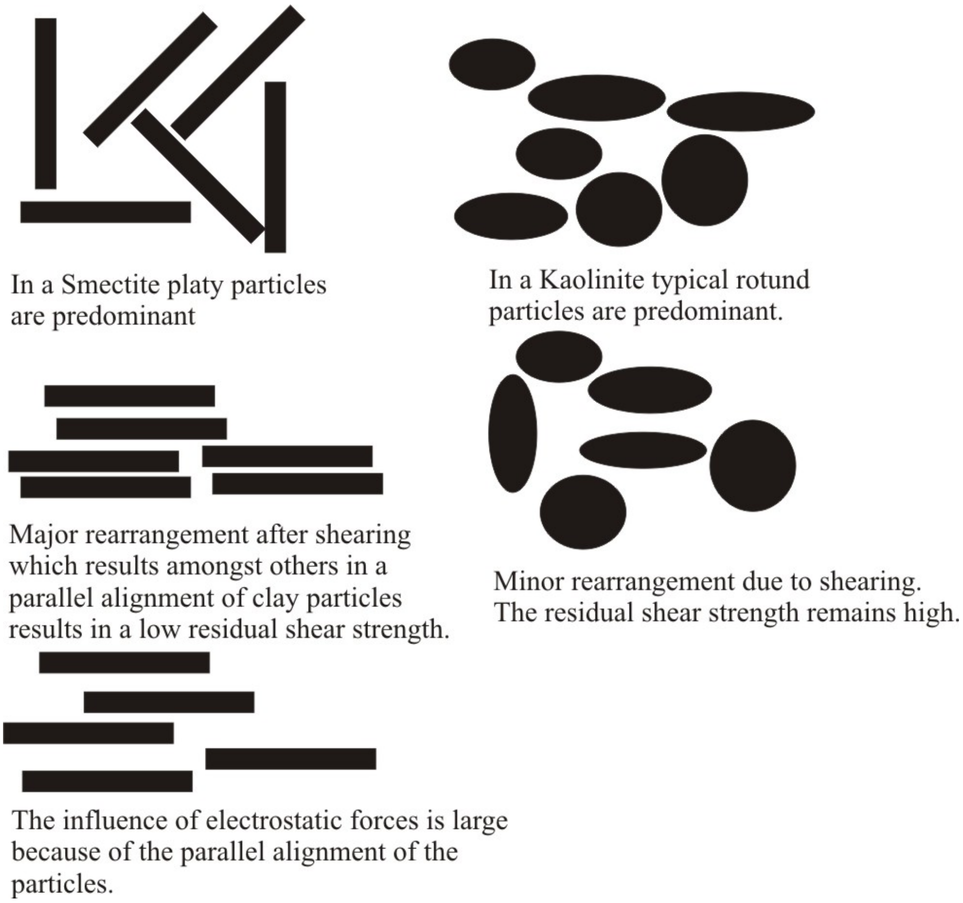

Figure: A4-2.

Different clay minerals, different morphology, different shear behaviour. Based on interpretation by Terzaghi (et al 1996).

A 4.4 Modification of the hydraulic conductivity

A 4.4.1 Introduction

Wienberg (1990) gave an important overview of the effects on the hydraulic conductivity found in literature. The most important feature that one can learn from the overview of the hydraulic conductivity tests is that important increases in hydraulic conductivity can occur, but that:

- *Considering double layer effects on the particle level*
  - If the boundary conditions are equal to those in a triaxial cell, no increase in hydraulic conductivity occurs when substances are added that decrease the diffuse double layer of clays (either a fluid with a lower relative permittivity or with a higher cation concentration than the original fluid contained in the clay).
  - If the increase in hydraulic conductivity occurs when a sample is tested under oedometer conditions in absence of exterior effective compressive stresses *i.e.* when clay particles are not moved together after a decrease of the repulsive forces between the clay particles then large increases in hydraulic conductivity can occur.
  - Organic substances with low water solubility hardly affect the hydraulic conductivity (although breakthrough is possible through individual isolated interconnected pores). Organic substances that are good mixable with water show effects only above a concentration of 80% (Wienberg 1990).

These aspects are analysed in more detail in **Part: C**.

- *Considering pore clogging effects on the particle level*
  - Pore clogging decreases hydraulic conductivity under triaxial and oedometric conditions.

Changes in hydraulic conductivity, the magnitude and direction (increase or decrease) can vary with the same clay - fluid type or substance contained in the contacting fluid, depending on which level: TOT/TO, interlayer or particle level changes occur. This depends amongst others on the boundary conditions and the instant when the fluid contacts the clay as will be explained in *e.g.* paragraph **C 6.4**.

A 4.4.2 The test conditions

In general the measurement of the influence of the leachates on the hydraulic conductivity is a very slow process, which can only be executed in the laboratory to a limited extent (Entenmann 1998). Many authors have indicated that measured field hydraulic conductivity on the completed liner can be as much as 1 or 2 orders of magnitude greater than the hydraulic conductivity obtained in the laboratory (Clark and Davies 1996).

The clays needs to be tested:

- Under conditions as similar as possible to the prevailing conditions in the clay barrier (degree of compaction, moisture content, stresses, fluid type) (ManWal 2000).
- With varying test conditions (ManWal 2000).
- By taking into account possible ion exchanges (ManWal 2000).
- With flexible wall (or triaxial) cells in the case the samples are undisturbed because the use of rigid wall permeameters may lead to spurious side-wall leakage and measurement of a hydraulic conductivity that is too high (Daniel 1987). This subject will be discussed in more detail in **Part: C**.
- The hydraulic conductivity should be determined using real leachates at a confining pressure of 4 bar (GDA 1997).

A 4.4.3 Overview: Origin of changes in hydraulic conductivity

Changes in hydraulic conductivity can be caused by:

- Clay mineral alteration *e.g.* collapse of the silicate layers by inclusion of pollutants into the interlayer space (Wagner 2000).
- Mineral transformation or formation of new minerals *e.g.* dissolution of calcite and precipitation of new mineral phases (Wagner 2000).
- Decrease of the thickness of the diffuse double layer by an increase in electrolyte concentration (Wagner 2000).
- Development of shrinkage and vertical fissures if freshwater clay liners are exposed to saline leachates (Fam and Dusseault 1999).
- Pure bases that increase the hydraulic conductivity (Hasenpatt 1988 lit rev)
- The oxidation of Fe(II) and Mn compounds that suffocate the pores of rocks and soils (Vogelsang 1988).
- Adsorption (Hasenpatt 1988).
- Change in dielectric constant (Hasenpatt 1988).
- Change in viscosity (Hasenpatt 1988).
- Bacterial activity (Hasenpatt 1988).
- Blocking of pores by waste products (Hasenpatt 1988).
- Precipitation and decrease of the grain size that can lead to choking of the pores and reduction of the hydraulic conductivity if clays are attacked by pure acids (Hasenpatt 1988 lit rev).

A 5 Conclusions

- Fluids or substances contained in the fluid permeating a clay barrier can change clays at the:

- Particle level.
- Interlayer level.
- TOT- or TO-layer level.

- On each level other physical mechanisms steering the geomechanical properties are important.

- On the particle level especially the theory of the diffuse double layer is illustrative to predict changes in properties if the clay is percolated by fluids with different cation concentrations or with other relative dielectric constants than the original fluid contained in the clay. Although the double layer theory is well established, there is no consensus how changes in double layer thickness can be linked to geomechanical properties. The different views found in literature have been classed into a simple system.

- One must rely on clay mineral analyses by X-ray diffraction to study changes on interlayer level. Many clay mineral alterations are possible but only a few will occur under geomechanical conditions. The most impressive changes in geomechanical properties are caused by the alteration of Illite into a Smectite or vice versa because this reaction involves a change from the interlayer level to a particle level.

- Changes on TO, TOT level need a long history of subsequent physical and chemical steps. But for a few, these have not been reproduced in the laboratory. Therefore one must rely on geological analogues to analyse these changes.

- Atterberg tests depend on the clay mineralogy but also on the chemistry of the fluid contained by the clay. It is a very potent tool to analyse the activity of clay - leachate interactions.

- Upon clay - fluid contact physical and chemical reactions take place on the TOT/TO-, interlayer and particle level of clays. Thereby geomechanical properties like the hydraulic conductivity can change. Changes on the particle level are the fastest and are therefore the first to occur (and to recognised) during testing. Depending on the boundary conditions the same fluid - clay combination can show different behaviour. These boundary conditions should correspond to those in a barrier to determine if the barrier will still function properly after *e.g.* leachate contact.

B Clay barrier in Vivo

B 1 Introduction

In part **A**, a literature overview of clay-leachate interactions was given. It was shown how fluids influence the mechanical behaviour of clay and on which levels: TOT/TO, interlayer or particle level reactions occur.

In part **B** this information is used to study the influence of landfill leachates on clay barriers in municipal landfills, the heart of the ARC[23] project. Like in a real case scenario natural clays were selected: Tournai clay and Soignies clay from the Walloon region and Kruibeke clay from the Flemish region and genuine landfill leachates originating from three different existing landfill sites in the Walloon region. Soignies and Tournai clay represent by their genesis, their availability (reserves and resources) and mineability, the potential clay-barrier source material in the Walloon-region. The third natural Belgian clay that was analysed is Kruibeke clay (large reserves and resources) from the Flemish region which is well characterised under the name Boom clay in geomechanical literature. A reference ("pure") Smectite and reference ("pure") Kaolinite were analysed as well to make a link to geomechanical literature discussing clay - leachate interaction, which is traditionally restricted to the analyses of pure clays.

Each step - excavation, construction of the barrier, mechanical loading and permeation of landfill leachates - stresses the clay barrier differently. Therefore all the steps - from the deposition of the clay to the construction of the barrier, the first leachate contact to the end of the technical life of the barrier - are described in geomechanical terms in this chapter (see **Figure: B1-1**).
In order to analyse the reactions between natural clays and leachates, batch tests like Atterberg tests were used. Clay mineral changes after leachate contact were analysed. Changes in hydraulic conductivity due to leachate contact were tested in oedometer and triaxial cells. Possible modifications of the shear strength after clay - leachate contact were analysed as well.

In more detail:
- In chapter **B 2** the depositional history of the clays is described. It is explained why differences in this initial phase of the clay are responsible for today's difference in geomechanical properties of the clays.
- In chapter **B 3** the evolution of the clay during the Holocene is described. This includes the changes provoked by the exposure to the present day's atmosphere in the quarry, the treatment on the landfill construction site, the mechanical loading by infill of

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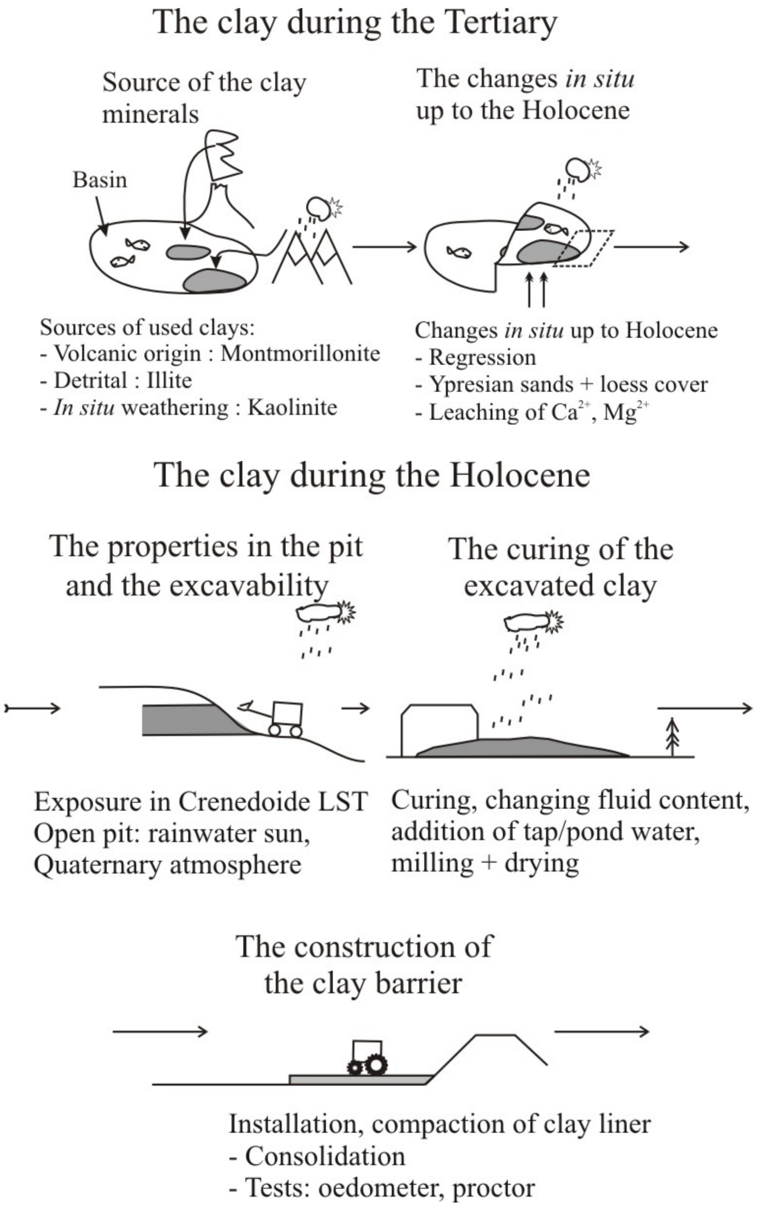
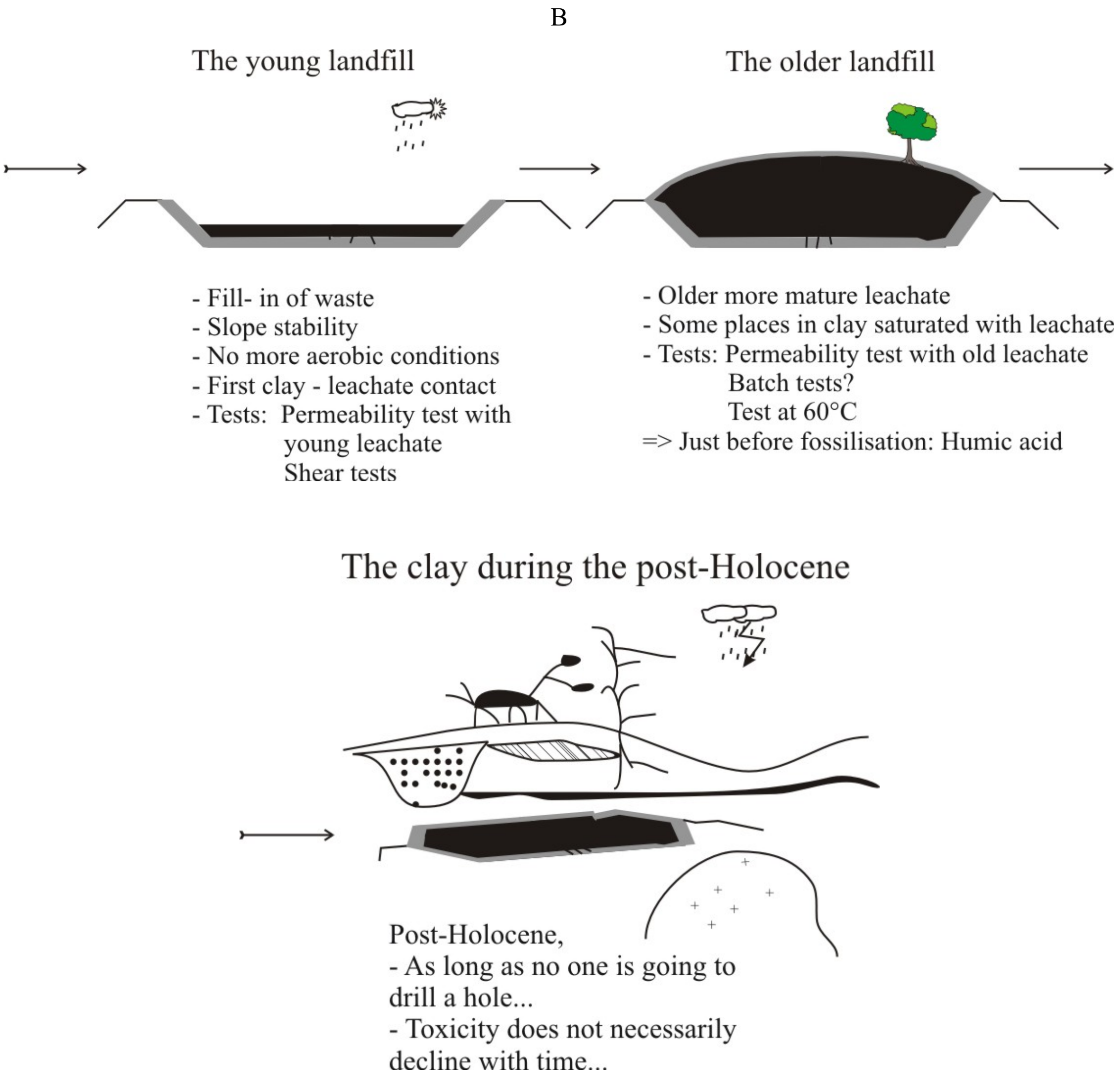
[23] *The advances in research related to the ARC project 99/04-243 "Confinement de centres d'enfouissement technique à l'aide de barrières argileuses" were reported annually to the "Communauté française de Belgique". The publications related specifically to the subject of this thesis can be found in: Schmitz (2004b, 2004c, 2003a, 2003b, 2002a, 2002b, 2001a, 2001b, 2001c, 2001d), Schmitz and Boukpeti (2002), and Schmitz and Collin (2001).*

the waste, the contact with the young landfill leachate, the steady rise of the temperature and the final permeation of the mature landfill leachate through the clay barrier.

- In chapter **B 4** the final stage in the life of the clay is presented in which the biological life of the landfill ends. The prediction of the long-term behaviour of the clay barrier is given by making a reference to nature by referring to natural analogues.
- In chapter **B 5** the conclusions concerning part **B** are given.

The tools developed in part **C** following part **B**, are partly developed on the basis of the results of part **B** and partly on the results with pure clays and pure fluids. Some of the tools developed in part **C** were used or are referred to in part **B**, to understand the clay-leachate interaction under landfill conditions.





The young landfill

- Fill- in of waste
- Slope stability
- No more aerobic conditions
- First clay - leachate contact
- Tests: Permeability test with young leachate
  Shear tests

The older landfill

- Older more mature leachate
- Some places in clay saturated with leachate
- Tests: Permeability test with old leachate
  Batch tests?
  Test at 60°C

=> Just before fossilisation: Humic acid

The clay during the post-Holocene

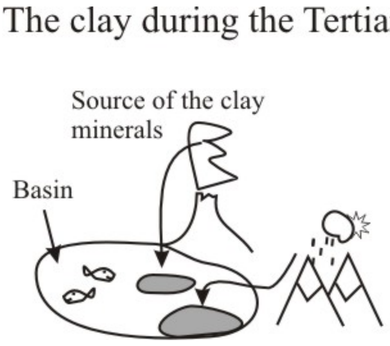
Post-Holocene,
- As long as no one is going to drill a hole...
- Toxicity does not necessarily decline with time...

Figure: B1-1.

All phases and changes involved in the different steps a clay takes during its origin in the basin through excavation and liner construction to its final waste containment function.

B 2 The clay during the Tertiary

B 2.1 The source of the clay



Keywords: Volcanic activity, weathering of rocky substratum, erosion, transport and sedimentation in a basin

The origin of the clay is analysed because it is the depositional history that explains:

- Certain differences in the clay mineral composition of different clayey soils.
- The degree of heterogeneity of a clay deposit.
- The presence of non-clay minerals, like pyrite, which can play an important role in the clay barrier.

As shown by previous detailed XRD analyses (ManWal 2000), the clay phases in the considered Tertiary deposits are characterised by rather complex assemblages with Illite, Kaolinite and non-swelling Illite-Chlorite and swelling Illite-Smectite mixed-layers; Chlorite generally occurs as a subsidiary mineral. Such clay mineral assemblages reflect a detrital multi-source.

<u>Origin of Smectite and Illite-Smectite mixed-layers:</u>
Active volcanic North-Sea produced ash transformed into Smectite, which was transported to the shelf where it was deposited (PC Thorez). A source of the volcanic activity is explained by Schmidt and Walter (1990): The mountain forming processes during the Tertiary were accompanied by a severe magmatic activity and were expressed through an acceleration of the sea floor spreading. The considered clay deposits include clay produced by halmyrolysis (weathering in sea water) of a former acidic volcanic ash in marine waters. After detailed XRD analyses completed with Li^+ and K^+ ion saturations (Anceau 1987) it was found that such a halmyrolytic clay was a Montmorillonite, the latter being thus volcanogenic and also neoformed. Cation saturation (Thorez 2000) enables to differentiate this halmyrolytic Montmorillonite from any other Smectite (*e.g.* Beidellite) produced by the alteration of a parent Illite.
This Montmorillonite has been incorporated into the detrital clay stock during transport and sedimentation in the Tertiary seas, particularly in Belgium. This Smectite became mixed with other detrital clay minerals during the sedimentation and final accumulation in karstic cavities. These clays fill huge karstic cavities developed at the top of upper

Tournaisian (Lower Carboniferous) limestones. Clays used in this thesis were sampled at a depth of several meters beneath the Quaternary loess cover.
The occurrence of clinoptilolite in Tournai clay further supports a volcanogenic origin of the Smectite, which matches, the genetic conditions as well as the mineralogical composition of a commercial Bentonite.

Of interest in the present study was the fact that the three selected clay materials (Tournai, Soignies and Kruibeke) contained volcanogenic, neoformed Montmorillonite and not Beidellite. Finally, as it will be indicated later, the Montmorillonite found in the Tertiary clays did not correspond to a pure mineral but rather to a random mixed-layer Illite-Montmorillonite (10-14m).

Origin of Kaolinite:
Kaolinite originated from the weathering of the Palaeozoic bedrock. The material was then transported and deposited on the shelf (PC Thorez).

Origin of Illite and Chlorite:
Both minerals, of unknown source(s) depict fresh material thus unaffected by chemical weathering. The minerals were eroded, transported and sedimented in the basin in association with other clay minerals (Montmorillonite, Kaolinite).

Origin of the mixed-layer Illite-Chlorite:
Again the source of this material cannot be reconstructed. Its origin can be related to a mild physico-chemical alteration of an Illitic structure.

B 2.2 The sedimentation

Keywords: The basin

Clay deposits from Soignies, Tournai and Kruibeke accumulated during a series of transgressions and regressions that developed towards the uplifted Belgian Ardennes in the south. The sediments consist of clay, silty clay, silt and fine sand deposited in near shore tidally (sub-tidal in the case of Kruibeke) influenced conditions. The Smectite (a neoformed volcanogenic Na-Montmorillonite) was developed by halmyrolysis of volcanic ash. Due to deposition in seawater a part of the original Na-Montmorillonite was transformed into a Ca-Montmorillonite (completed at a later stage, by leaching of Ca^{2+} ions originating from the loessic cover). This clay became mixed with detrital clay minerals such as: Illite, Illite-Chlorite mixed layers and Kaolinite, with a minor local contribution of Chlortire. The Ypresian clays were deposited in karst holes in the Tournaisian limestone. All three clays are dipping towards the North due to the morphology of the basin. **Figure: B2-2** gives an overview of the sedimentological history of the clay deposits.

General geological picture at the time of the sedimentation:
After the regression (sea-level drop) at the end of the Cretaceous, a transgression (sea level rise) by the North Sea followed. The old Anglo-Saxon basin split into separate units (London, Belgian and Paris basins), which the Atlantic Ocean and the North Sea regularly invaded. A regional depression of the North Sea basin (see **Figure: B2-1**) (Walter 1995) took place during the Tertiary.

The uplifted Ardennes, exposing Palaeozoic substratum, had been intensively weathered. In particular the Tournaisian limestone had been exposed, and karst had developed. The karst was eventually reached by the sea and filled by Tertiary sediments (Soignies, Tournai). Reworked Illite, Chlorite, mixed-layer Illite-Chlorite and minor Chlorite of detrital origins and sources were mixed with the volcanogenic Montmorillonite (PC Thorez).

The first regression occurred during the Eocene and a second one during the Oligocene (see **Table: B2-1**).

Table: B2-1

Transgressions during which the Tournai, Soignies and Kruibeke clay were deposited.

Period		Epoch	Stage	Deposit	Regression/ Transgression
Tertiary	Palaeogene	Oligocene	Rupelian 34-29MY	Kruibeke clay	Transgression
		Eocene	Ypresian 55-50MY	Tournai and Soignies clay	Transgression

(Pan Terra 1998, last column: Schmidt and Walter 1990)

Eocene:
The climate was tropical, and a subtropical coal-swamp and warm water fauna developed. During the Eocene the transgression reached its maximum extension. The Ypresian clays were deposited in the Belgian basin. On the bordering mainland in the south, lateritic erosion and extensive Kaolinisation developed (Schmidt and Walter 1990). During this epoch the Soignies and Tournai clays were deposited on the border of the Ardennes-continent.

Oligocene:
A second transgression occurred. The climate became cooler (Schmidt and Walter 1990). The Kruibeke clay was deposited in a tidal environment. Towards the end of this epoch the sea retreated to its present location. During the following Miocene short invasions of the Belgian coast still occurred whereas the Ardennes were definitely uplifted (Schmidt and Walter 1990).

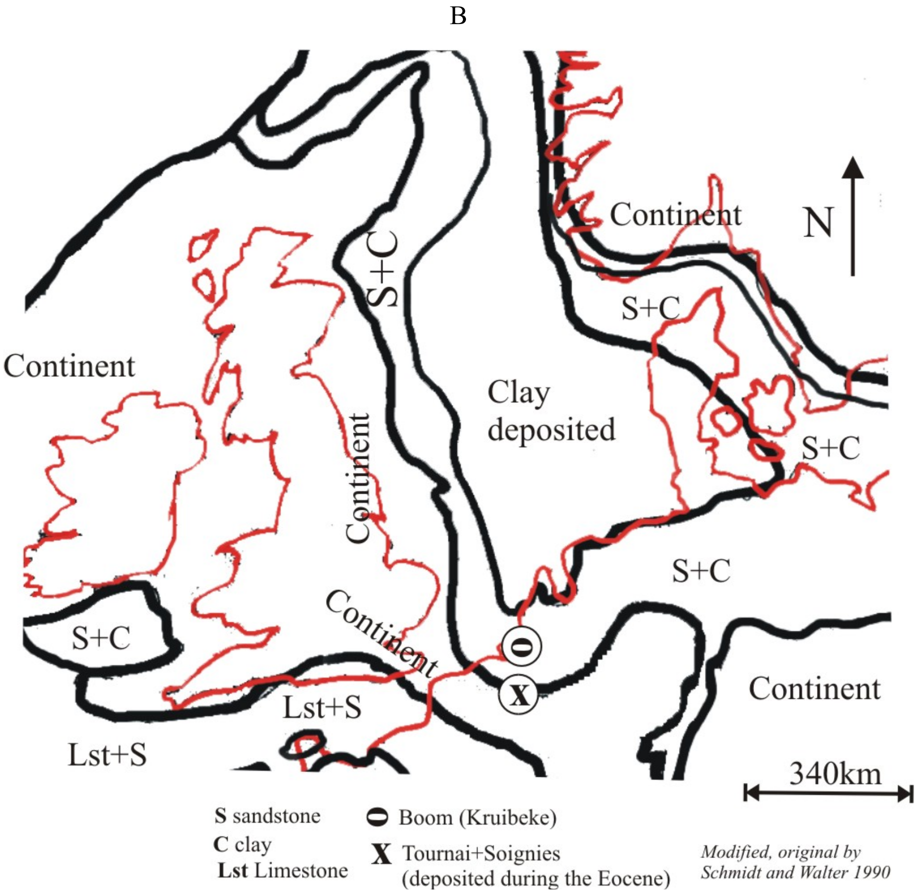


Figure: B2-1.

Distribution of land and sea in Europe during the Oligocene. In this figure the northern part of the European continent is shown at the time the Soignies and Tournai clays accumulated. In Belgium (except the emerging Ardennes), the Netherlands, northern Germany and Denmark large amounts of clays became deposited. The sand fraction in the clays increased towards inshore depositional environments.

B

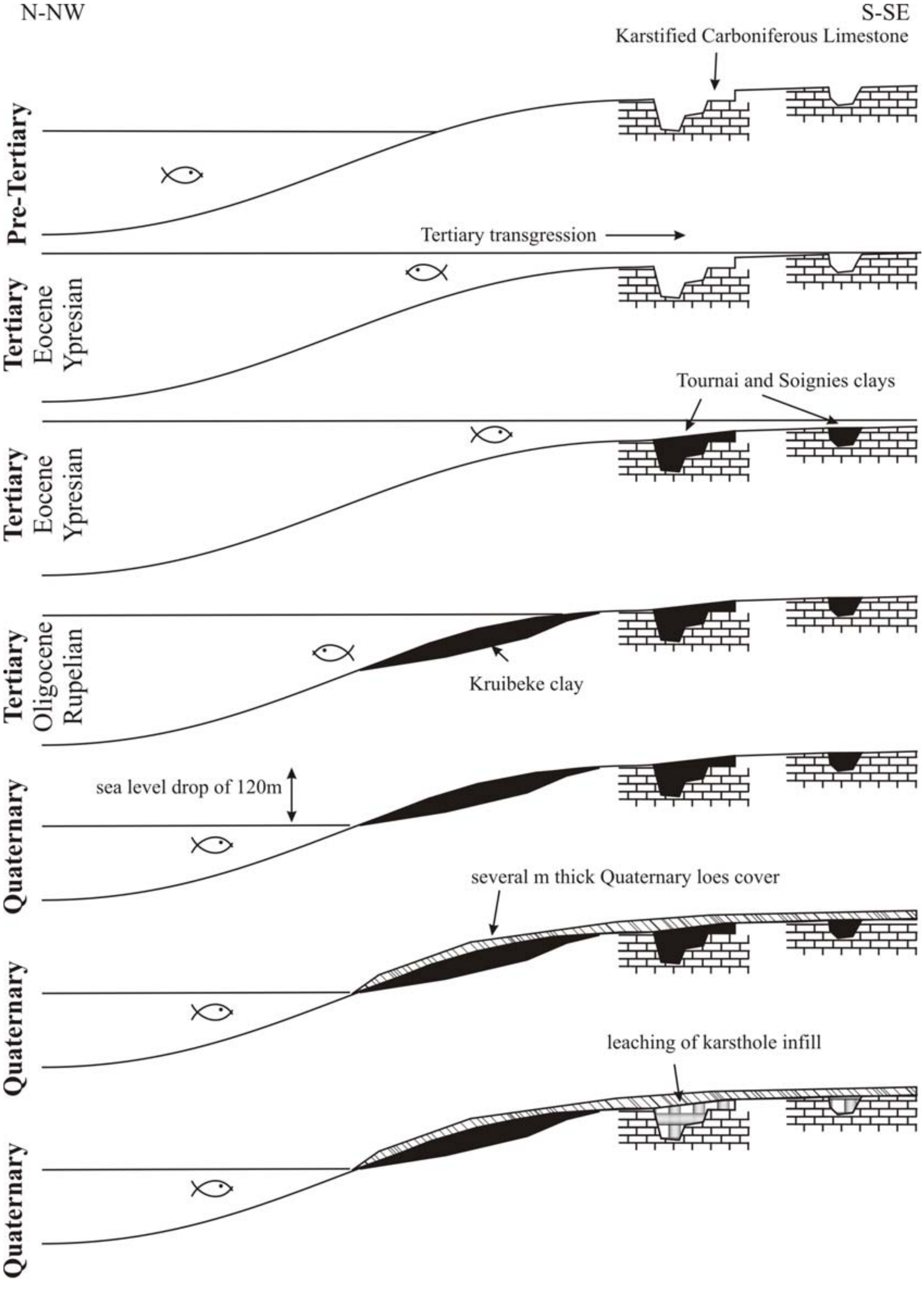
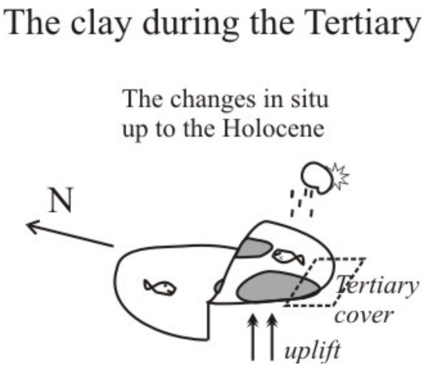


Figure: B2-2.

Overview of the transgressions and regressions of the Tertiary sea at the location of present Belgium. At this date the Ardennes formed the continent in the South. Its northern margins were covered by the sea. Soignies and Tournai clays were deposited near the coast in a previous karstified area invaded by a transgression. The Kruibeke clay was deposited more off-shore (PC Thorez).

B 2.3 The changes *in situ* up to the Holocene



Keywords: Loess, leaching.

From the Tertiary to the Holocene:

Soignies and Tournai clays:

After the clays were deposited a regression followed. Next the clays were covered by an extended Quaternary loamy (loessic) cover, with originally up to 20% of calcite. The thickness of this cover was at maximum 2-3 m (see **Figure: B2-3**). No other material covers Soignies or Tournai clays. Due to leaching the Ca^{2+} ions of the loess replaced the remaining Na^+ cations in the Smectite thereby completing the transformation of the original Na-Smectite into Ca-Smectite (**Figure: B2-3**). Therefore, the Soignies and Tournai clays excavated at present day contain Ca-Montmorillonites.

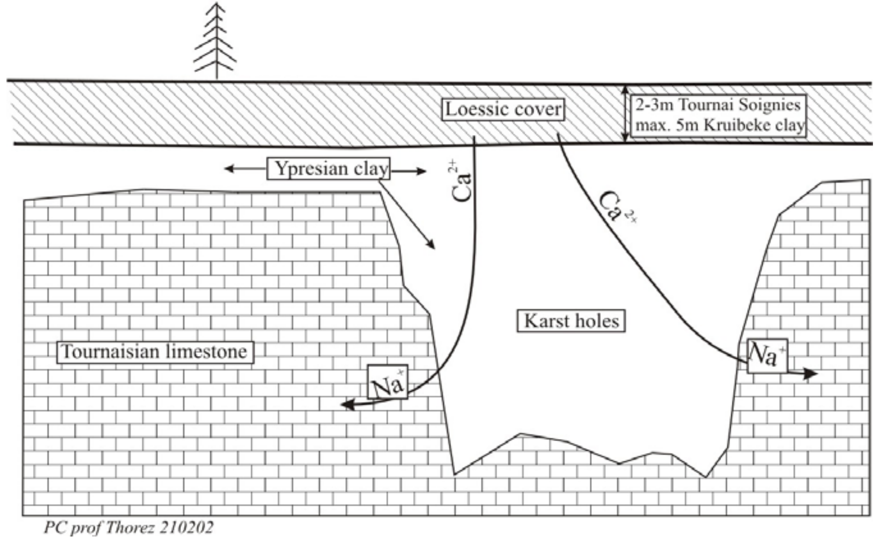


Figure: B2-3.

The Smectite of the Ypresian clay, a neoformed volcanogenic Na-Montmorillonite, was deposited in karst holes of the Tournaisian limestone. Loessic deposits, with originally a carbonate content of 20% up to 40%, covered these clays.

Kruibeke clay:

Similar to the depositional history of Soignies and Tournai clay, a regression followed the deposition of Kruibeke clay. The cover of Quaternary loessic sediments has never been thicker than 5m (PC Thorez). There has been no (leaching) alteration of the clay since the deposition: In Kruibeke clay there still occurs salt water from the Rupelian sea.
The formation to which the Kruibeke pit belongs, outcrops near Antwerp. In the underground laboratory (SCK-CEN) in Mol the formation can be found at 200 m depth. Here the clay from the same formation is known as the Boom clay (see **Figure: B2-4**).
In geomechanical engineering there are several clays that have gained legendary status, like *e.g.* the London, Boom, Opalinus and Pot clays. The Boom[24] clay belongs to the same formation as the Kruibeke clay. Boom clay samples that are often used in today's publications originate from the geomechanical laboratory below Mol at 230m depth. The Kruibeke clay was obtained in a quarry near Antwerp. Nevertheless, one can raise the question: Is the Kruibeke clay a Boom clay?
Like Kruibeke clay and Boom clay, Soignies and Tournai clay originate from the same formation. Soignies and Tournai clay, both Tertiary Eocene Ypresian clays, have completely different geomechanical properties (see *e.g.* **Figure: B3-6**). This shows that if two clays are considered that originate from an identical geological formation they do not necessarily have similar geomechanical properties.
Although both, the Boom and the Kruibeke clay, were deposited at the same time (29-34 million years ago):
1) Kruibeke clay and the Boom clay at Mol are located at different depths and reflect differences related to this: The one near to the surface faced surface erosion (exposure to weather, leaching), the other one at depth compaction.
2) The distance between Mol and Kruibeke is ~70 km. The clays were deposited in the same region but not exactly at the same spot; one clay may have been more influenced by tidal environmental influences than the other one. Conclusion: Kruibeke like Boom is a name for a clay material; both are obtained from the same formation but have like Soignies and the Tournai clay different geomechanical properties.

Taking these differences into account the Boom clay from the underground research laboratory in Mol could reflect the initial state of *e.g.* mineralogy and the pore water composition of the Kruibeke clay. The mineral composition and Atterberg properties of both clays have been given in **Table: B2-2**.

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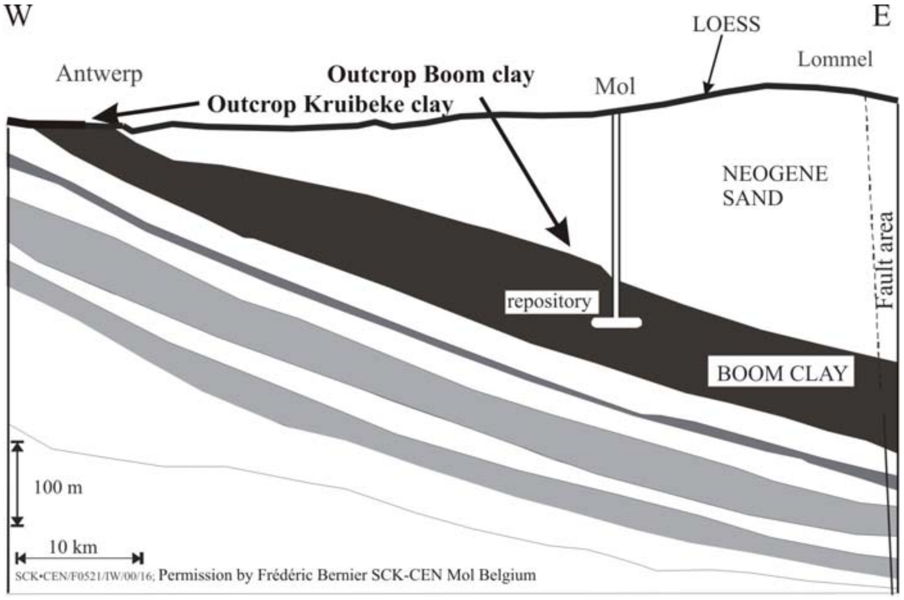
[24] *Boom is a village in Belgium next to the river Rupel, near Antwerp, century old centre of brick industry.*



SCK•CEN/F0521/IW/00/16; Permission by Frédéric Bernier SCK-CEN Mol Belgium

Figure: B2-4.

Is the Kruibeke clay a Boom clay? Both, the Kruibeke clay and the Boom clay, belong to the same formation (marked in black). The difference in post-depositional history, the proximity of the Kruibeke clay to the atmosphere, led to some geomechanical differences between Kruibeke and Boom clay.

Table: B2-2

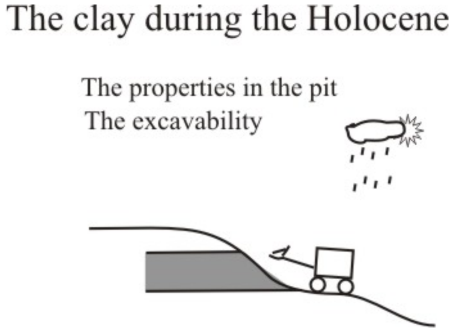
Comparison of index tests and clay mineralogy of the Boom clay at the underground laboratory in Mol and Kruibeke clay.

Clay type	LLcasa (%)	PI (%)	CF_{Illite}^{FOA} (%)	$CF_{(10\text{-}14c)}^{FOA}$ (%)	$CF_{(10\text{-}14m)}^{FOA}$ (%)	CF_{SmAl}^{FOA} (%)	$CF_{Kaolinite}^{FOA}$ (%)	$CF_{Chlorite}^{FOA}$ (%)	TCF^{TRP} (%)
Kruibeke clay average	63	34	28	18	17	5	13	19	71
Boom clay (Mol)	70	41	53	14	10	0	10	13	78

Except for the amount of Illite the mineral composition of the Boom clay and the Kruibeke clay are comparable. In the Kruibeke clay the Illite content is smaller: K^+ cations have been leached out and therefore the Smectite content (10-14m) is higher than in the Boom clay. This opening of the interlayers by the removal of K^+ cations allowed other substances to enter, thereby the Sm_{Al} and (10-14c) content was increased. In total this results in an EBS (equivalent basal spacing, see chapter **C 5**) that is a little higher for the Boom clay from Mol than for the Kruibeke clay, therefore the liquid limit (LL) is a little higher as well.

B 3 The clay during the Holocene

B 3.1 The clay mineralogy and other properties *in situ*



Keywords: Atterberg limits, grain size distribution of the natural samples.

B 3.1.1 Resources and reserves

Clays in Flanders (Kruibeke):

The Kruibeke (Rupelian, Tertiary) clay has a wide regional extension due to the original deposition conditions. Furthermore, it is characterised by a more uniform clay mineral composition and grain size. In Flanders, especially close to the border to the Walloon region, Tertiary marine sediments with a high amount of clay fraction are extracted at many places. The material is mainly used for production of bricks. Sedimentological and paleogeographical conditions seem to indicate large reserves compared to the material of the same age in the Walloon region. The mineralogy is also more homogeneous. The Tertiary clays consist of Illite, Smectite, Kaolinite, Chlorite and various mixed-layer clays (ManWal 2000). The clayey material is at present extensively mined.

Clays in the northwestern Walloon region (Soignies and Tournai):

The upper Ypresian forms the major part of the hills in Flanders, Brabant and in northern Hainaut. It consists of glauconite sands with intercalations of plastic clay. Towards the base clayey sand and sandy clays with regular interstratifications are found. The oldest unit consists of compacted plastic clays (lagoonal facies, Waddenzee deposit) with sandy intercalations. The lower Ypresian is found in the central and southern parts of the provinces West- and East-Flanders and in some parts of Hainaut. The lower Ypresian of Belgium and the north of France form one unit. This formation consists of fine clayey sand and compacted sandy clay at the base. The sand and the clay deposits of the lower Ypresian are not perfectly separated: Generally there is a transition consisting of a sandy micaceous clay zone or a zone with alternating clay and sand beds. The clay content of the Ypresian increases towards the west where the Ypresian reaches a thickness of more than 180m. In Hainaut and Brabant and the Campine (Kempen) the clay content is already strongly reduced and less homogeneous due to the presence of occasionally very sandy zones. The Ypresian ends in the Hainaut region as a thin, completely sandy formation with a littoral character (Fourmarier 1954). In Tournai and Soignies the major part of Ypresian (Tertiary) clay occurs as sedimentary fillings of huge karst cavities developed into the Tournaisian (Lower

Carboniferous) limestone. The clay body has a thickness reaching several meters but appears somewhat heterogeneous, with stacked clayey and silty layers; it dips slightly to the north.

The syn- and post-sedimentary activity and the present geomorphologic conditions led to the fact that the present Tertiary deposits only have a limited extent in the Walloon region and are characterised by a variable mineralogy. Therefore in the Walloon region and the neighbouring parts of Flanders and France all clay deposits that are considered for engineering use (and maybe even all layers) have to be characterised separately by XRD analyses (ManWal 2000).

B 3.1.2 Mineralogy *in situ*

B 3.1.2.1 Method

The mineralogy was determined at the Liège Clay Laboratory using a modified sample preparation (ManWal 2000) by analysing the total clay mineral fraction and not only the fraction smaller than 2 micrometer (see (SP-XRD 2004)). This method is called FOA (forced oriented aggregate). With the FOA the different clay species can be identified. Additionally the TRP (total random powder, an XRD plot of a non-orientated clay sample) is determined for each sample in order to analyse the non-clay minerals and the amount of clay material in the sample.

B 3.1.2.2 General mineral content of Kruibeke, Soignies and Tournai clay

All these samples contained (see **Table: B3-1**) a similar clay composition that comprises: Illite, a neoformed volcanogenic Montmorillonite, also some non-swelling random mixed-layers composed of Illite layers and Chlorite interlayers (10-14c) and natural pillared Smectites occur with Al-hydroxides in the interlayers, (Sm_{Al}), minor Chlorite and Kaolinite occurs in Kruibeke and Soignies clay materials. The Montmorillonite does not correspond to a pure mineral species but matches better to a random mixed-layer Illite-Montmorillonite (10-14m), wherein the Montmorillonite component is predominant. The v/p method (Thorez 1976) shows that the Montmorillonite does not fully expand to or near 100% (as a pure mineral) but to a maximum of 65%.

Table: B3-1

Average mineral composition of the natural Soignies, Kruibeke and Tournai of the first and second sampling.

Clay type:	CF_{Illite}^{FOA} (%)	$CF_{(10\text{-}14c)}^{FOA}$ (%)	$CF_{(10\text{-}14m)}^{FOA}$ (%)	CF_{SmAl}^{FOA} (%)	$CF_{Kaolinite}^{FOA}$ (%)	$CF_{Chlorite}^{FOA}$ (%)	TCF^{TRP} (%)
K_{nat} average	30,5	17,5	14,7	0	26,1	11,2	70,3
T_{nat} average	20	6,2	67,8	5,1	0,9	0	76,5
S_{nat} Average	39,5	22	13,5	0	21	4	50,6

Next to quartz other non-clay minerals are only present in small quantities. Other non-clay minerals present are:

In all three clays:
- A small amount of framboidal bacterial pyrite, (in Kruibeke only in natural state) formed during diagenesis (PC Anceau)
- Gypsum (few % of the TRP)
- Feldspars (few % of the TRP)
- Dolomite (few % of the TRP, most in Soignies clay)
- Calcite (several % of the TRP)

Only in Tournai clay:
- A small amount of the zeolite mineral clinoptilolite (traces)

Only in Soignies and previous batch Kruibeke clay:
- Cristobalite (few % of the TRP)

B 3.1.2.3 Example of an XRD-diagram

In **Figure: B3-1** a general XRD plot of Tournai clay is given. The X-ray diffraction analysis of the untreated (natural) Tournai clay, the Tournai clay exposed to ethylene glycol (EG) and the Tournai clay heated to 500°C show the following results:
In the natural state a large peak at 14 Å and a peak at 10 Å are clearly visible. Upon saturation with ethylene glycol the 14 Å peak shifts to 17 Å and collapses upon heating. This characterises a Smectitic behaviour. In all three states the 10 Å peak rests at its place; this corresponds to an Illite. The peaks between 10-14 Å and 17 Å that remain stable (at 14 Å) upon heating correspond to a mixed-layer Illite-Chlorite (10-14c) and a Smectite with pillars in the interlayer spaces (Sm_{Al}) respectively.

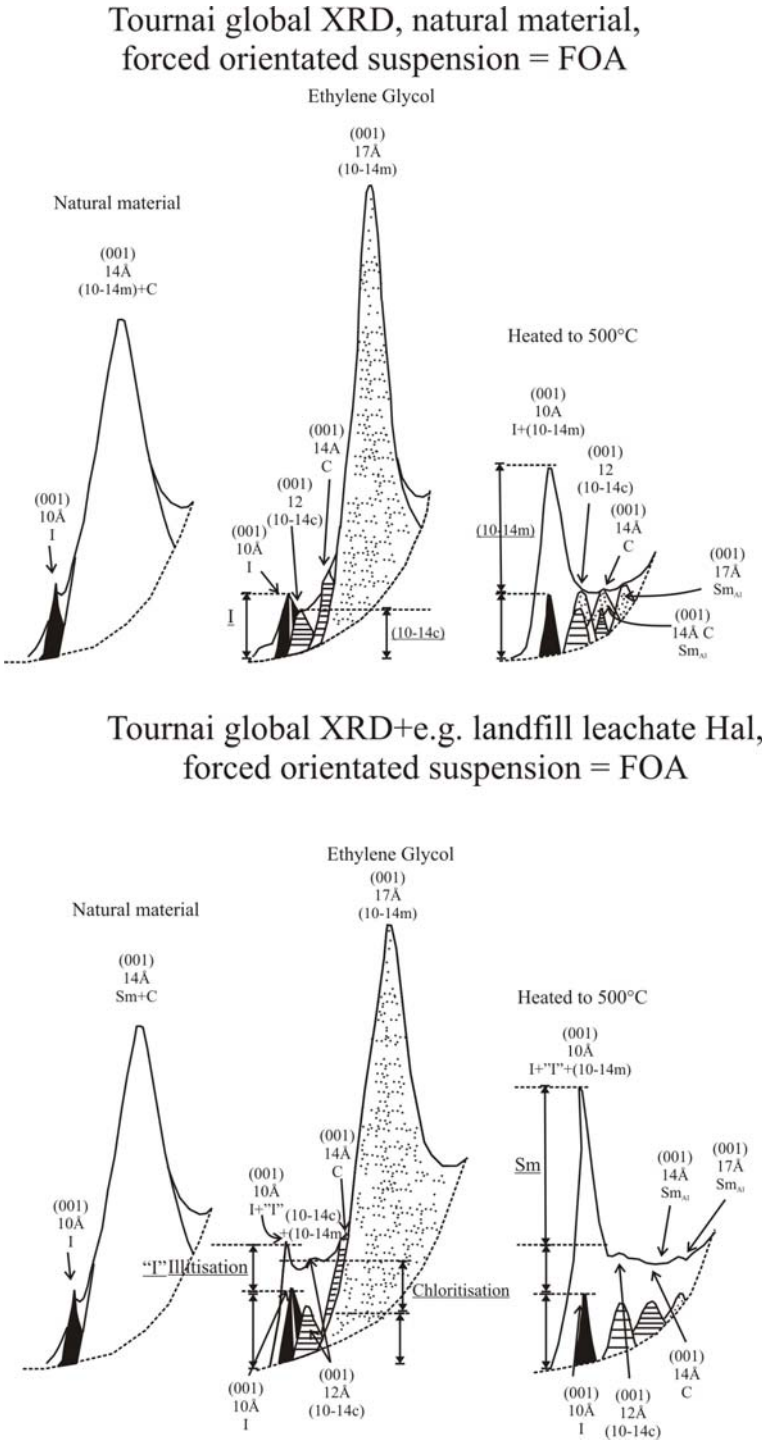


Figure: B3-1.

Semi quantitative analyses of the forced oriented aggregate (FOA) of the Tournai clay and the Tournai clay after contact with landfill leachate. In the figure the processes of Illitisation and Chloritisation are indicated. Note that by the Illitisation processes an open Illite, "I", is formed by the partial collapse of the interlayer spaces (by K^+ cations) of the Smectite, and that this process is reversible. The apparent Chloritisation is partially caused by the collapse of the Sm_{Al}, the Smectite with pillars in the interlayer spaces.

B 3.1.3 Geochemistry part I, *in situ*

The fluid phase of the clays squeezed-out at high pressure is analysed in order to determine:

- If the composition of the natural pore water of the clay will change due to a change in the chemical environment (*in situ* → exposure to air) during exposure in the pit and storage.
- If there are fundamental differences between the fluid contained in the three clays.
- The possible impact of landfill leachates on the clay and its geochemistry during the following stages in the life of clay.
- If the clay is in equilibrium with its pore water in the outcrop in the quarry.

The chemical composition of the altered fluid phase of the natural clay was obtained by squeezing the sample at high pressure (10 MPa). In **Figure: B3-2** the values of the squeezed-out clay-fluids are compared. Soignies clay contains the highest amount of ions of all measured fluids:
- From the values of the conductivity, resistivity, total amount of ions and cations it can be observed that: >[ions] in the order S>>K~T
- The pH increases in the order S<<T<K (**Table: B3-2**)

Only in the squeezed-out fluid of Kruibeke clay SiO_2 can be found (the origin of this mineral is discussed in paragraph **B 3.4.3**). The squeezed-out fluid of Soignies clay certainly contains much more ions and has a very low pH compared to the two other clay types (see **Table: B3-2**).

Table: B3-2

pH of the squeezed-out fluid of the natural clays.

Clay type	pH squeezed-out clay-fluid
Knat	4.5
Snat	2.2
Tnat	3.0

The pH of the pore water of all the three squeezed-out clay-fluids is very low. Is there an explanation for the low pH?
Hypothesis:

a) The clays have been deposited $30 \cdot 10^6$ years ago in an acid environment and have retained their original fluid phase.
b) The original fluid phase has been changed in the undisturbed material before anthropogenic activity started. Even if the hydraulic conductivity of the Soignies clay formation were as low as $1 \cdot 10^9$ m/s, surface fluids could arrive at the level where the clay was excavated, tens of meters below the surface, within short time delay on a geological scale.
c) The original fluid phase has been exposed to the present day's atmosphere (rainfall) because it outcrops due to the mining activity.
d) The squeezing method used to extract (by squeezing out the clay-fluid) causes changes or extracts more than the free fluid (Q_{II}) alone.

- Why to reject a):

A low pH of 2 as in the case of Soignies clay could cause degradation of the clay minerals themselves. During $30 \cdot 10^6$ years this would have caused degradation of all clay minerals.

- Why to reject b):

The time needed for fluids to penetrate from the surface to the clay at excavation depth (in the absence of a fracture system) is in the order of thousands of years (before the industrial revolution). Taking the local history into account it is not very likely that a concentrated acid penetrated the soil.

- The plausibility of c) and d) will be analysed in paragraph **B 3.4.3** and **B 3.6.2.4**.

Conclusion

The extreme acid values measured in the clay can be caused by the change in chemical "regime" due to the exposure to the Quaternary atmosphere:

It is known that such alterations can occur during the *in situ* exposure of the clay to the atmosphere at the excavation front, during storage and transportation to the construction site. Therefore the request that XRD analyses are made during excavation and just before construction is implemented into the new manual for landfill construction in the Walloon region (ManWal 2000).

B 3.2 The excavability *in situ*

Keywords: Liquid limit, natural fluid content.

Excavability and other aspects of the deposits

Only the excavability of the two Ypresian clays (Tournai and Soignies clays) is discussed because the Kruibeke clay was excavated before the arrival of the author and no data are available about its acquisition.

In the quarries from which the Tournai and Soignies clays were obtained limestone (Crenoid) of Upper Tournaisian age is actively mined. This limestone is better known as “Petite Granite” and is used in wide parts of Europe for ornamental purposes (have a look at your window sill).

The Soignies clay was more difficult to excavate than the Tournai clay. The Soignies clay could not be excavated using shovels because the material stuck to the equipment. Therefore the sample material was sampled with bare hands. The Tournai clay sample material was collected using a mechanical shovel. This material was subsequently manually filled into plastic buckets. If only the natural fluid content is considered (see **Table: B3-3**) it seems to be controversial that the Soignies clay was more difficult to handle than the Tournai clay.

Table: B3-3

Natural fluid content of Soignies and Tournai clay in situ.

Clay type:	W_{nat} (%)
Soignies	31
Tournai	65

If one takes a look at the values of the liquid limit, one is able to observe that the Soignies clay is expected to be more slurry-like, because its natural fluid content is nearer to its liquid limit (see **Table: B3-4**), under field conditions compared to the Tournai clay.

Table: B3-4

*Excavability of Soignies and Tournai clay expressed as the ratio of the natural fluid content and the liquid limit (extract from **Table: B3-8** and **Table: B3-3**).*

Clay type:	LL (%)	PI (%)	W_{nat}/LL
SEF1;X	38	19	0.82
TEF1;X	128	84	0.51

This simple example illustrates once again the value of the Atterberg limits. Note the following remark by Capper and Cassie (1963): "Except at the surface natural clay deposits have a moisture content between the plastic and the liquid limits". For the two examples presented here this can be validated.

The value of the consistency index can be related to a description of *e.g.* the excavability on the bases of experience *e.g.* see DIN 18 122 (see **Table: B3-5**).

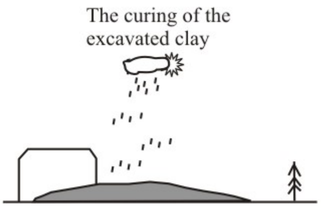
Table: B3-5

Excavability of Soignies and Tournai clay expressed in terms of the consistency index.

Clay type:	I_C (%)	description based on I_C value (Bell 1998)
Soignies	0.36	pulpy soil; easily penetrated to several centimetres by thumb
Tournai	0.75	firm, stiff soil; cannot be moulded in the fingers

This description coincides exactly to the situation that was experienced in the field.

B 3.3 The curing of the excavated clay



The clay during the Holocene

Keywords: Exposure to atmosphere, expulsion of natural fluid phase of clays.

Once the clay is excavated it will be stored unavoidably on the mining site or on the construction site. The changes that occur when Tertiary clay like Tournai clay is exposed to the Quaternary atmosphere will be discussed in this section.

Atterberg limits

Clays were exposed to present and simulated atmospheric conditions:

a) Clays were exposed to a sea climate (a climate similar to which the clay will be exposed in the quarry and on the landfill liner construction side) during a Belgian summer and autumn.
b) Clays were exposed to a sea climate during two Belgian summers, autumn, winter and spring.
c) Clays were exposed to simulated tropical conditions: One month at 50°C, with a constant moisture content equal to the natural fluid content of the clay.

Table: B3-6

The changes in Atterberg limits of Tournai clay if exposed to atmospheric conditions.

Exposure to:		LL (%)	PL (%)	PI (%)
Natural samples	$T_{nat}F$	96.0	46.0	50.0
Tropical conditions	$T_{nat}C;1$	112.6	50.7	61.9
Sea climate during one summer and one autumn	$T_{nat}F;6out$	131.6	65.1	66.5

Table: B3-7

The changes in Atterberg limits of Tournai clay if exposed to atmospheric conditions, compared to the LL of the natural clay (in fact the least exposed clay).

	The induced changes are expressed in terms of the original Atterberg properties	Sea climate summer autumn	Tropical conditions
Tnat	$LL_{exposure}/LL_{nat}$	1.37	1.17
	$PI_{exposure}/PI_{nat}$	1.33	1.24

Tournai clay:
The exposure causes an increase of the liquid limit and the plasticity index (see **Table: B3-6** and **Table: B3-7**). The change is large; the points lie outside the range (range = mean plus twice the standard deviation). The long-term exposure to the sea climate causes more changes than the exposure to tropical conditions.

If one interprets the increase in liquid limit with the concept of equivalent basal spacing (see chapter **C 5**) the increase in liquid limit in the case of exposure of Tournai clay to the atmosphere would indicate an opening up of the interlayer space (of any but not specified clay fraction). The only comparable (unpublished) experience with this matter was obtained in the Belgian brick industry (PC Thorez): Common practise was to leave the clay material after excavation outside for 1 to 6 months. This improved the quality of the bricks. But this aspect has never been analysed thoroughly.

B 3.4 The homogenised natural Tertiary clays

Keywords: Drying, grinding effect on Atterberg limits.

B 3.4.1 Introduction

Once the clay has been excavated it will be transported and stored at the construction site. Next the clay will be homogenised to different degrees in-plant or on-site *i.e.* open air. This pre-treatment includes the grinding of large lumps and the drying or wetting to obtain a fluid content near to the optimum fluid content. This was simulated in the laboratory by drying (30°C) and grinding the clay.

B 3.4.2 Atterberg properties and other properties of the homogenised natural clay

B 3.4.2.1 Atterberg properties

In **Table: B3-8** and **Table: B3-9** the Atterberg values of the standard clay samples after homogenisation are given:

Table: B3-8

Index test data (mean, standard deviation, coefficient of variation and natural heterogeneity) of the homogenised Tournai, Soignies and Kruibeke clays in contact with demineralised water.

Atterberg values standard samples		Mean (%)	COV (-)	S (%)	S_{rp} (%)	S_h (%)	C_{vh} (-)	$S_{h/}S$ (-)	Based on N° of samples:
TEF1;X	LL	128	0.06	7.91	4.86	6.24	0.049	0.79	11
	PL	44	0.12	5.24	1.79	4.92	0.11	0.94	11
	PI	84	0.06	4.65	3.24	3.33	0.040	0.72	11
KEF1;X	LL	60	0.03	1.69	2.35	x (3)	x (3)	x (3)	10
	PL	29	0.07	1.96	1.22	1.54	0.054	0.78	10
	PI	31	0.06	1.80	1.30	1.24	0.040	0.69	10
SEF1;X	LL	38	0.04	1.57	1.58	x (3)	x (3)	x (3)	9
	PL	20	0.05	0.98	0.89	0.42	0.022	0.43	9
	PI	19	0.09	1.74	0.86	1.51	0.080	0.87	9

Table: B3-9

Index test data of the homogenised Tournai, Kruibeke and Soignies clays with the 90% confidence interval (Data-set ***Table: B3-8****).*

Clay type:		Mean-2S	Mean	Mean+2S	Position with respect to A-line PI=0.73·(LL-20)
TEF1;X	LL (%)	112	128	144	Above
	PI (%)	75	84	93	
KEF1;X	LL (%)	57	60	63	Above
	PI (%)	27	31	35	
SEF1;X	LL (%)	35	38	41	Above
	PI (%)	16	19	22	

B 3.4.2.2 Grain size distribution

The grain size distributions of the Tournai, Kruibeke and Soignies clay after homogenisation are presented in **Table: B3-10**.

Table: B3-10

Grain size distribution of homogenised clay.

Tertiary homogenised clay	Clay size [<0.002mm] (% total mass)	Silt [0.002-0.06mm] (% total mass)	Sand [0.06-2mm] (% total mass)	Gravel [2-63mm] (% total mass)
T_{pow}	53.4	39.2	7.4	0
K_{pow}	23.7	59.8	16.6	0
S_{pow}	20.8	48.2	31	0

B 3.4.2.3 Activity of standard samples

In **Table: B3-11** the activity of the homogenised samples has been determined according to Skempton (1953) and is calculated as the ratio of plasticity index and percentage of the mass smaller than 0.02 mm.

Table: B3-11

The activity (Skempton 1953) of the homogenised Tournai, Kruibeke and Soignies clay (Data: ***Table: B3-9*** *and* ***B3-10****).*

Tertiary homogenised clay	Activity (-) homogenised clay
TEF1;X	1.6
KEF1;X	1.3
SEF1;X	0.91

B 3.4.2.4 Methylene blue adsorption values of standard samples

In **Table: B3-12** the methylene blue values for the Tournai, Soignies and Kruibeke clays are given. In absence of a large group of standard samples the values for the samples tested with various leachates are given. The COV is fairly low, therefore the average values will be considered to be standard MBA values for the Tournai, Kruibeke and Soignies clay.

Table: B3-12

The mean, coefficient of variation and standard deviation of the methylene blue adsorption values of the homogenised Tournai, Soignies and Kruibeke clay.

MBA (g/100g)	Mean (g/100g)	COV (-)	S (% W_c)	Based on N° of samples
T(E,O,H,M)(C,F)(0.5,1,2);1	15	0.070	1.04	19
K(E,O,H,M)(C,F)(0.5,1,2);1	5.3	0.082	0.43	20
S(E,O,H,M)(C,F)(0.5,1,2);1	2.8	0.042	0.12	19

B 3.4.2.5 Classification of the homogenised clays

Although many different soil classification systems are used by various institutions, most of these classification systems are based on the outcome of particle size distribution analyses and the results of the plasticity charts of Casagrande (Douwes-Decker 1991). **Table: B3-13** gives the classification of the three clays.

Table: B3-13

The classification into clay groups according to DIN and BS of the homogenised Tournai, Soignies and Kruibeke clay and their 90% confidence interval (Data-set ***Table: B3-8****).*

Tertiary homogenised clay	DIN 18196 (1)	BS 5930 (2)
TEF1;X ± 2S	TA: Distinct plastic clay	CE: Extremely plastic clay
KEF1;X ± 2S	TA: Medium plastic clay	CH: Clay of high plasticity
SEF1;X ± 2S	TM: Medium plastic clay	CI: Clay of intermediate plasticity

DIN and BS standards are described in (1) Wendehorst 1996 and (2) Douwes-Decker 1991.

If one compares the values of the index properties of the standard or near standard samples described above one can get an impression of similar clays whose mineralogical composition has been described in literature (see **Table: B3-14**).

The mineralogy obtained via the index tests based on literature does not correspond to the measured mineral content; therefore another tool (equivalent basal spacing) has been developed to link mineralogy to geomechanical index tests. This will be discussed in **Part: C**.

Table: B3-14

Attempts in existing literature (before introduction of the EBS (Schmitz et al 2002) to predict the clay mineralogy of the Tournai, Soignies and Kruibeke clay on the basis of literature (Using data ***Table: B3-8****,* ***Table: B3-10*** *and* ***Table B3-12****.*

Clay type - fluid combination	Bell 1998 (LL)	Matula et al. 1979 (PI)	Skempton 1953 (Activity)	Selby 1993 LL, PL, Activity, MBA)	Stapel en Verhoef 1989 (MBA)	The sample contains most likely the following clay mineral
TEF1;X T_{pow} T(E,O,H,M)(C,F)(0.5,1,2);1	Extra high plasticity	Extremely plastic	Active clay (e.g. Smectite)	Montmorillonite Allophane Halloysite	Bentonite	Bentonite
KEF1;X K_{pow} K(E,O,H,M)(C,F)(0.5,1,2);1	High plasticity	Highly plastic	Active clay (e.g. Smectite)	Kaolinite Illite Halloysite	Bentonite	Bentonite
SEF1;X S_{pow} S(E,O,H,M)(C,F)(0.5,1,2);1	Intermediate plasticity	Highly plastic	Normal clay (e.g. Illite)	Halloysite Kaolinite	Kaolinite	Kaolinite

B 3.4.3 Geochemistry part II, the homogenised clay

B 3.4.3.1 The pH (Brønsted) of the homogenised clay

The homogenisation process of the clays involves among others the drying of the clay. To analyse the chemistry and to measure the pH of such a clay powder three methods were applied:

i) In order to obtain a slurry with a fluid content equal to twice the value of the liquid limit of the clay in question, an appropriate dosage of demineralised water was added to the dried clay powder. Next the slurry was cured during one month. During this month the particles settled and the pH of the surplus fluid could be measured. This value of the pH is called: pH of the contact fluid (see **Table: B3-15**). This pH value is corrected for the difference between the fluid content of the contact fluid and that of the natural clay.

ii) Addition of demineralised water: 10g of the clay powder were mixed with 50g (approx. 50ml) demineralised water or with a diluted $CaCl_2$ solution[25]. This suspension was mixed during one hour, after that the pH was measured. This

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[25] *The measurements were done according to ASTM D4972 except that 10g air dry soil was mixed with 50g fluid and not the prescribed 10g of fluid because a soil to fluid ratio of 1:1 creates a slurry to dense to measure the pH.*

value of the pH is called: pH of the remnant fluid phase of the natural clay (see **Table: B3-16**). The measured pH value is corrected for the difference between the fluid content of the suspension and that of the natural clay.

iii) The homogenised clay was stored with a liquid, *e.g.* demineralised water during one month. Subsequently the clay was air-dried at ambient temperature and the pH was determined according to ii (see **Table: B3-17**).

Table: B3-15

This table shows the pH of the Tournai, Kruibeke and Soignies clay after homogenisation (drying at 30°C and subsequent grinding). To measure the pH the contact fluid method (i) was used. In the second column the measured pH is given, in the last column the pH is given at the natural fluid content of the clay.

Clay type	pH of the contact fluid	$[H^+]$ (mol/l)	Actual fluid content (%) (1)	Natural fluid content (%)	Multiplication factor $[H^+]$ at natural fluid content	Corrected $[H^+]$ (mol/l)	Corrected pH → pH at natural fluid content
KEF2;1	3.2	$6.31\cdot10^{-4}$	134	40	3.35	$2.11\cdot10^{-3}$	2.7
SEF2;1	6.9	$1.26\cdot10^{-7}$	73.7	31	2.38	$3.00\cdot10^{-7}$	6.5
TEF2;1	7.4	$3.98\cdot10^{-8}$	267	65	4.11	$1.64\cdot10^{-7}$	6.8

(1) fluid content is calculated from the known amounts of clay and fluid added

Table: B3-16

This table shows the pH of the Tournai, Kruibeke and Soignies clay after homogenisation (drying at 30°C and subsequent grinding). The pH was measured on a diluted suspension of Tournai, Soignies or Kruibeke clay in demineralised water (method ii). In the second column the measured pH is given. In the last column the pH is given at the natural fluid content of the clay.

Clay type	pH clay powder	$[H^+]$ (mol/l)	Actual fluid content (%) (1)	Natural fluid content (%)	Multiplication factor $[H^+]$ at natural fluid content	Corrected $[H^+]$ (mol/l)	Corrected pH → pH at natural fluid content
Kpow	4.33	$4.68\cdot10^{-5}$	525	40	13.1	$6.13\cdot10^{-4}$	3.2
Spow	7.33	$4.68\cdot10^{-8}$	510.8	31	16.5	$7.72\cdot10^{-7}$	6.1
Tpow	8.34	$4.57\cdot10^{-9}$	576	65	8.86	$4.05\cdot10^{-8}$	7.4

(1) fluid content is calculated from the known amounts of clay and fluid added

Table: B3-17

This table shows the pH determined according to method (iii). The measured pH values were corrected for the difference between the fluid content of the suspension and that of the natural clay. Results have been separated into the measurements obtained with a dilute $CaCl_2$ solution and the measurements obtained with demineralised water.

Clay type	Corrected pH at natural fluid content (10:50H2O)+ (10:50CaCl$_2$)				Corrected pH at natural fluid content pH (10:50H$_2$O)				Corrected pH at natural fluid content pH (10:50CaCl$_2$)			
	Mean	S	COV	N	Mean	S	COV	N	Mean	S	COV	N
KEF (0.5,1,2);1	2.20	0.12	0.05	6	2.11	0.06	0.03	3	2.30	0.06	0.03	3
SEF (0.5,1,2);1	3.03	0.61	0.20	6	2.90	0.65	0.23	3	3.16	0.66	0.21	3
TE(C,F) (1/2,1,2;(1,2)	6.91	0.11	0.02	16	6.96	0.13	0.02	8	6.86	0.07	0.01	8

Observations related to the comparison of the three methods to measure the pH of the homogenised clay:

- H^+ ions survive the homogenisation process, which consists of drying and grinding.
- Except for Soignies clay the three different methods give comparable results. The difference related to the pH of the dried slurry after leachate contact (method iii) provides an indication of processes that intervene and are developed during storage. These processes are the most prominent for Soignies clay: One noticed a drop of pH nearly back to the original value (*i.e.* pH of the natural clay). This is possibly related due to desorption of H^+ protons.
- Independent of the method used to measure the pH of the Tournai, Soignies or Kruibeke clay, the pH was lower than that of the landfill leachates (see **Table: B3-26** for the pH values of the landfill leachates which all have a pH > 7.9). Note that a low pH could affect the geomembrane in contact with the clay barrier. A question that can be raised is if this low pH of the Tournai, Soignies and Kruibeke clay is normal. In general in central Europe the pH of the groundwater is higher (between 5-8), depending on the soil/rock type (Vogelsang 1988). But cohesive soils like clay contain next to the clay minerals other substances that can react with leachates like: carbonates, organic substances, iron oxide and iron hydroxide, sulphates and sulphides (Holzlöhner and Meggyes 1998), marcasite and pyrite that are common in clay sediments (Vogelsang 1988). Exposure in outcrops causes H_2SO_4 to form which results in extremely acid soils, pH = 2.5 is common (Jackson 1964). Thus, such a low pH can occur and it should be recommended (Holzlöhner and Meggyes 1998) to limit the amount of sulphides and sulphates in the clay.

B 3.4.3.2 The pH (Brønsted) of the homogenised clay compared to that of the natural clay

In **Table: B3-18** the pH of the homogenised clay is compared to that of the natural clay.

Table: B3-18

pH of the natural fluid phase of the clay as a function of the extraction method used.

Sample type	Untreated clay	After homogenisation		
	pH squeezed-out clay-fluid	corrected pH → pH at natural fluid content method i)	corrected pH → pH at natural fluid content method ii)	corrected pH → pH at natural fluid content method iii)
Knat Kpow KEF2;1 KEF(0.5,1,2);1	4.5	2.7	3.2	2.2
Snat Spow SEF2;1 SEF(0.5,1,2);1	2.2	6.5	6.1	3.0
Tnat Tpow TEF2;1 TE(C,F)(1/2,1,2;(1,2)	3.0	6.8	7.4	6.9

Observations related to the comparison of the pH of the squeezed-out clay-fluid of the natural clay and the pH of the homogenised clay:

- By squeezing fluid out of the clay at high pressure more H^+ is freed from the clay than with the more subtle methods i, ii and iii (not only H^+ as is discussed in the next paragraph). Therefore the pH of the squeezed-out clay-fluid is lower than the pH of the homogenised clay, except for Kruibeke. In the latter no Pyrite was found after homogenisation (see paragraph **B 3.1.2.2**) but instead a very high SO_4^{2-} concentration (see **Table: B3-19**) indicating the complete oxidation of the pyrite fraction and further acidification of the clay-fluid due to homogenisation.
- The components of the natural fluid phase (low pH) and not the landfill leachates (high pH) must be held responsible for the processes related to a possible acid attack of clay particles during clay-leachate interaction.

B 3.4.3.3 Ions; the differences before and after homogenisation

The chemical composition of the homogenised clay was determined by analysing the surplus fluid above a homogenised clay - water slurry (method i described in paragraph **B 3.4.3.1**). This latter value was corrected for the fluid content in the natural clay. An overview of cations, resistivity and pH of the landfill leachates and the different fluids extracted from the Soignies, Kruibeke and Tournai clay is given in **Figure: B3-2** and **Table: B3-19**.

Table: B3-19

The concentrations (mg/l) of some important chemical components of several involved fluids (the contact fluid concentration has been corrected to the natural fluid content of the clays: measured concentration times 3.4 (Kruibeke) times 2.4 (Soignies) and times 4.1 (Tournai). The CEMC of leachate-H1(see ***Table: B3-29****) amounts to $2.8\cdot10^{2}$(mol/m^{3}).Leach. = leachate.*

	Leach. -C	Leach. -H2	Leach. -M	Tournai (squeezed-out)	Kruibeke (squeezed-out)	Soignies (squeezed-out)	Tournai (contact fluid)	Kruibeke (contact fluid)	Soignies (contact fluid)
pH	8.1	7.9	8.1	3.0	4.5	2.2	7.9	2.8	7.5
Ca^{2+} mg/l)	$9.4\cdot10^{1}$	$1.0\cdot10^{2}$	$1.1\cdot10^{2}$	$6.8\cdot10^{2}$	$4.6\cdot10^{2}$	$1.1\cdot10^{3}$	$6.1\cdot10^{2}$	$1.6\cdot10^{3}$	$1.1\cdot10^{3}$
Mg^{2+} mg/l)	$9.1\cdot10^{1}$	$9.3\cdot10^{1}$	$7.1\cdot10^{1}$	$1.7\cdot10^{2}$	$5.1\cdot10^{2}$	$2.3\cdot10^{3}$	$8.0\cdot10^{1}$	$2.7\cdot10^{3}$	$1.9\cdot10^{2}$
Na^{+} (mg/l)	$1.5\cdot10^{3}$	$6.1\cdot10^{2}$	$8.6\cdot10^{2}$	$7.7\cdot10^{1}$	$4.1\cdot10^{2}$	$3.9\cdot10^{2}$	$6.2\cdot10^{1}$	$2.7\cdot10^{2}$	$2.9\cdot10^{1}$
K^{+} (mg/l)	$6.1\cdot10^{2}$	$3.6\cdot10^{2}$	$5.3\cdot10^{2}$	0	$1.4\cdot10^{2}$	0	$7.2\cdot10^{1}$	1.7	$9.0\cdot10^{1}$
Fe^{3+} (mg/l)	0	0	0	$2.5\cdot10^{2}$	0	$3.0\cdot10^{4}$	0	0	0
NH_4^{+} (mg/l)	$3.1\cdot10^{2}$	$5.2\cdot10^{2}$	$1.1\cdot10^{3}$	$3.4\cdot10^{1}$	0	$3.5\cdot10^{2}$	0	0	0
SO_4^{2-} (mg/l)	$1.7\cdot10^{2}$	$1.0\cdot10^{-2}$	$1.0\cdot10^{-2}$	$2.9\cdot10^{3}$	$4.4\cdot10^{3}$	$9.0\cdot10^{4}$	$1.8\cdot10^{3}$	$1.5\cdot10^{4}$	$3.6\cdot10^{3}$
CO_3^{2-} (mg/l)	$2.0\cdot10^{1}$	$1.5\cdot10^{1}$	$3.4\cdot10^{1}$	$1.0\cdot10^{-2}$	$1.0\cdot10^{-2}$	$1.0\cdot10^{-2}$	1.2	$1.0\cdot10^{-2}$	$2.5\cdot10^{-1}$
HCO_3^{-} (mg/l)	$2.9\cdot10^{3}$	$3.2\cdot10^{3}$	$5.2\cdot10^{3}$	$1.7\cdot10^{2}$	$1.0\cdot10^{-2}$	$2.6\cdot10^{2}$	$2.5\cdot10^{2}$	$1.0\cdot10^{-2}$	$1.3\cdot10^{2}$
Cl^{-} (mg/l)	$2.0\cdot10^{3}$	$6.7\cdot10^{2}$	$8.6\cdot10^{2}$	$2.0\cdot10^{3}$	$2.2\cdot10^{1}$	$1.7\cdot10^{3}$	$5.3\cdot10^{1}$	$3.5\cdot10^{1}$	$5.5\cdot10^{1}$
SiO_2 (mg/l)	0	0	0	0	$2.1\cdot10^{1}$	0	$8.9\cdot10^{1}$	$4.4\cdot10^{2}$	$1.5\cdot10^{1}$
F^{-} (mg/l)	$1.0\cdot10^{-2}$	$1.0\cdot10^{-2}$	$1.0\cdot10^{-2}$	$1.0\cdot10^{-2}$	$1.0\cdot10^{-2}$	$1.0\cdot10^{-2}$	2.8	$3.9\cdot10^{1}$	$1.0\cdot10^{-2}$
CEMC (mol/m^{3})	$1.1\cdot10^{2}$	$7.7\cdot10^{1}$	$1.2\cdot10^{2}$	$6.6\cdot10^{1}$	$8.6\cdot10^{1}$	$1.9\cdot10^{3}$	$4.1\cdot10^{1}$	$3.1\cdot10^{2}$	$7.5\cdot10^{1}$

The highest concentration of cations can be found (but for a few in Kruibeke) in the squeezed-out clay-fluid. These ions were not found during the chemical analysis of the less brutally obtained surplus fluid (or the percolate as will be shown in **B 3.6.2.4**, Geochemistry part III) because these ions are either loss during the homogenisation process or because they were not freed from places they are more rigidly held (e.g. double or interlayers) by the more subtle extraction methods. Increases were nevertheless measured for some special substances:

- Tournai clay shows after homogenisation an increase of SiO_2, a slight increase in K^+ and F^- but the concentration of the other elements decreases.
- Soignies clay exhibits again an increase in SiO_2 molecules and in K^+ cations, thus the same processes as in Tournai clay.
- Kruibeke clay shows as additional complication a decrease of the pH, a relative increase (taken into account the dilution discussed in the previous section) of Ca^{2+} and Mg^{2+} cations.

These results have been summarised in **Table: B3-20.**

Table: B3-20

Type of ions which are present in higher concentrations in the contact fluid (after correction) than in the squeezed-out clay-fluid.

Clay type	[ion type] > in the corrected contact fluid than in the squeezed-out clay-fluid						
Tnat	HCO_3^-/CO_3^{2-}	SiO_2	F^-	K^+			
Snat	CO_3^{2-}	SiO_2		K^+			
Knat	SO_4^{2-}	SiO_2	F^-		Ca^{2+}	Mg^{2+}	Cl^-

Can one find an explanation for the increase of some substances in the contact fluid with respect to the squeezed-out clay-fluid?

SiO_2 molecules

A possible explanation is that SiO_2 has been freed due to the acid attack of the pore water which has been in dis-equilibrium since its contact with the atmosphere and due to the weathering induced by the homogenisation. According to Prof. Thorez (PC) it is not possible to free SiO_2 from the TOT/TO-layers by the homogenisation process that involves drying and grinding. He states that with drying and milling clay particles cannot be destroyed even not in combination with a pH of the fluid phase of clay near 2. Therefore another more plausible explanation is presented: SiO_2 was present in an amorphous form (therefore not detectable by XRD analyses) as small silica particles that accompany volcanic eruptions and was freed from the clay sample matrix due to the homogenisation process.

F^- anions

F^- is present as fluorite (note that in the karst of the Ardennes large fluorite crystals have been found but that their origin (detrital or volcanic) has not yet been explained (PC Thorez) but the material was freed from the clay sample matrix due to the homogenisation process.

K^+ cations

The high concentration of K^+ cations in the contact fluid could originate from a partial leaching of the open Illite present in the original clay. It be can checked if a partial opening of Illite can change the K^+ cation concentration significantly:

The LL of Tournai clay is 120% (**Table: C5-1**). The test was performed at a fluid content twice the liquid limit thus at a fluid to dry clay mass ratio of 2.4 : 1. If it is assumed that the density of the fluid is close to 1 g/cm^3 one deals with $2.4 \cdot 10^{-3}$ l fluid/g dry soil. In the fluid fraction a concentration of 72 g/l K^+ can be found, before correction (conservative estimate) 18 mg/l (**Table: B3-19**). This corresponds to $4.3 \cdot 10^{-5}$ g K^+/g dry soil or $1.1 \cdot 10^{-6}$ mol K^+/g dry soil.

Literature values (Lagaly 1993) give a cation exchange capacity of 1.6 to 2.3 meq/g for the interlayer space of an Illite. Thus the amount of K^+ cations needed to obtain the measured concentration of K^+ cations can easily be reached by the opening up of 0.06% of the Illite minerals present in the Tournai clay.

Ca^{2+} cations

The natural clay contains pyrite, due to the oxidation during homogenisation *etc.* transition to sulphuric acid occurred and dissolution of calcite took place (PC Thorez). One can check if a partial dissolution of $CaCO_3$ can change the Ca^{2+} cation concentration significantly:

The LL of Kruibeke clay is 63% (**Table: C5-1**). The test was performed at a fluid content twice the liquid limit thus at a fluid to dry clay mass ratio of 1.26 : 1. If it is assumed that the density of the fluid is close to 1 g/cm^3 one deals with $1.26 \cdot 10^{-3}$ l fluid/g dry soil. In the fluid fraction a concentration of 1600 mg/l Ca^{2+} can be found, before correction (conservative estimate) 471 mg/l (**Table: B3-19**). This corresponds to 5.94 g Ca^{2+}/g dry soil, 1.48E-5 mol Ca^{2+}/g dry soil, $1.48 \cdot 10^{-5}$ mol/ g dry soil thus $1.48 \cdot 10^{-3}$ g $CaCO_3$/g dry soil thus 0.15 mass% $CaCO_3$. For Tournai and Soignies clay the same order can be found.

The range of measured $CaCO_3$ values (XRD) varied between 2 and 7%. Thus only a fraction of the $CaCO_3$ needs to be dissolved to obtain the measured concentration of Ca^{2+} cations.

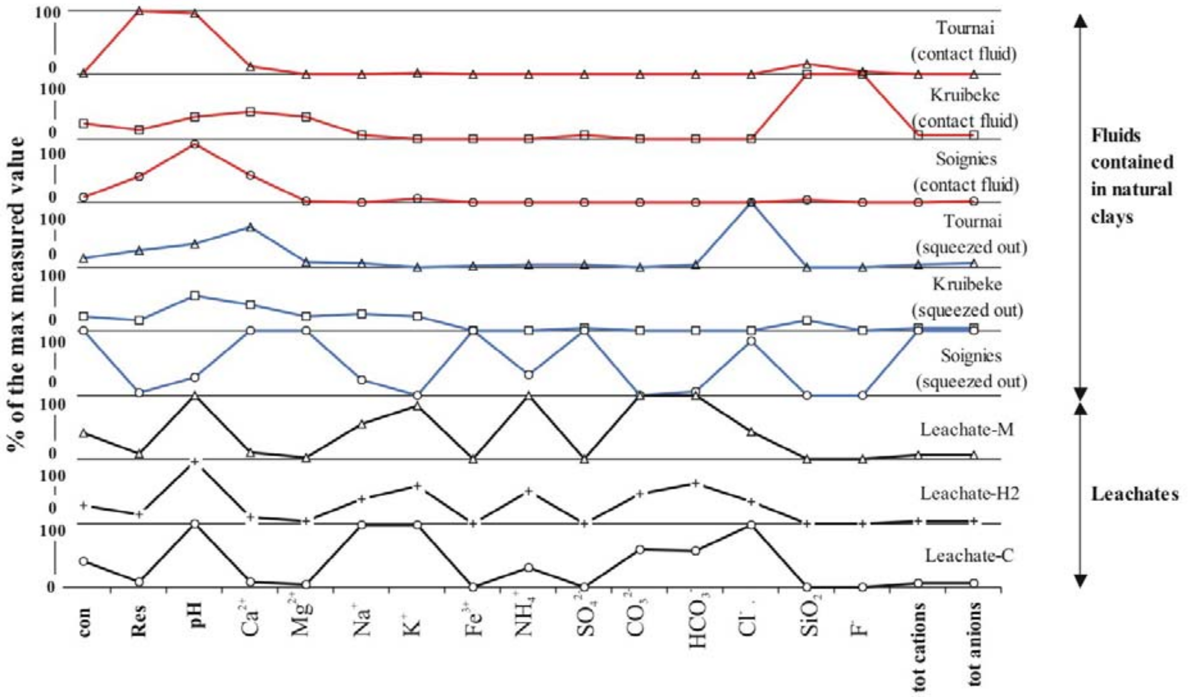
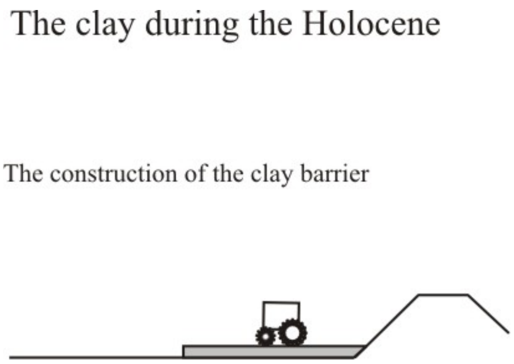


Figure: B3-2

The concentrations of some important chemical components of several involved fluids are given in percentages (100% indicates the highest concentration of the specific compound measured in any fluid). The highest conductivity (con) is found for squeezed-out fluid of Soignies clay ($2.6\cdot10^4$ microS/cm). The highest resistivity (res) is found for the contact fluid of Tournai clay ($1\cdot10^3$ Ohm·cm). The values are expressed in percentages of the maximum value of a component measured in any fluid. E.g. most Ca^{2+} cations are found in the squeezed-out fluid of Soignies clay. Therefore the value of Ca^{2+} cations is 100% in leachate-M. The concentration of Ca^{2+} cations is only one tenth of the concentration in the squeezed-out fluid of Soignies clay. Therefore the value for Ca^{2+} cations of leachate-M in this graph is 10%. Not that the contact fluid concentrations have not been corrected for the difference in fluid content with the natural clay.

B 3.5 The construction of the clay barrier



Keywords: Soil class, Proctor density.

B 3.5.1 Related geomechanical properties of the homogenised natural clays

The homogenised clay can be compared to clays which belong to the same class and whose suitability for various applications in civil engineering is known (see **Table: B3-21**):

Table: B3-21

*Correlation of the Tournai, Soignies and Kruibeke clays to other geomechanical properties via the link provided by the soil classification according to DIN18196 (Wendehorst 1996) (Data-set **Table: B3-8**).*

Clay type	Soil class	Description	Consistency index Ic (-) (1)	Specific weight above the water table (kN/m^3) (2)	Specific weight below the water table (kN/m^3)	Effective friction angle (°)	Effective cohesion (kPa)	Cohesion of the undrained soil (kPa)
TEF1;X KEF1;X	TA	Inorganic cohesive soil with distinct plastic properties, LL>50%	>0.5 <0.75	18.0	8.0	17.5	0	15
			>0.75 <1	19.0	9.0	17.5	10	35
			>1	20.0	10.0	17.5	25	75
SEF1;X	TM	Inorganic cohesive soil with properties that are slightly plastic, 35 %<LL<50%	>0.5 <0.75	19.0	9.0	22.5	0	5
			>0.75 <1	19.5	9.5	22.5	5	25
			>1	20.5	10.5	22.5	10	60

(1) values transferred from text to number using DIN 18 122 (2) Not specified in the standard but the values correspond to those of a saturated soil.

The ManWal (2000) gives workability limits for clays that are deemed to be suitable as liner material: Liquid limit: LL<80% and Plastic limit: 10%<PI<40%.. The standard Soignies and Kruibeke clay fulfil this criteria but Tournai clay not (see **Figure: B3-3**).

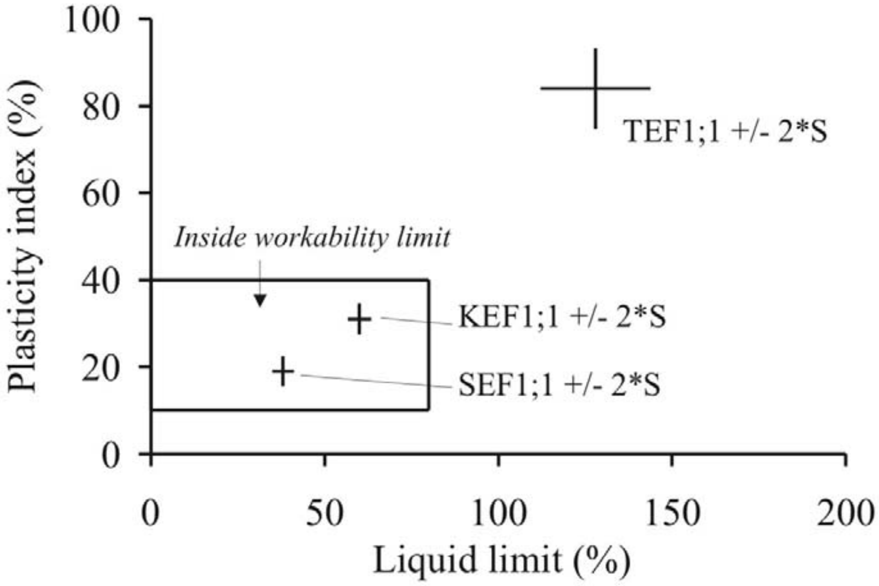


Figure: B3-3

The ManWal (2000) gives workability limits for clays that are deemed to be suitable as liner material: Liquid limit: LL<80% and Plastic limit: 10%<PI<40%.. The Soignies and Kruibeke clay fulfil this criteria but Tournai clay not (Modified after Schmitz et al 2002a). The average Atterberg limits +/- twice the standard deviation have been indicated.

B 3.5.2 Suitability of the natural homogenised clays for construction

Tournai, Kruibeke and Soignies clay can be used as sealing material according to the classification (**Table: B3-22**) and previous experience found in literature related to this classification as was shown in the previous paragraph. These materials should not be used if danger of erosion exists (*e.g.* do not use it as top liner). There is a risk of freezing damage. Thus, the liner should be installed and covered before winter. With all three clays considerable settlement can be expected. However, in case they are used as liner below a landfill their settlement will be negligible with respect to the settlement of the waste. Compaction will be difficult but special tools for clays *e.g.* sheep foot rollers are available but not recommended (because of the random orientation of the clay particles, see part **C**). The Tournai clay is however unsuitable as liner material if the workability limits are taken into account.

The Proctor density[26] of the three clay powders mixed with water were determined (Kruibeke in Gembloux, Tournai and Soignies clay in Liege) because this is an important construction parameter. In **Table: B3-23** the results of the Proctor tests and its related variables are given.

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[26] *Normal Proctor density with CBR mould, LCPC: Mode Opératoire Essai Proctor 1966*

Table: B3-22

The suitability of Tournai, Soignies and Kruibeke clays as construction material based on the soil classification according to DIN18196 (Wendehorst 1996) (Data-set ***Table: B3-8****). TA and TM are defined in* ***Table: B3-13****.*

Clay type	TEF1;X - KEF1;X	SEF1;X
Soil class according to DIN 18196	TA	TM
Shear resistance	very low	small
Ability to compact	very bad	bad
Compressibility	very large	large to moderate
Hydraulic conductivity	negligible	negligible
Susceptibility to weathering and erosion	intermediate	large to intermediate
Susceptibility to freezing	low to moderate	large to moderate
Subsurface for foundations	moderately suitable	suitable
Construction material for earth roads and roads on construction sites	not suitable	not very suitable
Construction material for roads and train embankments	not very suitable	moderately suitable
Construction material for earth dam seals	not very suitable	very suitable
Construction material for earth dams, structural support	not suitable	not suitable
Construction material for drains	not suitable	not suitable

Note: In classifying fine-grained soils the term compressibility refers to the slope of the virgin pressure - void ratio curve and not to the actual condition of the undisturbed soil which may be partly dried or otherwise be preconsolidated (Casagrande 1947 and DIN 18196 Bodenklassifikation für bautechnische Zwecke; Wendehorst 1996).

Table: B3-23

Some geomechanical properties needed for barrier construction of the Tournai, Kruibeke and Soignies clay.

	T at ρ_{OPT}	T at $0.95 \cdot \rho_{OPT}$	K at ρ_{OPT} (1)	K at $0.95 \cdot \rho_{OPT}$	S at ρ_{OPT}	S at $0.95 \cdot \rho_{OPT}$
w_{OPT} (% fluid content)	38.9	44.3	28.2	32.0	16.4	22.5
Dry unit weight (kN/m^3)	9.74	9.25	14.3	13.6	14.1	13.3

(1) Ourth and Verbrugge (1999a)

In **Table: B3-24** the prediction of the Proctor density based on the liquid limit and the plastic limit (by Kolymbas 1998) is given and compared to the actual Proctor density. Good predictions of the fluid content at the optimum Proctor density results are obtained with the relationship:

$$W_{OPT} = PL - 4 \qquad \textbf{(B3 - 1)}$$

Table: B3-24

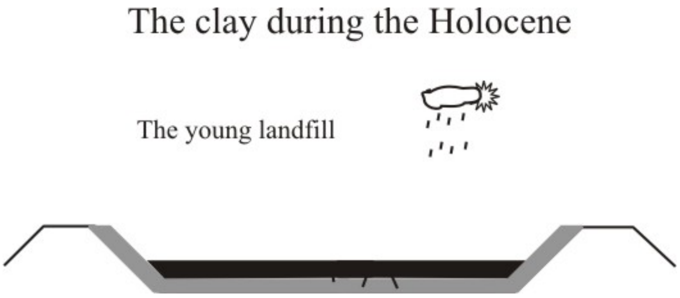
Some geomechanical properties needed for barrier construction predicted on the basis of correlations with the index properties of the Tournai, Kruibeke and Soignies clay.

	T at the optimum Proctor density	K at the optimum Proctor density	S at the optimum Proctor density
w_{OPT} (%)	38.9	28.2	16.4
LL/2	64	30	19
PL-2	42	27	18
PL-4	40	25	16
w_{OPT}/(LL/2)	0.6	0.9	0.9
w_{OPT}/(PL-2)	0.9	1	0.9
w_{OPT}/(PL-4)	1	1.1	1

Summary

Tournai clay will have the lowest permeability, but will be too difficult to handle. All clays have a low shear strength. This has to be taken into account designing any sloping parts of the landfill barrier. Compaction will not be easy. Especially Soignies clay will be susceptible to freezing damage. The optimum Proctor density of the clays can be estimated satisfactory with relationship **(B3 - 1).**

B 3.6 The young landfill, first layers of waste and first leachate contact



Keywords: Leaching tests, with first expulsion of the fluid phase of clays.

B 3.6.1 The clay *in vivo*, what happens?

The clay liner has been installed near its optimum Proctor density. The first layers of waste have been filled in. Although the waste is covered with a layer of soil after each working day, the influx of meteoric water is still large. When more and more waste is stored on the landfill site the production of landfill leachate increases.

Pressure characteristics

The total pressure on the clay liner increases from initially zero to the maximum pressure of $3 \cdot 10^5$Pa when the landfill is filled. The pore pressure remains zero (if waste is filled in slowly). If the geomembrane is fissured the pore pressure increases from initially zero to a value depending on the functionality of the drainage system.

Fluid characteristics
The composition of the fluid within the clay has changed from the Tertiary clay-fluid towards the contemporary clay-fluid due to contact with the present atmosphere (meteoric water). Subsequently it was modified during the curing and installation (tap or pond water added). As a function of the amount, composition and biological activity of waste the fluid within the clay will change more or less quickly but unavoidably from rainwater to landfill leachate.

This landfill leachate will change depending on the phase of decomposition of the waste. The final composition will, in the case of domestic waste resemble that of humic acid. The first fluid that will leave the clay (barrier or sample) facing the biosphere will not resemble the composition of the fluid that went in on the other the side of the clay (barrier or sample) facing the waste: First the natural (or modified) clay-fluid will be driven out. And only after that the results of the batch tests (in which homogenised clay was mixed with landfill leachate) will be applicable to the complete section of the barrier.

Evolution of landfill leachate (extract from Schmitz et al 2001):
When the landfill is sealed off at the top, the amount of meteoric water infiltrating the landfill will decrease. The landfill as a kind of large bioreactor starts up and landfill leachate is produced. Municipal solid wastes (MSW) buried in landfills may be considered as a cellulosic substrate undergoing biological degradation processes. Indeed, cellulose is the most important carbon source in landfills, contributing to 90% of the total methane produced by the anaerobic degradation. Jointly with the bioconversion process of cellulose into a biogas, a mechanism of organic matter stabilisation takes place, *e.g.* the humification process. Humic and fulvic acids are the complex macromolecules produced by such a process. In addition to biogas emission, important volumes of leachate are generated in landfills. Leachates are generated by an excess of rainwater and by waste constitutive water that percolate through the waste layers. The combination of physical, chemical and microbiological processes transfers organic and mineral compounds from the waste material to the percolating water.

Four different samples of leachate-H1, -H2, -M1, and -C originating from three MSW landfills in Wallonia were selected[27]. Information about the period during which the different landfill cells were performed are shown in **Table: B3-25**.

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[27] *Although the three landfill leachates-C, -H and -M are different, they are qualitatively representative of domestic landfill leachates in general. Quantitatively differences exist. These differences are smaller between countries with an identical standard of living and climate. Substances that influence the double layer thickness like cations and fluids with a low relative dielectric constant are not consumed nor produced during the biological degradation process of municipal landfill waste, except* NH_4^+ *which is actively involved in this biological degradation process (PC Rodriguez).*

Table: B3-25

Period of exploitation of the different landfill cells where the landfill leachates-C, -H and -M were collected (in 2000).

Leachate reference	Duration of exploitation	Date of sampling
H1	1989-1999	2000
H2	1999-still active	2000
M1	1987-1993	2000
C	1989-2000	1998

The biochemical characteristics of the leachates are shown in **Table: B3-26** the inorganic composition in **Table: B3-19**. In comparison to typical range values of pH (7,5-9) and chemical oxygen demand (COD) (500-4500 mg O_2/l) for methanogenic landfills, the analysed leachates showed characteristics of old methanogenic leachates even if two of them are originated from young landfill cells (**Table: B3-25**).

Table: B3-26

Biochemical analyses of the leachates (n.d.: not determined)

Parameter	Unit	leachate-H1	leachate-H2	leachate-M	leachate-C
COD	mg O_2/l	2425	1076	1135	1247
NO_3^-	mg N- NO_3^- /l	1.4	0.96	0.96	1
NO_2^-	mg N- NO_2^-/l	12	n.d.	n.d.	0

The situation towards the end of the biological activity of the landfill is discussed in chapter **B 4**. In that case the more representative leachate is humic acid instead of the genuine landfill leachates.

B 3.6.2 Hydraulic conductivity of the clay barrier

B 3.6.2.1 Observations related to the hydraulic conductivity

Observations related to the hydraulic conductivity of natural clays and genuine landfill leachates and water have been summarised in **Table: B3-27**. All clays fulfilled the limits given by the European Union Directive (1999) and the ManWal (2000): K_{hc} $<1\cdot10^{-9}$m/s.

The hydraulic conductivity measured in the laboratory is however always more favourable (less permeable) than the overall hydraulic conductivity in the field. To obtain the required
$K_{hc} <1\cdot10^{-9}$m/s in the field, the $K_{hc} < 5\cdot10^{-10}$m/s at i=30 in the laboratory (TaSi).

To test the influence of the leachate on the hydraulic conductivity the tests were repeated using a leachate (**Table: B3-27**) instead of water. For all the three clays measured with various methods, the effect of the leachate was either no change or a decrease of the hydraulic conductivity, if the clay was prepared with water and was permeated with a leachate instead of water. The moment the clay was cured before the test with leachate and permeated with leachate after sample consolidation the K_{hc} was larger than the K_{hc} of the sample cured with water consolidated and tested with water (see BOAC chapter **C 6.4**).

B

Clay type	Fluid type	ρ (·10^3kg/m^3)	W_c (%)	CP (MPa)	σ_3 (MPa)	P_i (MPa) or i	K_{hc} (·10^{-10}m/s)	Observed changes in hydraulic conductivity
natural Tournai	tap water leached with H1	1.7	43-55	1.1-1.7	0.4	0.22 - 0.34 i = 220-340	0.3 - 0.5 0.09 - 0.2	slightly lower hydraulic conductivity with leachate
natural Soignies	tap water leached with H1	2.0	21				7.3 - 67 2.0	slightly lower hydraulic conductivity with leachate
Kruibeke clay powder	cured and leached with H_2O	1.7	48	-	rigid wall	i = 7-14	3.9-15 av.8.9	slightly lower K_{hc} with landfill leachate
		1.8	63			i < 50	8.0	
		2.0	63			i < 50	2.7	
	cured with H_2O leached C	1.7	48		rigid wall	i = 7-14	1.2-5.6	
		1.9	63			i < 50	2.0	
		2.0	63			i < 50	0.85	
	cured and leached with C	1.7	48	-	rigid wall	i = 7-14	0.88-2.2 av.1.4	if mixed with leachate before test slightly higher K_{hc} at higher sample density
		1.8	67			i < 50	6.4	
		1.9	67			i < 50	3.9	
Soignies clay powder	cured and leached with H_2O	2.1	35		rigid wall	i < 50	8.1	slightly lower K_{hc} with landfill leachate
		2.2					2.2	
	cured with H_2O leached C	2.0	37	-	rigid wall	i < 50	4.8	
		2.1					2.0	
	cured and leached with C	2.0	35	-	rigid wall	i < 50	5.9	slightly lower K_{hc} if mixed with leachate before test
		2.1					0.82	
Tournai clay powder	cured and leached with H_2O	1.6	126	-	rigid wall	i < 50	0.71	no difference in K_{hc} with landfill leachate
		1.72					0.22	
	cured with H_2O leached C	1.6	127	-	rigid wall	i < 50	0.93	
		1.7					0.24	
	cured and leached with C	1.6	127	-	rigid wall	i < 50	1.6	slightly higher K_{hc} if mixed with leachate before test
		1.7					0.43	
	cured and leached with H2	1.5	127	-	rigid wall	i < 50	2.3	slightly higher K_{hc} if mixed with leachate before test
		1.7					2.2	

Table: B3-27

Hydraulic conductivity of Tournai, Soignies and Kruibeke clay (modified from Schmitz et al. 2001)

ρ = *Apparent volumetric mass at the given hydraulic conductivity*
W_c = *Initial fluid content*
CP = *Compaction pressure*
σ_3 = *Confining stress during test*
K_{hc} = *Hydraulic conductivity of the system in equilibrium*
i = *Hydraulic gradient*
P_i = *Injection pressure fluid*

Note that:
- Natural samples tested in flexible wall cells were statically compacted with a compaction pressure of 1.1-1.7MPa. Their dry density was higher than the Proctor density and the confining pressure during the hydraulic conductivity tests in a triaxial cell was 4MPa (results P. Illing & Ch. Schroeder Geomac)
- Homogenised Kruibeke clay at a volumetric weight of $1.7\cdot10^3 kg/m^3$ *was tested in a modified oedometer cell. The sample was compacted up to 80% of the optimum Proctor density before the test (raw data: A-S Ourth, Gembloux).*
- All other homogenised clays were tested in standard oedometer cells. The samples were cured during at least one month with demineralised water or landfill leachate at a fluid content equal to the liquid limit before the test.

The clays fulfilled the standards with demineralised water and with landfill leachate[28]. But why does the hydraulic conductivity decrease when the test is performed with landfill leachate instead of demineralised water?
Possible explanations for the reduction of the hydraulic conductivity observed in the various tests are analysed in the following paragraphs on which the focus will be on:
1) Viscosity and density differences of leachate versus water (paragraph **B 3.6.2.2**).
2) Alteration of minerals along flow pathways (paragraph **B 3.6.2.3**).
Followed by additional analysis:
3) Examination of the percolate (Geochemistry part III, paragraph **B 3.6.2.4**)).
Finally a theory describing the changes observed above is developed in:
4) Chapter **C 6** and **C 7**

B 3.6.2.2 Viscosity

As can be seen in **Table: B3-28** the viscosity (dynamic and kinematic) of the genuine landfill leachates is slightly higher than the viscosity of demineralised water. The density is comparable. Assuming that the intrinsic permeability is identical before and after permeation with landfill leachate the differences in measured hydraulic conductivity upon permeation with water or leachate (**Table: B3-27**) can be expressed in terms of density and viscosity differences (**Table: B3-28**):

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[28] *That the landfill leachates could even have a favourable effect on the hydraulic conductivity was first published in Schmitz (et al 2001).*

$$\frac{K_{hc\ leachate}}{K_{hc\ H_2O\ LIG}} = \frac{\rho_{leachate} \cdot \eta_{H_2O}}{\rho_{H_2O} \cdot \eta_{leachate}}$$

The maximum change in $K_{hc\ max}$ between permeation with water and landfill leachates on the basis of density and viscosity differences is a factor 1.2 (**Table: B3-28**) whereas the measured K_{hc} differences vary with a factor. 1 - 33 (**Table: B3-27**). Apparently other factors play a role besides differences in viscosity and density. This will be analysed in more detail in the following paragraphs.

B 3.6.2.3 Alteration of minerals along flow pathways

Decrease in hydraulic conductivity:

A possible mineralogical explanation for the decrease in hydraulic conductivity, for the unaffected structural stability and the overall small changes in Atterberg properties and clay mineral content could be:

- A partial Smectitisation along preferential pathways in the remoulded natural clay (right hand side **Figure: B3-4**).
- An overall slight modification of the clay mineral content, that affects the hydraulic conductivity of the sample; only measurable after curing (**Figure: B3-4** left hand side lower part) of the dried and ground homogenised clay with a leachate during a certain period of time (terms of months) and tested at a low stress level (**Table: B3-27**). This effect was not measurable if the clay was quickly permeated by the landfill leachate without previous long-term storage (part of the BOAC model, see **C 6.4** or Schmitz *et al* 2004b).

Table: B3-28

Viscosity, density and the resulting multiplication factor to compare the hydraulic conductivity of leachates to demineralised water assuming that the $K_{intrinsic}$ remains constant. Demin. = demineralised water. Temp. = temperature.

	Dynamic viscosity (mPa·s)	Cinematic viscosity (mm²/s)	Density (g/cm³)	Temp. (°C)	$\frac{K_{hc\ leachate}}{K_{hc\ H_2O\ LIG}}$	$\frac{K_{hc\ leachate}}{K_{hc\ H_2O\ LGIH}}$
Leachate-H1	1.1494	1.1401	1.0082	21	0,94	0,97
Leachate-H2	1.2979	1.3023	0.9966	21	0,83	0,85
Leachate-M1	1.0923	1.0969	0.9958	22.5	0,98	1,01
Leachate-C	1.2499	1.248	1.0015	21	0,86	0,88
Tap water LGIH	1.1013	1.099	0.9979	21		
Demin. water LIG	1.0732	1.0754	0.998	21		

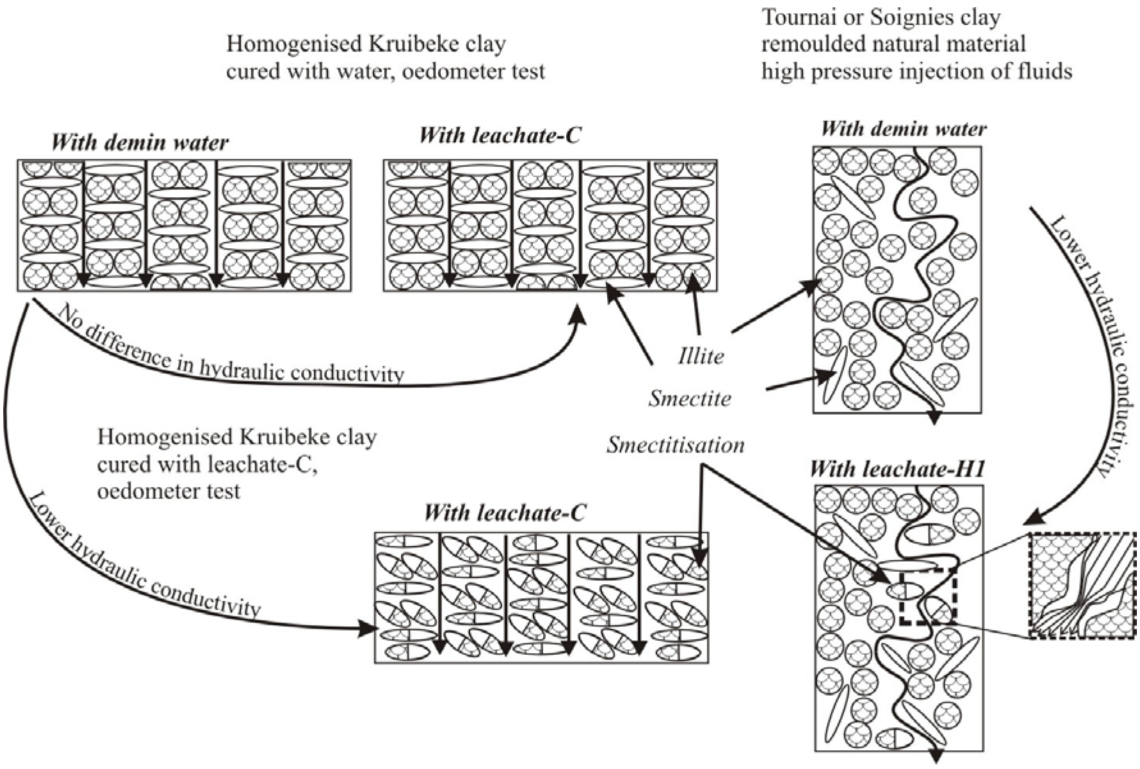

Figure: B3-4.

A possible explanation for a measured decrease of the hydraulic conductivity without any other change in geomechanical properties could be attributed to localised clay mineral alterations along the flow paths.

B 3.6.2.4 Geochemistry part III, examination of the percolate

During a hydraulic conductivity one can focus on the determination of the hydraulic conductivity but additionally one can analyse the evolution of the chemical composition of the fluid that has percolated through the clay barrier or on a smaller scale a clay sample. This latter aspect is discussed in this paragraph. As illustrative example Soignies clay containing the most interesting natural clay-fluid (see paragraph **B 3.4.3** and paragraph **B 3.1.3**) was chosen.

The results showed that three different leaching patterns can be identified, depending on the relationship between the concentration of different substances within the leachate or the natural clay-fluid (see **Table: B3-29**) :

i) The concentration of a specific chemical was larger in the leachate than in that of the natural clay-fluid (see **Figure: B3-5 A-D**).

ii) Reversed to that of i), *i.e.* the concentration was larger within the natural clay-fluid (see **Figure: B3-5 E-H**).

iii) The concentration in both fluids was comparable (see **Figure: B3-5 I & J**).

Table: B3-29

Concentration of different substances within the leachate or the natural clay-fluid and pH values.

	Leachate-H1	Soignies squeezed-out clay-fluid
conductivity at 25°C (microS/cm)	$2.4 \cdot 10^4$	$2.6 \cdot 10^4$
pH	8.7	2.2
Ca^{2+} (mg/l)	$4{:}8 \cdot 10^1$	$1.1 \cdot 10^3$
Mg^{2+} (mg/l)	$5.6 \cdot 10^1$	$2.3 \cdot 10^3$
Na^+ (mg/l)	$2.6 \cdot 10^3$	$3.9 \cdot 10^2$
K^+ (mg/l)	$2.1 \cdot 10^3$	0
Fe^{3+} (mg/l)	$1.3 \cdot 10^1$	$3.0 \cdot 10^4$
NH_4^+ (mg/l)	$2.0 \cdot 10^3$	$3.5 \cdot 10^2$
SO_4^{2-} (mg/l)	$2.8 \cdot 10^2$	$9.0 \cdot 10^4$
HCO_3^- (mg/l)	$1.1 \cdot 10^4$	$2.6 \cdot 10^2$
Cl^- (mg/l)	$2.8 \cdot 10^3$	$1.7 \cdot 10^3$
SiO_2 (mg/l)	4.3	0

Pattern i):

*The evolution of the pH (**Figure: B3-5-A**)*

- If the leachate is landfill leachate-H1:

The ejected fluid has initially the same low pH as the natural fluid of Soignies clay. After an amount of leachate 1.5 times the initial pore volume had been injected the value of the pH rose quickly to pH = 8, the pH of leachate-H1.

- If the leachate is tap water (TW):

In the case that tap water is used even after an amount 3 times the initial pore volume, of tap water had been injected the pH remained low.

*The evolution of the concentration of Na^+ cations (**Figure: B3-5-B**)*

- If the leachate is landfill leachate-H1:

The concentration of Na^+ cations in the ejected fluid rises quickly to the value of the leachate. The concentration remains lower even after an amount 3 times the initial pore volume of leachate passed through the Soignies clay sample.

- If the leachate is tap water (TW):

The concentration of Na^+ cations in the ejected fluid remains near zero. It is apparently difficult for water to remove/exchange Na^+ cations from the clay-fluid (in the double layer or adsorbed on the clay particles?).

*The evolution of the concentration of K^+ and NH_4^+ cations (**Figure: B3-5-C** and **D**)*

- If the leachate is landfill leachate-H1:

The concentration of K^+ or NH_4^+ cations in the ejected fluid rises less quickly to the value of the leachate as the Na^+ cations do.

- If the leachate is tap water (TW):

The concentration of NH_4^+ cations in the ejected fluid remains near zero. It is apparently difficult for water to remove (exchange is not possible) NH_4^+ cations from the clay-fluid (in the double layer or adsorbed on the clay particles?). K^+ is not available in the original Soignies clay.

Pattern ii):

*The evolution of the concentration of Ca^{2+} cations (**Figure: B3-5-E**)*

If the leachate is landfill leachate-H1 or tap water (TW) the concentration of Ca^{2+} cations in the percolate remains constant. Such a phenomena was not observed before with any other cation. At the point where the pH rose to 7 and 8 (see **Figure: B3-5 A**) the dissolution of calcite ($CaCO_3$ molecules) stopped. Apparently the small amount of calcite that was present in the natural clay (see **B 3.4.3.3**) was dissolved by the <u>migrating</u> front of the altered (remember the oxidation of Pyrite) natural fluid phase of the natural clay. When the neutral to basic landfill leachate replaces the altered fluid phase of the clay the dissolution of calcite stops.

*The evolution of the concentration of Mg^{2+}, Fe^{3+} and SO_4^{2-} ions (**Figure: B3-5-F, G** and **H**)*

- If the leachate is landfill leachate-H1:

In the profiles of pattern ii) (see **Figure: B3-5-F, G** and **H**) it can be observed, that after 1.5 times the pore volume was leached through the sample, the largest part of the natural clay-fluid has been expelled from the sample. Here both, samples leached with landfill leachate or tap water, converged to the same final concentration → 0. The characteristics of leaching Mg^{2+}, Fe^{3+} and SO_4^{2-} are comparable, except for the absolute values.

- If the leachate is tap water (TW):

The results are comparable to those with leachate-H1 as permeating fluid but the concentration of Mg^{2+}, Fe^{3+} and SO_4^{2-} ions is less, not all ions are removed.

Pattern iii):

*The evolution of the concentration of Cl^- anions (**Figure: B3-5-I**)*

- If the leachate is landfill leachate-H1:

The concentration of Cl^- anions in the ejected fluid rises quickly to the value of the leachate. Comparable to Na^+ in **Figure: B3-5-B** but the value of the leachate is reached faster.

- If the leachate is tap water (TW):

The concentration of Cl^- anions in the ejected fluid remains near zero. It is apparently difficult for water to remove Cl^- cations from the clay-fluid.

*The evolution of the concentration of SiO_2 (**Figure: B3-5-J**)*

SiO_2 is neither present in the initial clay-fluid of the natural Soignies clay (obtained by squeezing the sample) nor in the leachate. Still a large concentration of SiO_2 can be found in the percolate.

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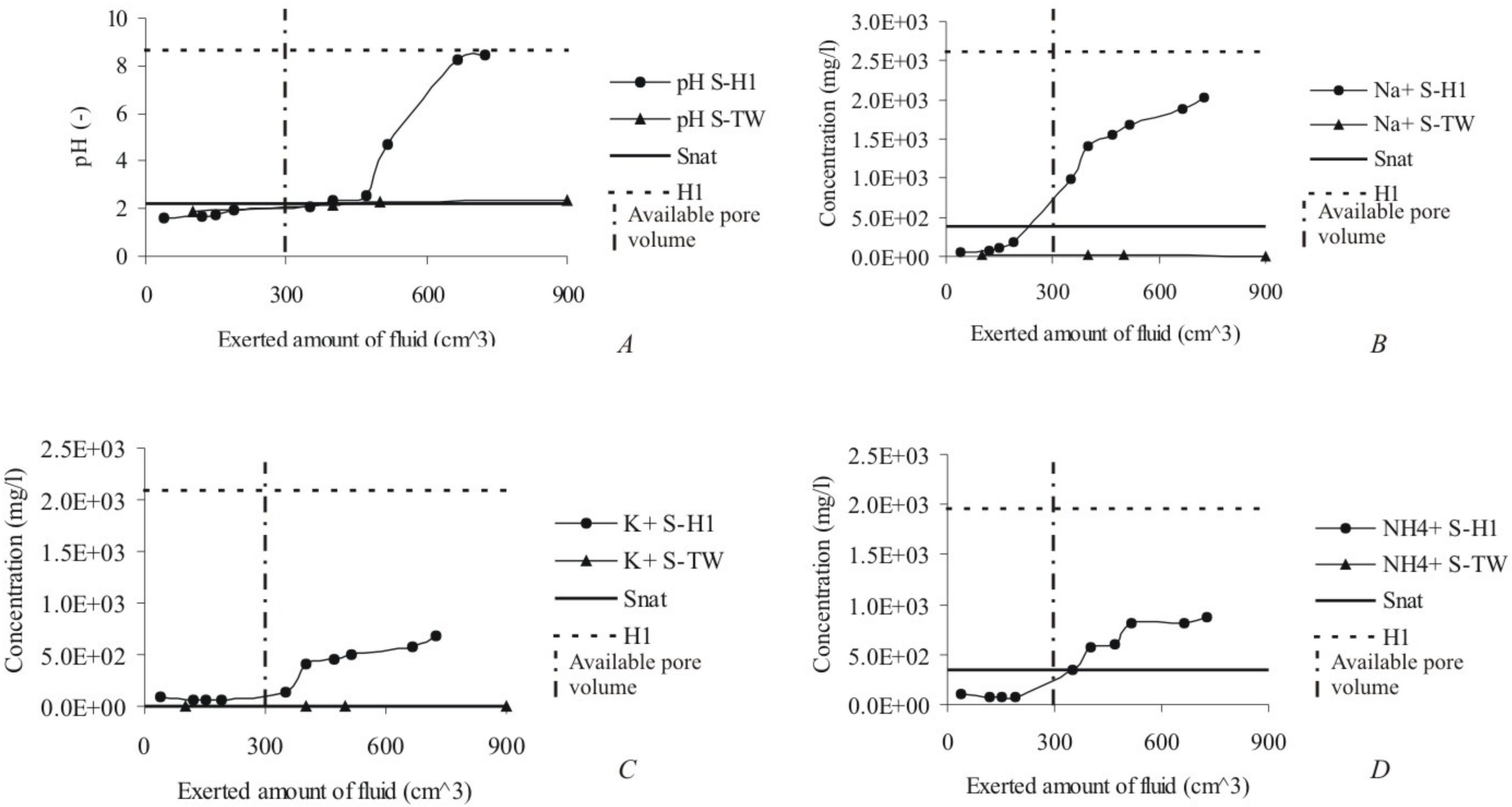

Figure: B3-5 A to D

This figure shows an example of pattern i). The concentration in leachates is higher than in natural pore water.

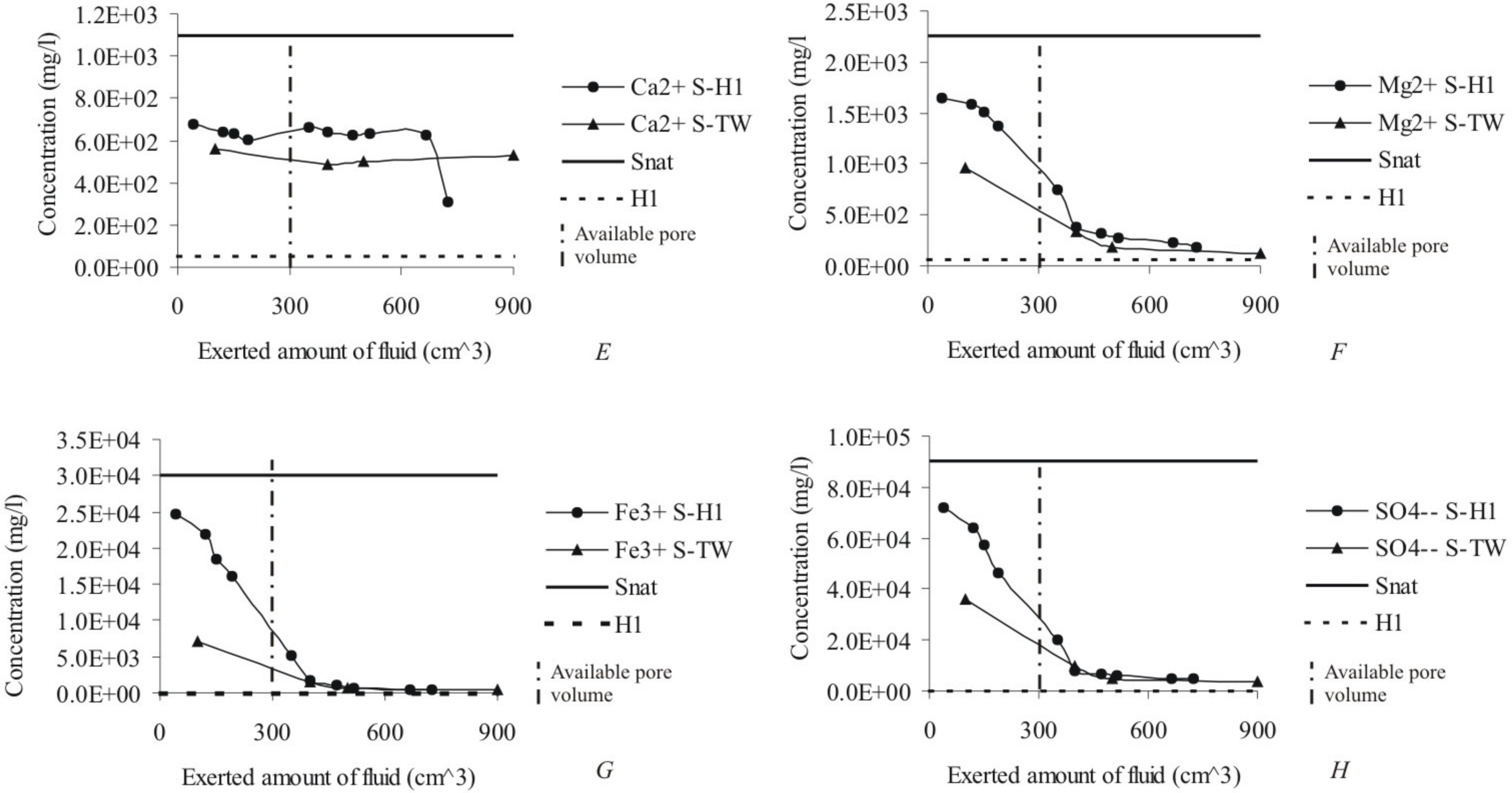

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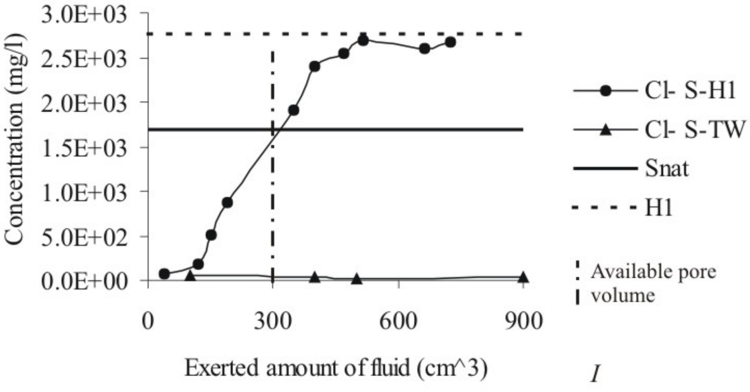
Figure: B3-5 E to H



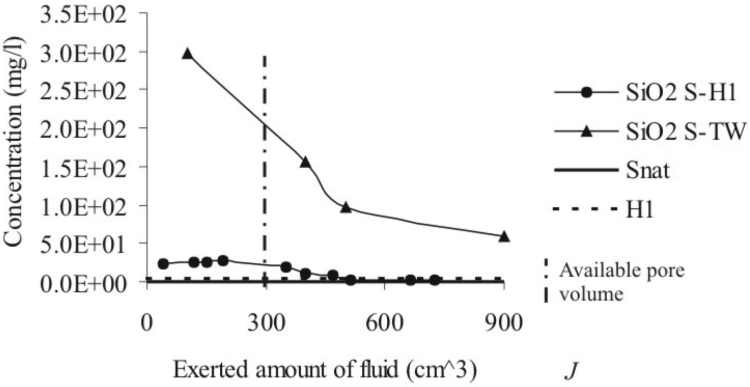


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Figure: B3-5 I to J

Discussion patterns i), ii) and iii):

a) When tap-water is used as leachate virtually no Na^+, NH_4^+ or Cl^- but little more H^+, Mg^{2+}, Fe^{3+} and SO_4^{2-} is removed from the clay-fluid of the natural clay.

b) When leachate-H1 is used as leachate, Na^+, K^+, NH_4^+ and Cl^- are leached through the sample. The rate decreases in the order: Cl^-, Na^+, K^+ and NH_4^+.

c) When leachate-H1 is used as leachate, Mg^{2+}, Fe^{3+}, SO_4^{2-} are partly removed (more effectively than with tap-water) from the sample.

These observations suggest that:

- A part of the cations and anions (H^+, Mg^{2+}, Fe^{3+} and SO_4^{2-}) is held outside double layers or in interlayers in places where fluids (like water not containing cations, or leachates containing predominantly monovalent cations) can remove them easily (Q_{II}).
- A part of the cations and anions (Na^+, NH_4^+, Mg^{2+}, Fe^{3+}, Cl^- and SO_4^{2-}) is held inside double layers or interlayers in places (Q_I) where fluids cannot remove them easily.
- Flow takes place partly outside (Q_{II}) and partly inside (Q_I) domains in which double layer or other attraction occurs attract cations.
- The method to determine the chemical composition of the clay by analysing the juice obtained by squeezing the sample at high pressure (10 MPa) is an excellent method to obtain an overview about all ions present in the clay whether they are contained inside

(Q_I) double layers or interlayers or outside (Q_{II}) these places.

d) The concentration of SiO_2 molecules rose to values larger than those found in either the leachate or the squeezed-out clay-fluid.
Possible sources of SiO_2 molecules could be quartz, decomposed clay and most probably amorphous silica or cristobalite as had been suggested in Geochemistry part II (paragraph **B 3.4.3**).

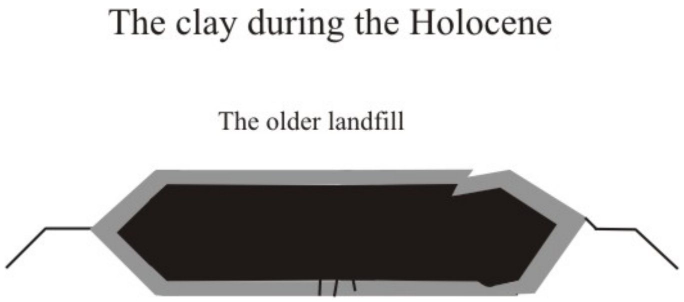
Suggestions:
- When a clay liner is constructed and the concentration of substances in the fluid in a drainage layer below this liner is measured one has to choose the time of sampling well (time in terms of the history of the clay - leachate permeation). Additionally one has to know the chemical composition of the clay-fluid in the clay liner to be able to draw relevant conclusions. As was shown in this paragraph only after 1.5 times a volume equal to the volume of pores in the clay liner has been displaced by landfill leachate one starts to measure the composition of the leachate that enters the barrier on the other side. Depending on the adsorbing capability of the clay (K^+, NH_4^+ cations) or accompanying minerals ($CaCO_3$) even after 1.5 times a volume equal to the volume of pores in the clay liner has been displaced by landfill leachate the original fluid present in the clay will mask the exact nature of the leachate entering the clay on the side (facing the biosphere) of the barrier.
- Knowledge of the fluid phase composition of the clay that will be used as barrier is needed to avoid wrong conclusions about breakthrough moments of landfill leachates.
- Next to XRD analyses other investigations of the clay matter are needed like the identification of amorphous glass (frequent in Bentonites and Bentonites are frequently used as barrier material) to be able to interpret leaching results correctly.
- Knowledge of the Eh-pH (redox potential - acidity) conditions in the clay barrier under a landfill is needed. Tests in the laboratory should ideally be performed at the same condition as prevailing during the life of the barrier because some components (like Ca^{2+} calcite) loose their mobility drastically if one of these properties changes.

B 3.6.2.5 Summary

In the previous paragraphs the observations related to the hydraulic conductivity of natural clays (Soignies, Kruibeke and Tournai) have been discussed. For all the three clays measured with various methods, the effect of the leachate (added to the sample prepared with water and consolidated and subjected to a exterior compressive effective stress like in a barrier) was either no change or a decrease of the hydraulic conductivity.
Possible explanations for the reduction of the hydraulic conductivity observed in the various tests were analysed:
1) Viscosity and density differences of leachate versus water certainly play a role, but these differences are too small to explain the measured difference in hydraulic conductivity.
2) Alteration of minerals along flow pathways is a possibility but no direct proof is available. Observed was that the clay needed to be cured before the test with the leachate to observe the largest effect of the leachate on the hydraulic conductivity. This supports BOAC (**C 6.4**) concept.
3) Examination of the percolate (Geochemistry part III) showed that flow with leachate removes ions contained naturally in the clay and displaces the natural fluid by the

leachate. Ions are not only removed or introduced in the sample via inert conduits (Q_{II}) or flow channels (for definition see **C 6.3.6**) but as well from or into double layers or interlayer spaces (Q_I) (in which of the two is discussed in **C 6.4**).
4) These observations led to models proposed in chapter **C 6**, **C 7** and finally the applications in **C 8** and the summary in **C 8.3**.

B 3.7 The older landfill, waste filled in, landfill sealed off



Keywords: Tests at 50°C, oedometer tests to test consolidation, triaxial tests for slope stability.

B 3.7.1 The clay *in vivo*, what happens?

Now the pressure rises. The barrier is sealed off. The biodegradation works at maximum power: The heat rises to 60°C. Leachate is produced. The geomembrane starts to suffer in the next tens of years: Locally it will start to fissure. If clogging of the drainage system occurs, nothing will help and the pore pressure will rise. The maximum amount of waste is filled in. The total (before fissuring of the geomembrane the effective stress) pressure on the barrier is about $3 \cdot 10^5$ Pa.

B 3.7.2 Adequate laboratory tests

Adequate laboratory tests must test the:

- Influence of leachates at 50°C, not only to analyse the reactions at a temperature close to that in a landfill, but - assuming the validity of Arrhenius' law (Huette 1996) - to speed up reactions.
- The consolidation characteristics and the shear strength of the clay at landfill conditions.
- Post-meteoric time; landfill leachate prevails; after leachate production (still) some time was needed for the first leachates to enter the clay barrier and to replace the existing fluid. At this stage one can assume that this has happened. It will be analysed how the leachate attacks the clay.

A difference with respect to the situation in an actual barrier, an open system, is that the batch tests were performed in a closed system. In an open system the following processes take place:

- Removal of exchanged cations.
- Removal of anion partners of acids.
- Acidification.

B 3.7.3 Atterberg batch tests, representative of the older landfill

B 3.7.3.1 Introduction

The results of the different tests were displayed by referring to plasticity charts for laboratory classification of fine-grained soils showing the liquid limit (LL) versus the plasticity index (PI). Anticipated large shifts in soil classes after leachate contact could not be observed. It appeared that one was dealing rather with small shifts of Atterberg properties than with large transitions from one to another soil class after having added leachates (**Figure: B3-6**).

B 3.7.3.2 General overview results

Taking a closer look at the shifts, the results were plotted as a function of leachate type, storage temperature and initial fluid content (**Figure: B3-7**). The changes were not that straightforward and varied to a large extent as a function of the clay type. The Tournai clay was apparently more affected by the variation of parameters than the other two clays. Factors like storage temperature did not seem to affect the clays in the same way. However, there was an evident dependence of the Atterberg properties on the initial fluid content.

The influence of the variables that could be discerned were summarised in **Figure: B3-8**. Before and after leachate contact one can (still) recognise:
- The clay group to which a clay-leachate combination belonged.
- The initial amount of fluid involved within the data of only one specific clay type.
- The storage temperature, with the knowledge of the parameters: Clay group and initial amount of fluid.

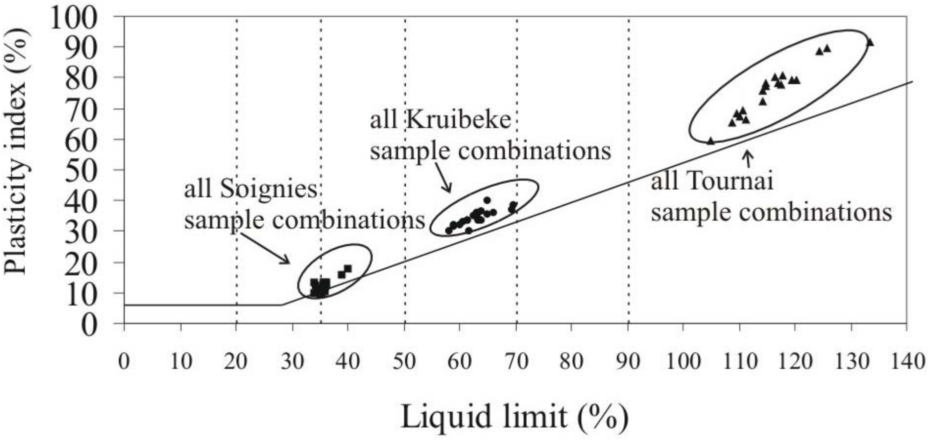


Figure: B3-6

Results of a test in which the three natural clays (after homogenisation) were exposed to different leachates, cured at different temperatures and different initial fluid contents. The position of the three clouds of data is controlled by the clay composition; no other observation related to e.g. the influence of a leachate could be made at this stage.

B

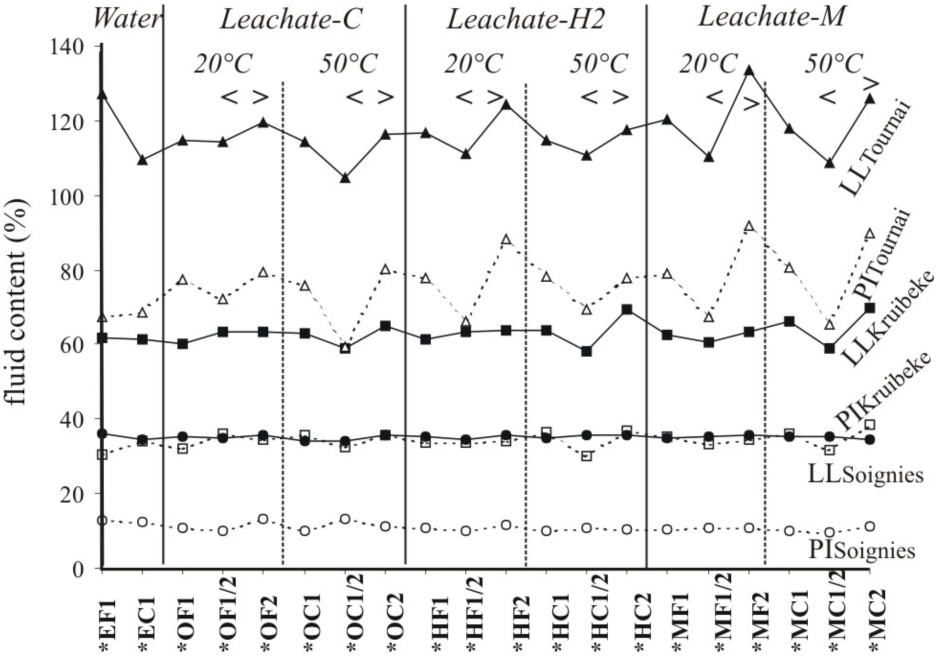


Figure: B3-7

The values of liquid limit (LL) and plasticity index (PI) are plotted as a function of the variable conditions to which the clays were exposed. The type of exposure is indicated by a code along the horizontal axis. The < symbol refers to samples stored at an initial fluid content equal to 0.5LL; the > symbol to 2LL, no symbol to LL.

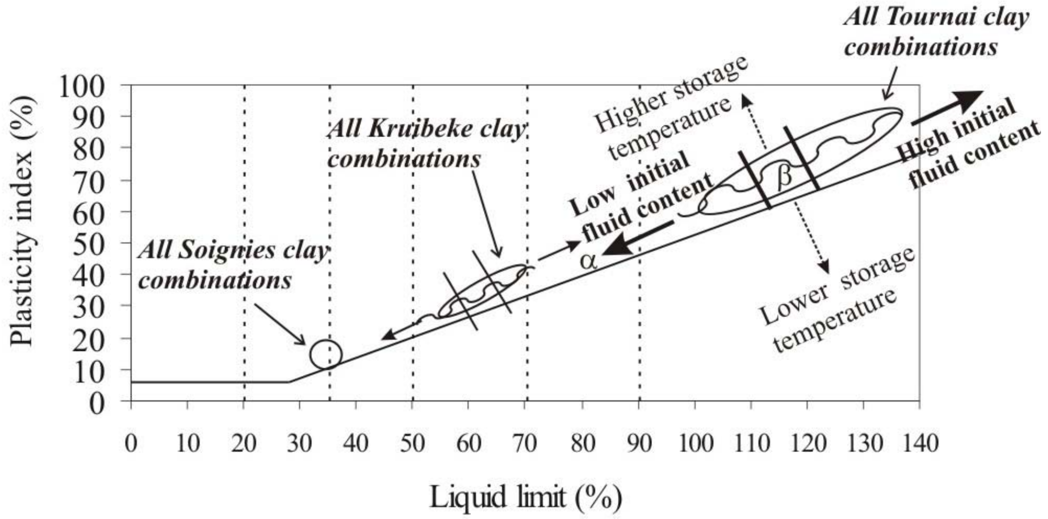


Figure: B3-8

Taking a closer look at the scattered Atterberg data of several homogenised natural clays tested with 3 genuine landfill leachates one is able to differentiate, once the clay type is known, the samples stored at a high initial fluid content (high is twice the liquid limit value) and those stored at a low (half the liquid limit) initial fluid content. Once these two properties were known another, less persistent, differentiation could be made on the basis of the temperature. The variability within the Soignies clay group is too small to allow making such observations.

Table: B3-30

Mean values, coefficient of variation, standard deviation and heterogeneity of natural homogenised Tournai clay samples stored with various landfill leachates.

LL	Mean (%)	COV (-)	S (%)	Srp (%)	S_h (%)	C_{vh} (-)	S_h/S (-)
T(E,O,H,M,U) (C,F)0.5;X	111	0.029	3.26	4.22	x	x	X
T(E,O,H,M,U) (C,F)1,2;X	123	0.060	7.43	4.66	5.78	0.047	0.78

In **Table: B3-30** the mean values of natural homogenised Tournai clay (Tournai as example because it showed the largest reactivity) samples that were stored with various landfill leachates are shown: The samples stored at a fluid content equal to half the liquid limit, have a mean liquid limit that is lower than that of samples stored at a higher fluid content (see **Figure: B3-8**). These phenomena are directly related to the influence of the natural fluid phase (chemical composition was discussed in paragraph B3.4.3.3). This will be analysed in more detail in chapter **C 3**.

B 3.7.3.3 Atterberg batch tests, older landfill - diluted leachates

As to assume that the processes were related to the amount of fluid and not to the type of leachate the tests were repeated with Tournai clay (the most “active” one, largest EBS) with the same, but in this case diluted leachate-C. Leachates were diluted by a factor 2 and 4. After this dilution the leachates were mixed again with the clay powder up to the liquid limit.

If the type of fluid determined the position in the LL-PI field, the diluted samples would be located at other liquid limit - plasticity index coordinate than the non-diluted samples. But it turned out that their LL-PI coordinates were located next to the samples stored at an - initial fluid content near the liquid limit - tested previously. Such an observation raised some serious questions about the chemical composition of the involved fluids, especially about the role of the leachates. These problems will be analysed in the light of the inorganic substances of the used fluids in chapter **C 3**. The chemical composition of leachates, with respect to the natural fluid phases of the clays, was discussed in *e.g.* **B 3.4.3** (Geochemistry II) and **B 3.6.2.4** (Geochemistry III).

B 3.7.3.4 Atterberg batch tests, older landfill - the effect of contact time

In several batch tests the homogenised clays (powders) were mixed with landfill leachates. The slurry obtained in this way had a fluid content equal to the liquid limit of the reference clay and was stored at room temperature.

The results are shown in **Figure: B3-9**. The change in the Atterberg limits as a function of time is rather small for all types of fluids.

Apparently the difference in liquid limit of clays cured during different time intervals (from 1 month to three years) is not very large in terms of the standard deviation of the liquid limit determination (see **Table: B3-9**), usually 5% sometimes 10%. The processes occur either within a time period smaller than one month, or could be expected in a time interval exceeding 3 years.

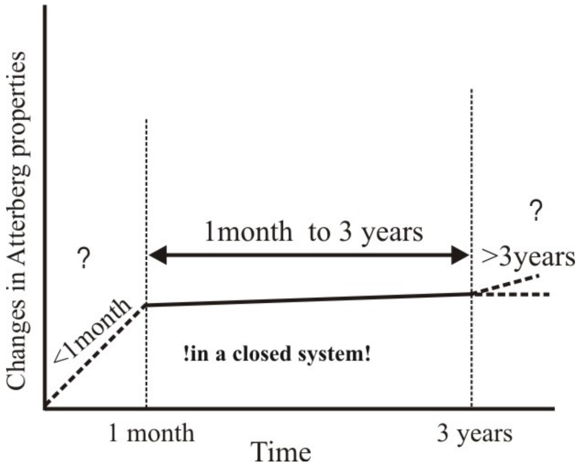


Figure: B3-9

In a closed genuine leachate-natural clay system the index properties hardly change even after three years of mutual contact.

B 3.7.3.5 Atterberg batch tests, older landfill -summary of the results

A summary of the results of Atterberg limits using landfill leachates-C, -H2 and -M1 with the natural but homogenised Soignies, Tournai and Kruibeke clays at fluid contents equal to the liquid limit of the clay or half or twice this value, cured at room temperature or at 50°C is given below:

- Variable: Clay type:

$LL_{TXXX}>>LL_{KXXX}>>LL_{SXXX}$ **(B3 - 2)**
$PI_{TXXX}>>PI_{KXXX}>>PI_{SXXX}$ **(B3 - 3)**

- Variable: Leachate type: **(B3 - 4)**

$LL_{\alpha M>1\delta}>LL_{\alpha H>1\delta}>LL_{\alpha O>1\delta}$ with δ=C or F if α=T else δ=C if α=K

- Variable: Fluid content: **(B3 - 5)**

$PI,LL_{\alpha\beta\gamma 2}>PI,LL_{\alpha\beta\gamma 1}>PI,LL_{\alpha\beta\gamma 0.5}$ with α=T or K
β= X or M or H or O
γ=C if α=K else γ=X if α=T

- Variable: Temperature: **(B3 - 6)**

$LL_{\alpha\beta F\delta}>LL_{\alpha\beta C\delta}$ with α=K or T
β=M or H not O
δ=0.5 or 1 or 2 if α =T or δ=0.5 α =K

$LL_{\alpha\beta C\delta}>LL_{\alpha\beta F\delta}$ with α=K **(B3 - 7)**
β=M or H or O
δ=1 or 2

- Variable: Dilution of leachates: **(B3 - 8)**

$LL_{T\beta\gamma 1(1/8)}>LL_{T\beta\gamma 1(1/4)}>LL_{T\beta\gamma 1}$ with β=O or H
γ=C or F

B 3.7.3.6 Atterberg batch tests, older landfill - conclusion

It can be concluded that:

- The Tournai clay has the highest Smectite content and the largest EBS (equivalent basal spacing) and conform literature shows the largest leachate dependency, Soignies contrary the lowest.
- The LL-PL plots show that there are large differences between the 3 clay types.
- The activity of the Tournai clay > Kruibeke clay > Soignies clay.
- If the initial fluid content and the leachate type is known a distinction can be made between samples stored warm (50°C) or cold (room temperature) (for the Tournai clay this is more evident than for the Kruibeke clay).
- A higher initial content of leachate causes an increase of the liquid limit and plasticity index, an initial lower fluid content causes a decrease.
- The influence of the leachates is lower than the influence of the initial fluid content. This is related to the fact that the leachates are not "aggressive" with respect to the initial fluid contained in the clays. The leachates do not modify the nature of the clays. The remnants of the natural altered fluid phase are more aggressive (especially at low initial fluid content).

B 3.7.4 Analyses of clay mineral alteration pathways

Doing batch tests using clay powder and landfill leachates a long contact time between clay barrier and landfill leachates was simulated[29]. An extensive overview of clay mineral alteration processes was given previously by the author (Schmitz 2001a). The same clays were exposed to young and old domestic landfill leachates. The results showed (see **Figure: B3-1**) that, although one did not observe any major shift in clay mineral compositions, one was dealing with the following processes (**Figure: B3-10**): Smectitisation (left image), Illitisation (pathway A, right image), secondary Chloritisation (pathway B), Al-pillaring (pathway D) and Kaolinisation. The most dominant processes in terms of magnitude were Illitisation and Smectitisation.

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[29] *In **Part: C** it will be shown that batch tests do not necessarily present long-term leaching tests because these tests depend on completely different physical processes. It is shown that the liquid limit depends on reactions on the interlayer and the particle level. Because effects on a lower level - here the interlayer level - are more powerful than changes on a higher level - here represented by the particle level - reactions on the interlayer level may mask reactions on the particle level. During batch tests the interlayer is more accessible than during percolation tests during which a mechanical stress is applied (see paragraphs **A 3.2.2** and **C 6.4**). Therefore the results presented here must not be interpreted as long-term behaviour sensu stricto, thus not as a continuous evolution from the results measured on a short-term (months in lab) on a particle level. But the results must be interpreted more (vaguely) as long-term effects when the interlayers will have become more accessible due to a lower effective stress (after rise pore pressure, after failure of the geosynthetic, see e.g. overview in Schmitz 2001a) or after a long history of leaching that ravels the clay particles and renders them more accessible (thus one should be prudent to Atterberg limits as "first insight" into clay - leachate interactions as was proposed e.g. by (Schmitz (et al 2002c)).*

If clay is brought into contact with leachates there are no substantial changes in the mineralogy. Changes are caused, however, in the amount of each mineral present in the soil. Tournai, Soignies and Kruibeke clay show an increase in Illite due to leachate contact. In Tournai and Soignies clay this is caused by Illitisation of the Smectite. The amount of Smectite subsequently decreases. In Kruibeke and Soignies clay small amounts of Chlorite are transformed into Kaolinite.

A summary of the behaviour of different clay minerals after contact with domestic landfill leachates, the modifications affecting the interlayer space and inducing clay mineralogical changes (supported by the BS characteristic) of the basal reflection are shown in **Figure: B3-10**. Some of these processes concerned separately or in combination or in a stepwise sequence:

- Illitisation (pathway 2A): Insertion of potassium into the interlayers of Montmorillonite (10-14m): These interlayer spaces collapsed and gave rise to a so-called open Illite ("I"). As a consequence the relative content of Illite in the final clay assemblage increased.
- Smectitisation (pathway 1B): A reverse process through leaching of potassium out of the interlayer space; the relative content of (10-14m) increased in the final clay composition.
- Secondary Chloritisation and Al-hydroxilisation (pathways 2B and 2D): Due to the polymerisation of aluminium ions in an acid environment, affecting the interlayer spaces of an open Illite or Montmorillonite, a secondary Chlorite showing the XRD characteristics of either a mixed-layer Illite-Chlorite (10-14c) (increasing thereby the relative content in (10-14c)) (pathway 2B) or of a pillared Smectite (pathway 2D) by increasing the original content of Sm_{Al} was formed.
- Neoformation (pathway 5A): Dissolution of Chlorite, in an acid environment, generated a Kaolinite, with subsequent increase of the latter in the final clay assemblage.

Some of these processes were reversible (like the collapse of Smectite into an open Illite) while others are not (*e.g.* the transition of Montmorillonite to a mixed-layer Illite-Chlorite) under the conditions as prevailing in a landfill liner. In terms of magnitude the most dominant processes were Illitisation and Smectitisation, whether or not followed by the subsequent formation of mixed-layers, by insertion of organic or inorganic substances into the interlayer spaces of Smectite.

Why does one only observe the onset of clay mineral alteration processes?

Why only the onset of clay mineral alteration processes is observed and not a complete alteration is discussed in more detail for one of the most dominant (and geomechanically most important processes as was explained in paragraph **A 3.2.3** and **A 3.2.4**) mineral alteration processes: Illitisation.

In all combinations there is an increase in Illite if leachates are added. In **Table: B3-19** the chemical composition of the leachates is given: The leachates contain indeed a high concentration of small cations like K^+ or NH_4^+ which could cause Illitisation if these substances enter the interlayer space of Smectite. Note that the amount of K^+ cations in the natural fluid phase is very low and that the leachates are needed as a source of K^+ cations to explain Illitisation.

A 2N K^+ cation solution (78g/l) is sufficient to saturate a Smectite (PC Thorez). In **Table: B3-31** the concentration of the "small" ions[30] that cause Illitisation, like $NH_4^+$and K^+, is given for each landfill leachate. For leachate-C, -H2 and -M the combined concentration of K^+ and NH_4^+ cations is a factor 100 smaller than the required K^+ concentration sufficient to saturate a leachate and for leachate-H-1 this is a factor 1. A complete collapse is on the basis of these data unlikely and did not occur.

Table: B3-31

Availability of small cations in the genuine landfill leachates.

Type of ion:	Average leachate-C	Leachate-Hl	Leachate-H2	Leachate-M
K^+ (mg/l)	$6.1\cdot10^{+2}$	$2.1\cdot10^{+3}$	$3.6\cdot10^{+2}$	$5.3\cdot10^{+2}$
NH_4^+ (mg/l)	$3.1\cdot10^{2}$	$2.0\cdot10^{+3}$	$5.2\cdot10^{+2}$	$1.1\cdot10^{+3}$
K^+ (mol/l)	$1.6\cdot10^{-2}$	$5.3\cdot10^{-2}$	$9.3\cdot10^{-3}$	$1.4\cdot10^{-2}$
NH_4^+ (mol/l)	$1.7\cdot10^{-2}$	$1.1\cdot10^{-1}$	$2.9\cdot10^{-2}$	$6.1\cdot10^{-2}$
ions causing collapse (mol/l)	$3.3\cdot10^{-2}$	$1.6\cdot10^{-1}$	$3.8\cdot10^{-2}$	$7.5\cdot10^{-2}$

Are leachate-type and clay-type dependent or independent?

The author showed previously (Schmitz 2001a) that variables like clay type (Tournai, Soignies or Kruibeke), leachate type (leachate-C, -H or -M), temperature (room temperature or 50°C) and initial fluid content of the clay (0.5, 1 or twice the liquid limit of the clay) are independent. The analyses of each variable separately gives the same results as the analyses of a combination of variables. Therefore it is not likely that the variables clay type, leachate type, storage temperature or initial water content amplify each other differently and their effect is thus linearly cumulative. This is one of the observations that lead to develop the equivalent basal spacing (EBS) which will be discussed in chapter **C 5**.

B 3.7.5 Consolidation characteristics of the clay liner: How are these properties modified once the leachate permeated the barrier?

Several slurries of Kruibeke clay powder were prepared with water and with the leachate-C. The samples were tested in oedometer cells at room temperature and at 50°C. The results are shown in **Figure: B3-11.** Tests at ambient temperature on Soignies, Tournai and Kruibeke clay are shown in **Figure: B3-12**.

Assuming a normal distribution, 68% of all results will fall within an interval defined by the mean +/ - the standard deviations, thus in a range: $58\% < LL < 64\%$, corresponding using the correlation above to a maximum range: $0.43 < C_c < 0.49$.

This range incorporates the variation in the measured consolidation coefficient and shows that the differences of the compression index after leachate contact are comparable to those of the liquid limit, not only for Kruibeke clay (**Figure: B3-11**) but as well for Soignies and Tournai clay (**Figure: B3-12**).

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[30] *Hydrated ion radius (Å) (Mitchell 1995): K^+ 3.8-5.3 ; NH_4^+ 5.4 ; Na^+ 5.6-7.9 ; Li^+ 7.3-10 ; Ca^{2+} 9.6 ; Mg^{2+} 10.8*

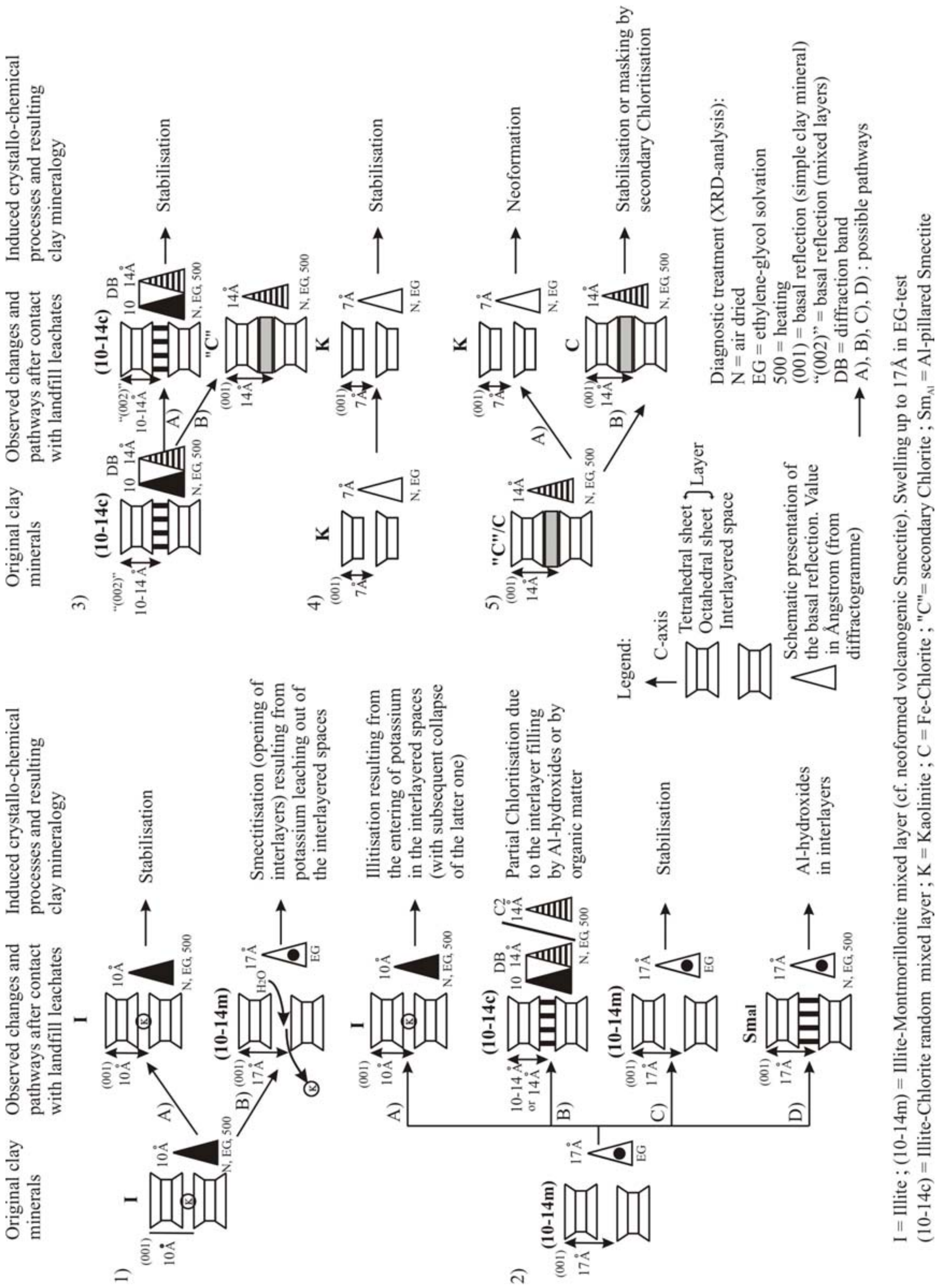
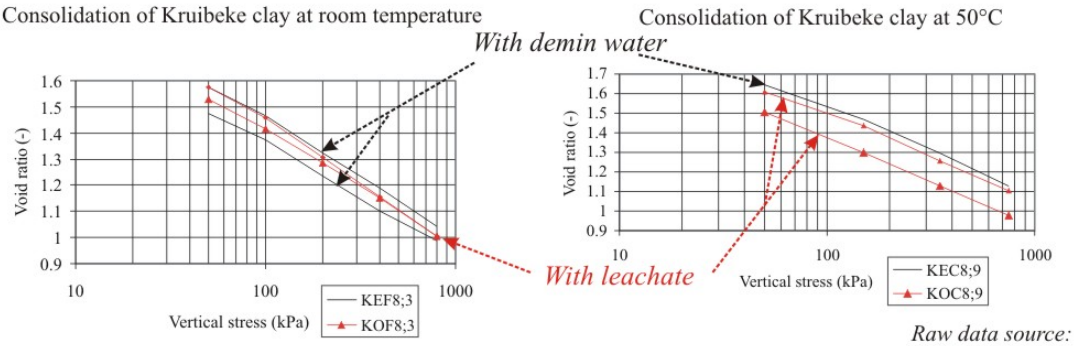


Figure: B3-10

This overview shows all the different mineral alteration pathways observed during the tests with the Kruibeke, Tournai and Soignies clay in contact with leachates-C, -M and -H. The Liège Clay Laboratory sample preparation method was used.



Raw data source:
PC Ourth

Figure: B3-11

Consolidation of homogenised Kruibeke clay exposed to demineralised water and leachate-C at room temperature and at 50°C. Oedometer tests on Kruibeke clay powder, mixed with leachate or demineralised water (clay:fluid ratio 1:5), cured for 3 months (the samples that were tested at 50°C have been stored for 9 months). Compacted within the cell to the 80% of the optimum Proctor density values.

The figures showed that the difference between the void ratio-vertical stress behaviour of Kruibeke clay treated with landfill leachate and demineralised water, was not large. This could have been expected on the basis of the Atterberg results which showed that Kruibeke clay is quite unaffected by the leachate. Values of the Atterberg limit and the compression index for remoulded clays can be related to various index tests. Sridharan and Nagaraj (2000) showed on theoretical and experimental basis that a correlation between the compression index (C_c) and the plasticity index or preferably the shrinkage limit (SL) are more suitable than the correlation between the liquid limit and the plastic limit often found in literature. Many other correlations exist, but the first and simplest correlations, proposed by Terzaghi and Peck (1967, note that this correlation has been changed in more recent editions of their book) suits the best:

$$C_C = 0.009 \cdot (LL - 10)$$

The average value of the Cc obtained by using **Figure: B3-11** is 0.44 for both, the samples stored with leachate-C and the samples stored with demineralised water. The maximum value is 0.45 and the minimum Cc is 0.43, apparently not related to the use of leachate or water.

If the correlation relating the liquid limit and the compression index given above are used:
LL, Kruibeke clay cured with water (**Table: C2-1**), mean = 60%, empirical standard deviation = 1.69%
LL, Kruibeke clay cured with landfill leachates do not change the mean but increase the empirical standard deviation (**Table: C2-1**), mean = 61%, empirical standard deviation = 2.97%.

Apparently, the range of Cc and Atterberg values can be related but for both, the effects of the leachate on this clay were apparently too small to induce measurable changes of the slope of virgin compression or of the corresponding Atterberg limits.

B 3.7.6 Shear strength characteristics of the clay liner: How are these properties modified once the leachate permeated the barrier?

The shear strength of the homogenised clays were tested during CU tests at effective stresses (backpressure was 400KPa) of 200, 300, 400kPa - thus the pressure level expected in the clay liner of a completely filled landfill. The results of the triaxial tests[31] are given in **Figure: B3-13**. A summary of the data in q-p' diagrams are given in **Figure: B3-13-A to C**. The reproducibility of a triaxial test on Tournai clay, tested and cured with demineralised water, was good as can be seen in **Figure: B3-13-A**. When the same clay was cured with landfill leachates C and leachate-H2 the shear strength decreased slightly. However the changes are small, and the parameters related to the structural strength remain largely unchanged. Soignies and Kruibeke clay that were tested with a young landfill leachate and water gave the same angle of internal friction (see **Table: B3-32**). The permeation with leachate will not weaken the clay liner (important to the sloping parts of the landfill).

Table: B3-32

Average elastic and Mohr-Coulomb parameters of homogenised Tournai, Kruibeke and Soignies clay measured during consolidated undrained triaxial tests (see ***Figure: B3-13****). The samples were preconsolidated at* $4 \cdot 10^5$ *Pa leading to an* I_C *of all clays before test > 0.8, effective constant cell pressure during the test varied from 200 - 400kPa.(1) Determined during loading - unloading of deviatoric stress.*

Homogenised	Fluid	ϕ°	E (MPa) (1)
Tournai clay	demineralised water	28	35
	demineralised water	28	37
	leachate-C	27	37
	leachate-H2	26	40
	sat. NaCl	31	-
	sat. KCl	30	
Kruibeke clay	demineralised water	31	50
	leachate-C	31	53
Soignies clay	demineralised water	29	-
	leachate-C	33	-

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[31] *Consolidated undrained tests on homogenised Tournai clay samples that were preconsolidated isotropically to 400kPa and tested at cell pressures of 600, 700 and 800kPa with a backpressure equal to 400kPa. In all cases the clay powder was mixed thoroughly with the fluid at a fluid content equal to the LL of clay. Next the slurry was allowed to cure at room temperature during at least one month.*

B

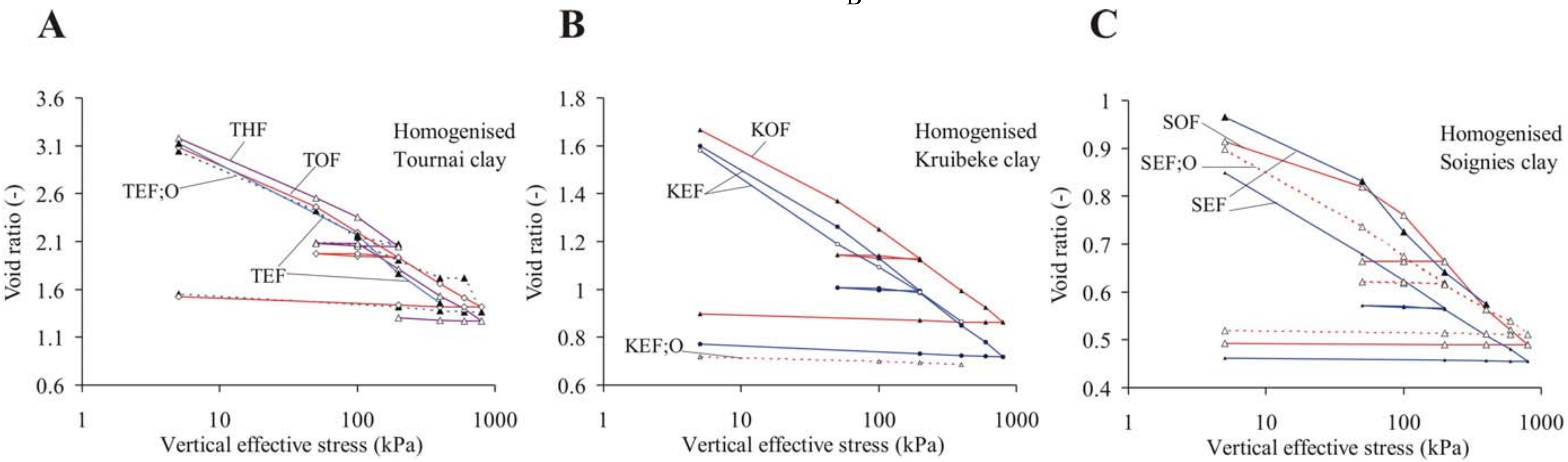
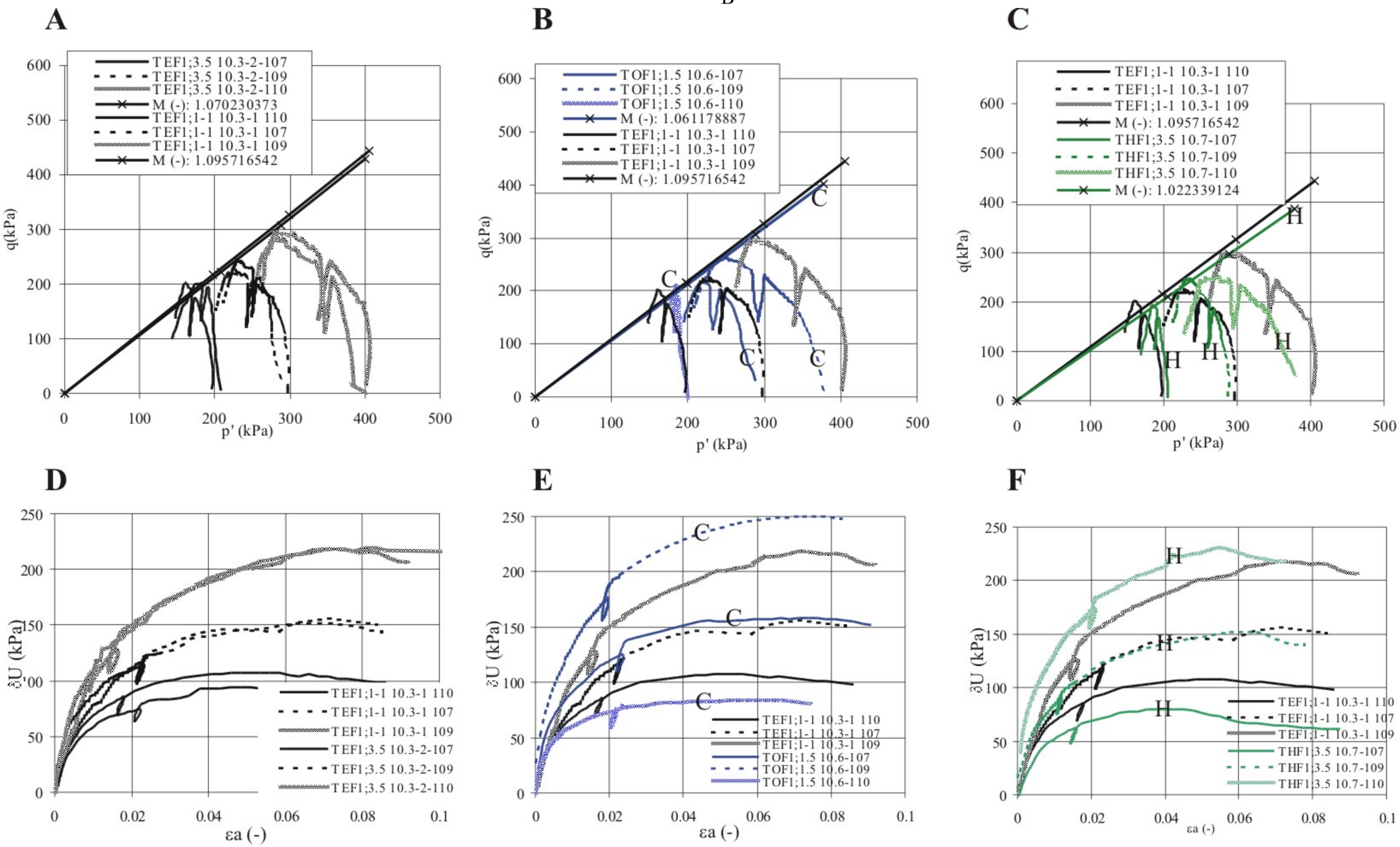


Figure: B3-12

Oedometer test results of homogenised Tournai, Kruibeke and Soignies clay exposed to various landfill leachates

B


A
q(kPa)
p' (kPa)
TEF1;3.5 10.3-2-107
TEF1;3.5 10.3-2-109
TEF1;3.5 10.3-2-110
M (-): 1.070230373
TEF1;1-1 10.3-1 110
TEF1;1-1 10.3-1 107
TEF1;1-1 10.3-1 109
M (-): 1.095716542
0
100
200
300
400
500
600
B
TOF1;1.5 10.6-107
TOF1;1.5 10.6-109
TOF1;1.5 10.6-110
M (-): 1.061178887
TEF1;1-1 10.3-1 110
TEF1;1-1 10.3-1 107
TEF1;1-1 10.3-1 109
M (-): 1.095716542
C
C
C
C
C
THF1;3.5 10.7-107
THF1;3.5 10.7-109
THF1;3.5 10.7-110
M (-): 1.022339124
H
H
H
H
D
∂U (kPa)
εa (-)
0
0.02
0.04
0.06
0.08
0.1
50
150
250
E
F

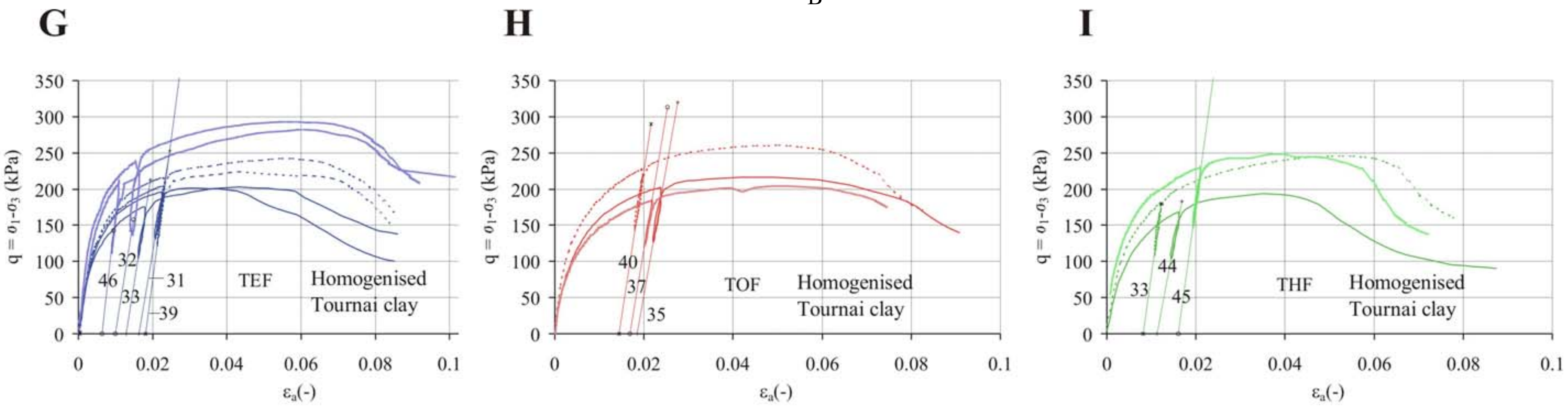


Figure: B3-13

The figures show test results of undrained triaxial tests on homogenised Tournai clay brought into contact and cured during at least one month with demineralised water or landfill leachates or brines.

- (p'-q) plane - A: Tournai clay mixed with demineralised water before the test. B: Tournai clay mixed with leachate-C before the test compared to Tournai clay mixed with demineralised water. C: Tournai clay mixed with leachate-H before the test compared to Tournai clay mixed with demineralised water.

- (variation pore pressure - axial strain plane) - D: Tournai clay mixed with demineralised water before the test. E: Tournai clay mixed with leachate-C before the test compared to Tournai clay mixed with demineralised water. F: Tournai clay mixed with leachate-H before the test compared to Tournai clay mixed with demineralised water before the test.

- (q-axial strain plane) - The numbers indicate the Young's modulus measured during an unloading - loading cycle in MPa - G: Tournai clay mixed with demineralised water before the test. H: Tournai clay mixed with leachate-C before the test. I: Tournai clay mixed with leachate-H before the test

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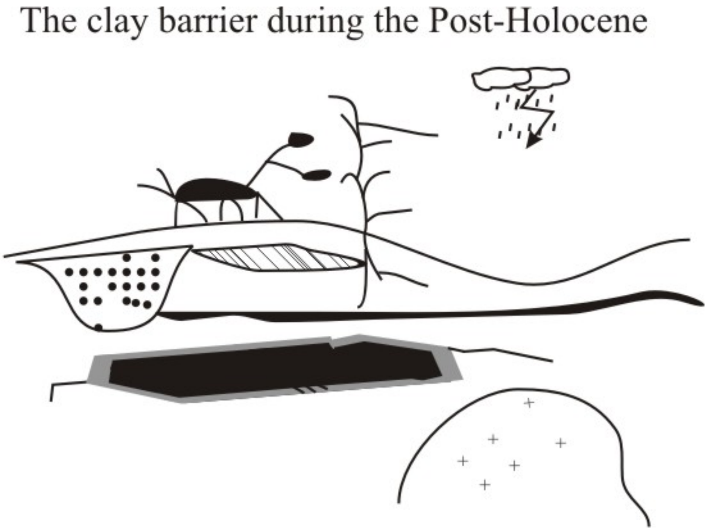
B 4 The barrier during the post-Holocene



Keywords: Geological analogue, humic acid.

B 4.1 Introduction

Towards the end of the biochemical active life of waste, a landfill barrier containing the waste will have been thoroughly permeated by landfill leachates. In addition the composition of the leachate produced by the waste will change. Humic acid is the last leachate that will be produced. This will be the last fluid the clay barrier has to resist. At the same time this will be the longest contact between a particular fluid and the clay barrier. Additionally, environmental boundary conditions will start to change. The confinement period starts to be "noticeable" on a geological time scale: Nearly every possible geological phenomenon could affect the boundary conditions of the landfill.

First, the long-time permeation and the resemblance with natural (pedological) analogues will be discussed, followed by the analysis of a humic acid - clay barrier contact.

B 4.2 Leaching tests and natural analogues

Tournai clay and Soignies clay were exposed (former LGIH, today's Geomac department) to long-term (laboratory scale) leaching tests (during months) with genuine landfill leachates. During the test the chemical composition of the percolate was analysed. Thin sections of the sample were made and the clay mineralogy was determined at different levels of the sample (from the leachate entry to the percolate exit). The test and the description of the natural analogue are based on Thorez (*et al.* 2001).

B 4.2.1 Leaching test

B 4.2.1.1 Set-up

The changes in hydraulic conductivity (triaxial boundary conditions) and of clay mineralogy affecting two different Tertiary clayey materials when leached with a complex domestic waste fluid have been studied within a hydraulic cell (see **Table: B4-1**). The tests conditions can be summarised as follows:

- High confining (400 kPa) and injection (200 kPa) pressure.
- Upward leaching-H1.
- Test duration two months.
- Compacted Tournai and Soignies clay materials.
- Samples were 10 cm high and had a diameter equal to 5 cm.

Table: B4-1

Leaching of leachate-H1 through remoulded Tournai and Soignies clay samples: Test conditions.

Clay sample	Bulk density (kg/m^3)	Initial fluid content (%)	Injection pressure (MPa) (1)	Hydraulic conductivity (m/s)
Tournai	1658	50.46	0.26/0.34	1.9 10^{-11}
Soignies	2113	21.20	0.25	2.0 10^{-10}

(1) Corresponds to 25-30m leachate table.

B 4.2.1.2 XRD analyses

Forced oriented aggregate (FOA) X-ray diffraction analyses were performed after leaching on three different “heights” in the sample.

Mineralogical trends of Tournai clay:
Illite and Illite-Chlorite mixed-layer (10-14c) decreased from the entry (high pressure) to the exit (low pressure). The decrease of Illite in Tournai clay from the entry to the exit implied that this mineral underwent a structural alteration due to the leaching. The percolate reached a pH of 2,5 at the exit of the cell and really acted like a true acid affecting the clay minerals.
The simultaneous decrease of Illite and (10-14c) was compensated by a parallel increase in Smectite and by the development and increase of “Chlorite” (the original sample does not contain any Chlorite); this double trend indicates that the leaching process generated a kind of secondary “Chloritisation”. Additionally one observed a decrease in the Sm_{Al} content, meaning that some of the original Al-pillars became leached from the volcanogenic Montmorillonite.

Mineralogical trends of Soignies clay:
In contrast, for Soignies clay there is only a small decrease of Illite, practically no change in the original (10-14c) content, a decrease in Montmorillonite but without any further “Chloritisation” of the latter clay component.

Amorphous matter in Soignies and Tournai clay:

When looking carefully to the diffractograms of both samples, one observed a “hump” affecting the base line towards the high angle side (around 3 Å and 5 Å). This indicates the occurrence of a certain amount of “amorphous” matter. This occurrence implicated that the alteration of clay minerals and the accompanying decrease of the total amount of clay minerals, generated a certain amount of amorphous matter as compensation. This hypothesis is indeed well supported by the poor quality of the diffractograms related to the upper interval in the tested clay sample.

B 4.2.1.3 Analyses of thin sections

A thin section of the leached Tournai clay was manufactured and analysed. The results demonstrated local destratification of the compressed clay material and the development of a diffuse, nebulous “leaching” front near the middle of the sample. Small and elongated irregular voids, fringed by a thin blackish isotropic matter occurred in association with this front. The occurrence of this matter can be compared to quasi-mangane and quasi-ferrane in Podzols (characterising the boundary between the E and B horizons in a natural Podzol (see **Figure: B4-1**). In parallel these voids and their edges with concentrated isotropic matter are probably the very sites of the main destructuration of the clay minerals (like Smectitisation, secondary Chloritisation). The voids seem also to be somewhat interconnected, meaning by this that these correspond to interconnected channels assuring the percolation of leachate through the compressed sample.

B 4.2.2 Podzolisation as a natural analogue?

B 4.2.2.1 Podzolisation in nature

Podzolisation develops downward through a soil and produces, from the surface to the depth of the Podzol, the classic (see *e.g.* Singer and Munns 1996) trilogy (see **Figure: B4-1**):

- Black O-A- horizon (O = organic; A = humus bearing horizon).
- Yellow or white E-horizon (with removal of most of the clay this in parallel to its intense weathering = eluviation).
- Red Brown B_{Fe}-horizon (accumulation of Fe- and Mn-hydroxides = illuviation).

Podzolisation necessitates a low pH during percolation of acid fluids associated to the degradation of humic matter and of the clay minerals. The acid character and high production of humic acids favour indeed the rapid and finally complete alteration of the parent clay minerals as well as of other silicates (feldspars, ferromagnesians), if present.

Smectitisation and secondary Chloritisation- processes result from the percolation of and leaching by humic acids; the latter eliminates all available cations (K^+, Ca^{2+}, Mg^{2+}) from the upper A and O soil horizons, by extracting them from the clay structures while blocking and concentrating residual “amorphous” components (such components are not materialised as reflections in a diffractogram).

B 4.2.2.2 Podzolisation induces changes on the interlayer level of clay minerals

Step 1:
Due to leaching (of humic acids) in nature associated to relative open conditions, a soil may undergo a:

- Partial to total Smectitisation which affects the parent Illite (which undergoes an opening of the interlayers due to the removal of the potassium)
- Vermiculitisation readily affects the Chlorite (if present).

Thus the alteration (degradation) operates at the level of the interlayer spaces through a progressive leaching of potassium, magnesium, in Illite and Chlorite, respectively.

Step 2:
A Vermiculite may undergo a secondary Chloritisation in the upper horizons A and B of a soil. This latter process produces a secondary Chlorite: A clay structure which, during X-ray diffraction analyses of samples treated with EG and heated to 500°C, behaves similarly as a true Chlorite.
The distended interlayers of a degraded Illite may become filled with Al-hydroxides as to produce a random mixed-layer Illite-Chlorite (10-14c) and eventually if continuously leached a "Chlorite".
Chloritisation may also affect a former Smectite and may "transform" the latter structure into a kind of mixed-layer (10-14c).

B 4.2.2.3 Podzolisation causes changes on the TOT/TO level

Podzolisation yields at the end, the complete degradation of the parent silicates (*e.g.* TOT clay minerals) and leaves as end-product a Kaolinite (a TO clay mineral). However, before Kaolinite becomes fully established and substitutes for the other original clay minerals, intermediate Smectitisation and later secondary Chloritisation phases develop.

B 4.2.3 Comparison of Podzolisation in nature to the results of the leaching test

In the case of the described experiments conducted in a hydraulic cell in which a clay sample is submitted to an upward leaching under pressure, a kind of forced, but upward "eluviation" process develops during the passage of the domestic leachate. The mineralogical effects due to this "eluviation" clearly induces the weathering of some (fractions of) original clay minerals along either a Smectitisation or a secondary Chloritisation pathway or a combination of both (depending on the origin of the investigated materials, Tournai or Soignies clay). This mimics a kind of Podzolisation.

In other words, the leaching developed under high confining and fluid injection pressure allows the upward transfer (through the core) of the domestic fluids (containing organic matter) and is analogous to the downward Podzolisation as this occurs in nature. The final Kaolinisation is not reached in Tournai and Soignies clay samples because of the short duration (on a geological scale) of the experiment. However, the occurrence of amorphous matter in the upper interval of the Soignies clay sample, and the Chloritisation within the same interval in Tournai clay sample are indicative of intermediate stages as found in/during natural Podzolisation.

However, the imposed laboratory conditions as well as time constraints do not entail a complete Podzolisation of the parent clay minerals; the very first stages of “Podzolisation” are specifically indicated by the development of secondary Chlorite.

The X-ray diffraction results obtained during the experiments may be compared also to some extents to a Smectitisation and/or secondary Chloritisation processes well-known in case of pedogenesis like Podzolisation. The resemblance to Podzolisation is supported, for Tournai clay sample, by a petrographical study.

By “forcing” the injection pressure within a hydraulic cell, one can envisage and forecast what kind of alteration of clay minerals would occur and develop between the clay barrier and the leachate during several decades on the site of the domestic waste dumps. The results may serve as mineral and geomechanical indicators, and certainly would indicate, anticipatively, what kind of damages may or would occur if developed within a clay barrier during a sufficiently long time, by taking into account also the composition of the parent clayey material and that of the leachates.

B 4.2.4 Conclusion

The upward clay mineral alteration finds some mineralogical similarities and trends as developed during a downward pedogenetic alteration and mimics the first stages of leaching and destructuration that occur during a Podzolisation.

The final stage of a Podzol yields the formation of Kaolinite. If the test conditions mentioned above apply to the situation towards the end of the life of the landfill the clay barrier has been partially transferred to its final stage: A Kaolinite. This situation can be modelled by using the geomechanical properties of a Kaolinite. These results will then simulate the final stage of the landfill barrier.

How Podzolisation can be interpreted in terms of equivalent basal spacing is explained in **Part: C 5** of this thesis.

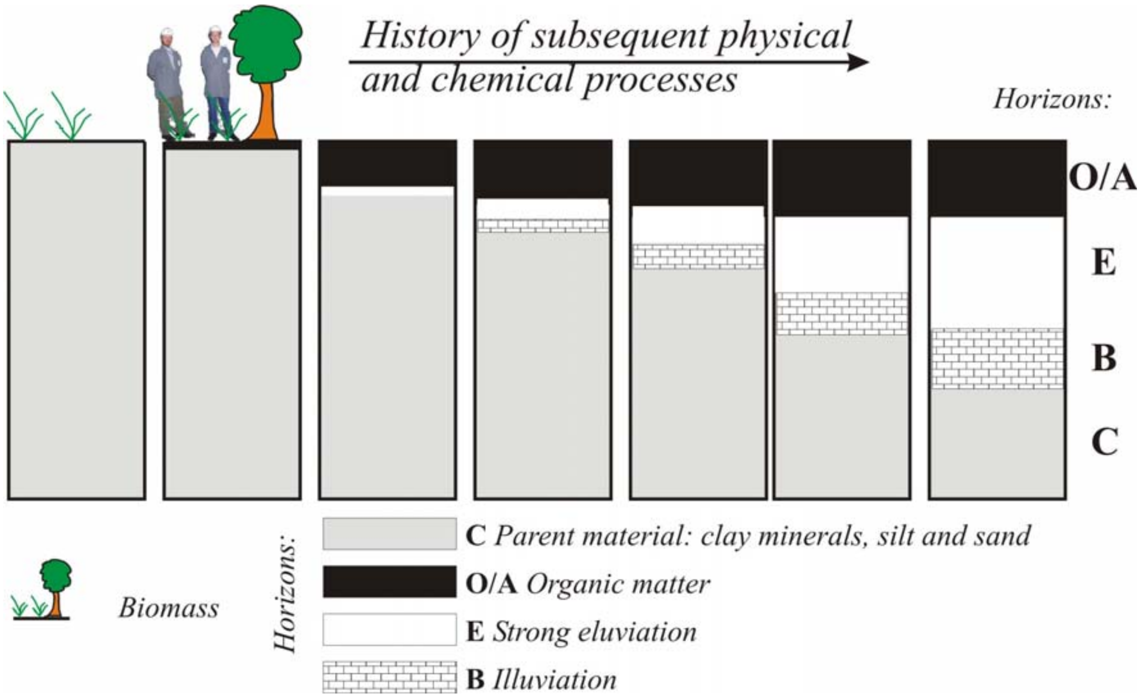


Figure: B4-1

The evolution of different soil horizons during Podzolisation.

B 4.3 Humic acid

Batch tests where clay was exposed to humic acid showed that the humic acid does not affect Tournai, Soignies and Kruibeke clay. The reference Smectite in contrast showed a decrease of the liquid limit with an increasing concentration of humic acid. The mineralogical analyses did not show a modification of the clay mineralogy.
These results show that if humic acid is the last leachate that will be produced by the waste and depending on the rate of decomposition, even the longest contact between clay barrier and fluid will be that between clay and humic acid. This will not result in any modification of the clay.

However, attention has to be paid, that by the time humic acid will be formed the clay has not been transformed into a new clay by action of other leachates. Reactions between humic acid and the “new” clay (see *e.g.* **B 4.2**) cannot be excluded.

B 5 Conclusions

- The hydraulic conductivity of the Tertiary Tournai, Kruibeke and Soignies clays, does not change or decreases slightly, when percolated by landfill leachates (representative of domestic landfill leachates in humid regions) with respect to the hydraulic conductivity measured with water. Other geomechanical properties, elastic (*e.g.* Young’s modulus) and plastic (*e.g.* friction angle) are barely affected by landfill leachate percolation.

- Dominant clay mineral alteration processes caused by landfill leachate contact are secondary Illitisation and Smectitisation. The clay mineral alterations of the Tertiary clays caused by the different leachates is similar, irrespective of the age of landfill leachate that is used.

- The chemical composition of the natural fluid phase of the Tertiary clays remains important even after homogenisation of the clay. If the fluid phase of the clays is acid the clay-leachate combinations are acid even if the landfill leachates themselves are basic. This fluid phase in its original or modified form is responsible for the clay mineral alteration processes of Kaolinisation and removal of organic material from the interlayer space of Smectite.

- Although some chemical substances that are present in the natural clay are lost during the homogenisation of the clay, the concentration of others increases: F^- and SiO_2. These two components - of volcanic origin and deposited with the neoformed Montmorillonite - were freed from the matrix during the homogenisation process.

- Presence of landfill leachate in the fluid phase of the clay will not weaken (Mohr-Coulomb and elastic properties) the clay.

- The clay mineral alteration processes and changes in geomechanical properties are small. Tournai clay remains Tournai clay, Soignies clay remains Soignies clay and Kruibeke clay remains Kruibeke clay. The alteration processes introduce scatter but not substantial change.

- The difference in clay mineralogy and geomechanical properties between the two Ypresian clays (Soignies and Tournai clay) is sometimes even larger than the difference between an Ypresian clay and the Rupelian clay (Kruibeke). The data of one lithological unit as a whole is only of limited use. Thus a detailed analysis (clay mineralogical and geomechanical) of each outcrop is needed.

- Once the clay mineral alteration processes during permeation of domestic landfill leachate through the Tertiary clay barrier are recognised comparison to natural analogues can be made to predict the behaviour of the clay barrier on the long-term. Based on this knowledge suitable clay deposits can be chosen to limit the changes in geomechanical and clay mineral alteration properties during the technical life of the clay barrier.

Suggestions when constructing clay barriers:

- To avoid processes related to an acid attack (*e.g.* on short-term the Kaolinisation of Chlorite and removal of organic material from the interlayer space of Montmorillonite) the clay has to be installed directly after excavation. If the clay is not pretreated, the clay has to be installed and covered directly after excavation to avoid oxidation of *e.g.* pyrite. Note that the pH of domestic landfill leachates in humid regions is nearly neutral.

- Next to a compulsory investigation into the nature of the leachates and the mineralogy of the clays, one must also pay attention to the nature of the composition of the clay-fluid for each batch of excavated clay separately.

C New tools

C 1 Introduction

In part **A**, a literature overview of clay-leachate interactions was given. It was shown how fluids influence the mechanical behaviour of clay and on which levels interactions occur. It was shown why it is comfortable to analyse possible interactions at three different levels: The particle, interlayer and TOT/TO levels.

In part **B**, the influence of landfill leachates on clay barriers in municipal landfills, the heart of the ARC project, was studied. Like in a real case scenario, natural clays were selected: Tournai clay and Soignies clay from the Walloon region, Kruibeke clay from the Flemish region as well as genuine landfill leachates originating from three different existing landfill sites in the Walloon region.

Part **C** represents the spin-off of this thesis.

In chapter **C 2** the natural heterogeneity of the clays used in the experiments is discussed in relationship to the influence of different leachates. In chapter **C 3** the variations of the LL are analysed in a new approach, which consists in the implementation of the chemical composition of the fluids contained in the clay into the analysis of clay - leachate interactions. In chapter **C 4** correlations between Atterberg test parameters are sought. In the same chapter correlations between mineral phases of the clay exposed to landfill leachates are used to confirm mineral alteration pathways described in part **B 3**. In chapter **C 5** it is explained how changes on the interlayer level *i.e.* changes of the clay mineralogy (natural clays and reference Smectite[32] and Kaolinite) can be related to geomechanical properties. Therefore the equivalent basal spacing (EBS) is defined. In the remainder of the chapter it is shown how the EBS can be used to predict the behaviour of clay when heated, when exposed to salts and mixed with other clays *etc.* In chapter **C 6** it is explained how a clay sample can be discretised as a homogenous assembly of discrete clay particles on the basis of various geomechanical and petrographical tests. It is shown how the dimensions of clay particles and their orientation are deduced from these tests. On the basis of these interpretations it is shown that test results and models determined on "pure" Smectites do not necessarily apply to natural clays. Additionally the interlayer accessibility of clays under barrier conditions is examined.

In chapter **C 7** the clay - leachate interaction on the particle level is analysed. A constitutive law relating the interparticle spacing to external stress and fluid chemistry is explained. Finally, it is shown how this constitutive law was introduced into the finite element code *LAGAMINE* to predict the evolution of the hydraulic conductivity during

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[32] *As was discussed in chapter **B 2**, the Smectite fraction contained in the Tournai, Kruibeke and Soignies clay is a neoformed volcanogenic Montmorillonite. A suitable reference Smectite should have the same origin (neoformed or transformed) because the origin of the Smectite determines to a large extent the reversibility of clay mineral alteration processes like e.g. Illitisation (see paragraph **A 3.2.4**). In chapter **C 5** it will be discussed why this is as well important from a geomechanical point of view. Such a reference Smectite was found and used as a reference in the following chapters.*

permeation of a clay barrier. Additionally an extrapolation approach was developed. In chapter **C 8** examples are shown how the information contained in Parts **A**, **B** and **C** can be used to determine the impact of clay - leachate interactions on clay barriers.
In chapter **C 9** conclusions concerning part **C** are given.
Part **C** is followed by a conclusion and a synthesis of the thesis.

C 2 The heterogeneity of the homogenised clays and the reference Smectite with respect to the influence of the leachates

C 2.1 Introduction

During the lifetime of a landfill the landfill leachates[33] might permeate the clay barrier: This situation and its consequences were discussed in **Part: B**. During the leachate-clay interactions the changes in Atterberg properties were measured. It was shown that these changes were rather small. Additionally all geomaterials are likely to possess an inherent heterogeneity. In this chapter it is analysed to which extent the measured changes are due to the heterogeneity or to the interaction with landfill leachates by using the approach of Réthási (1988) presented in paragraph **A 4.2.5**.

C 2.2 Analyses

C 2.2.1 Data

In **Table: C2-1** it is shown that if the liquid limit of all clay-fluid combinations is considered as being part of one database (row: All clay-fluid combinations) this database possesses a natural heterogeneity that is as large as its standard deviation. If other databases are considered which consist of one clay type only, one remarks that this natural heterogeneity decreases drastically. Therefore the different clay types, fluids added to the clay *etc*. are analysed separately.

Table: C2-1

Analyses of the natural heterogeneity (based on the liquid limit) of the clays that were used
S = empirical standard deviation measured in Liège laboratories; S_{rp} *= standard deviation characterising the reproducibility of Atterberg tests in general;* S_h *= standard deviation characterising the natural heterogeneity; COV = coefficient of variation;* C_{vh} *= coefficient of variation describing the natural heterogeneity; (1)* $S_{rp} = 0.0365 \cdot LL_{mean} + 0.175$ *(Borus and Rév 1968). (2)* $s_h = \sqrt{s^2 - s_{rp}^2}$ *(Réthási 1988). (3) No result because* $S<S_{rp}$*. (4) A strong heterogeneity in the database is reflected by surpassing the criteria mentioned in this cell.*

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[33] *The composition of the leachates has been discussed in paragraph B3.4.3.*

C

All clay - fluid combinations (row numbers are referred to in the text)	LL (18/07/02)	Mean (%W_c)	S (% W_c)	S_{rp} (1) (% W_c)	S_h (2) (% W_c)	COV (-)	C_{vh} (-)	S_h/S (-)	S/S_{rp} (-)	COV>0.1; S/S_{rp}>2; C_{vh}>0.1; S_h/S>0.8 (4)
	XXX;X	114	139.15	4.34	139.1	1.22	1.22	1.00	32	4 criteria surpassed
Tournai clay row 1	TEF1;1	127	7.93	4.79	6.31	0.06	0.050	0.80	1.7	1 criterion surpassed
Tournai clay row 2	TEF1;X	128	7.91	4.86	6.24	0.06	0.049	0.79	1.6	1 criterion surpassed
Tournai clay row 3	TEXX;X	123	9.82	4.68	8.63	0.08	0.070	0.88	2.1	2 criteria surpassed
Tournai clay row 4	T(E,O,M,H,U)F1;X	125	11.7	4.74	10.7	0.09	0.086	0.91	2.5	2 criteria surpassed
Tournai clay row 5	T(E,O,M,H,U)XX;X	122	9.23	4.64	7.98	0.08	0.065	0.86	2.0	2 criteria surpassed
Tournai clay row 6	T(E,N,K)F1;X	117	22.4	4.44	22.0	0.19	0.19	0.98	5.0	4 criteria surpassed
Tournai clay row 7	(T,Tnat)(E,-)F(1,-);X	127	9.40	4.82	8.07	0.07	0.063	0.86	2.0	2 criteria surpassed
Kruibeke clay row 1	KEF1;X	60	1.69	2.35	x (3)	0.03	x (3)	x (3)	0.7	no criterion surpassed
Kruibeke clay row 2	KEXX;X	60	2.50	2.37	0.80	0.04	0.01	0.32	1.1	no criterion surpassed
Kruibeke clay row 3	K(E,O,M,H)XX;X	61	2.97	2.40	1.75	0.05	0.03	0.59	1.2	no criterion surpassed
Kruibeke clay row 4	K(E,N,K)F1;X	60	12.9	2.38	12.7	0.21	0.21	0.98	5.4	4 criteria surpassed
Kruibeke clay row 5	(K,Knat)(E,-)F(1,-);X	65	10.7	2.55	10.4	0.16	0.16	0.97	4.2	4 criteria surpassed
Soignies clay row 1	SEF1;X	38	1.57	1.58	x (3)	0.04	x (3)	x (3)	1.0	no criterion surpassed
Soignies clay row 2	SEXX;X	38	1.80	1.56	0.91	0.05	0.02	0.50	1.2	no criterion surpassed
Soignies clay row 3	S(E,O,M,H)XX;X	37	2.04	1.52	1.36	0.06	0.04	0.67	1.3	no criterion surpassed
Soignies clay row 4	S(E,N,K)F1;X	39	5.21	1.59	4.96	0.13	0.13	0.95	3.3	4 criteria surpassed
Soignies clay row 5	(S,Snat)(E,-)F(1,-);X	41	4.16	1.65	3.82	0.10	0.094	0.92	2.5	4 criteria surpassed
Ref. Smectite row 1	CEF1;X	665	2.52	24.4	x (3)	0.00	x (3)	x (3)	0.1	no criterion surpassed
Ref. Smectite row 2	CEXX;X	659	41.4	24.2	33.5	0.06	0.05	0.81	1.7	1 criterion surpassed
Ref. Smectite row 3	C(E,O,M,H)XX ;X	571	113	21.0	111	0.20	0.20	0.98	5.39	4 criteria surpassed
Ref. Smectite row 4	C(E,N,K)F1;X	356	338	13.2	337	0.95	0.95	1.00	25.6	4 criteria surpassed

C 2.2.2 Reference Smectite

The coefficient of variation (COV) and heterogeneity (S_h) of the liquid limit (LL) of the reference Smectite samples stored with water at the liquid limit is extraordinary low (**Table: C2-1** lines: Reference Smectite). This reflects that this clay (in contrast to the other investigated clays collected *in situ* by the author) is a well-homogenised industrial product. The dramatic increase in heterogeneity with varying fluid contents (second row reference Smectite) is related to the changes in concentration of the remnant fluid phase of the clays (discussed in chapter **C 3**). The enormous heterogeneity obtained when the reference Smectite is mixed with landfill leachates (third row reference Smectite) reflects the sensibility of the nearly pure commercial Smectite to the leachates (due to the higher equivalent basal spacing see **C 5**, the absence of a fluid phase comparable to the composition of the leachates discussed in chapter **B 3.4.3** and the large number of interparticle voids with respect to the number of interlayer, see **C 6.3.4**). The changes caused by the leachates are of the same order as the changes caused by the addition of salt solutions to the other clays. The addition of salts to this clay (last line reference Smectite) causes the COV to be equal to 1 and the $S_h/S = 1$: The comparison of Smectite treated with and without salt is similar to a comparison of two different clay types.

C 2.2.3 Kruibeke and Soignies clays

Both the curing time with water and the amount of water added to the clays do not change the coefficient of variation (COV) much. The values remain below 0.05. The natural heterogeneity of these clays is low (**Table: C2-1** lines: Kruibeke and Soignies clay). When leachates are added the heterogeneity increases, the COV remains nearly constant. The leachates introduce some scatter but do not change the liquid limit as the salt solutions do. The COV increases rapidly (like for Tournai clay) when salts are added. With a ratio S_h/S near to 1 it can be stated that in contrast to the leachates, the salts change the behaviour of the clay dramatically (row 4 Kruibeke or Soignies clay). The same observation can be made for the homogenisation process (row 5 Kruibeke or Soignies clay), from which the Kruibeke and Soignies clay suffer more than the Tournai clay (row 7 Tournai clay).

C 2.2.4 Tournai clay

The coefficient of variation (COV) of the homogenised Tournai clay (row 1 and 2 Tournai clay) is near 0.05, which indicates that the mean of the liquid limit is determined with a small uncertainty. The standard deviation ($S = 7.9$) is however larger than the normal standard deviation for a clay with a comparable liquid limit ($S_{rp} = 4.9$). The ratio S_h/S is rather large; this means (following Rétháti 1988) that the overwhelming part of the standard deviation is not due to faults of the tests but to the natural heterogeneity (including the homogenisation during sample preparation) of the soil - even for the samples tested only with water.

A very high COV can be found if saturated salt solutions are added (row 6 Tournai clay). Even the difference between the natural Tournai clay and the Tournai clay after homogenisation is less (last row). The addition of salt causes in terms of liquid limit a shift from one into another clay type. The other factors like the addition of different landfill leachates *etc.* cause a considerable increase in heterogeneity and COV, although less in the case of Tournai clay than in the case when the reference Smectite is considered, but more than for Soignies and Kruibeke clays.

C 2.3 Conclusions

If the following criteria are taken as indications (last column **Table: C2-1**) of substantial changes in geomechanical parameters represented by the liquid limit when the clay is homogenised or leachates are added:

- COV>0.10
- $S/S_{rp} > 2$
- $C_{vh}>0.10$
- $S_h/S > 0.8$

Four of these criteria are trespassed if:

- Brines are added to homogenised clays.
- Clays are homogenised by drying (30°C) and grinding (except Tournai clay which is less affected).
- Landfill leachates are added to the reference Smectite.

Two of these criteria are trespassed if:

- The fluid content is changed in homogenised Tournai clay.
- Landfill leachates are added to Tournai clay.

On this basis one can conclude that:

- Considering that (see chapter **C 5**) the equivalent basal spacing increases in the order Soignies, Kruibeke, Tournai clay and reference Smectite, the clays with a high equivalent basal spacing are most affected by landfill leachates and changes in fluid content (only natural clays).
- Clays are seriously affected by the homogenisation process.
- Clays are seriously affected by the presence of brines.
- Tournai clay possesses the largest natural heterogeneity.

C 3 The effect of variations in fluid content on the liquid limit

C 3.1 Introduction

In **Part: B** it was shown that both the chemical composition of the leachates but especially the initial fluid contained in the clays have an important influence on the Atterberg tests.

Therefore the chemical composition of the fluid contained in the clay has been tested at several stages during the life of the clay in a landfill. Surprisingly, the concentration of many components (different polyvalent cations) was even higher in the natural pore water of the clay than in the leachates.

This raised the question if the leachate is “aggressive” with respect to the natural fluid phase? This will be discussed in the current chapter on the basis of the diffuse double layer theory.

C 3.2 Changes in concentration within the clay

Observations related to a varying liquid limit with varying clay to fluid ratios can be related to changes in concentration of substances present in the clay. *In situ* such changes in fluid content of the clay occur during exposure of the clay in the quarry, during transport and construction of the barrier on the landfill construction site.

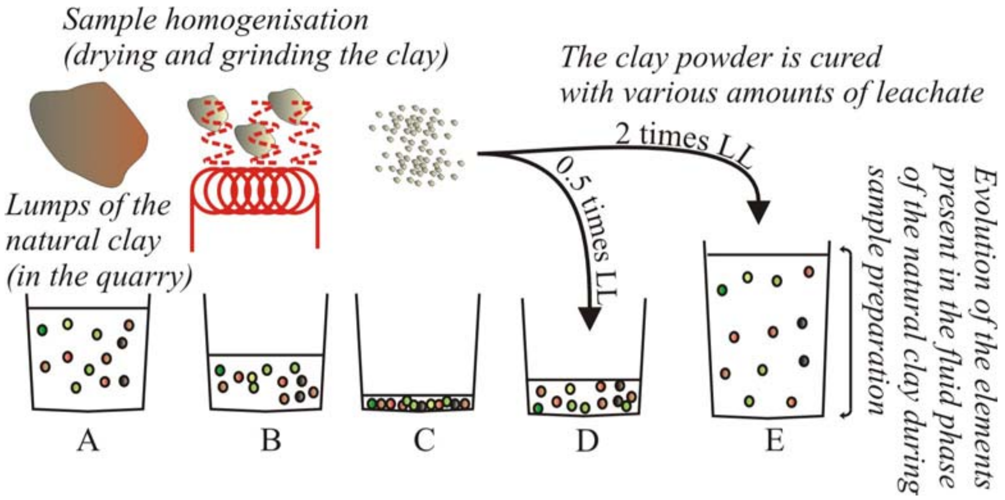

Figure: C3-1

Observed dependency on the initial fluid content is based on the high (with respect to the leachates) concentration of substances found in the natural clay. Further increase of the concentration is caused by the homogenisation process and testing methods, not unlike the conditions the clay will experience in situ.

During drying (from **A** to **C** in **Figure: C3-1**) the concentration of the substances in the fluid phase of the clay reached a maximum value once the clay has been stored as powder. Note that the alteration processes are dormant in the case of a virtual absence of fluid that serves as a transport agent. The amount of fluid (*e.g.* of leachate) added to the clay during the subsequent step fixed the concentration of the inherited substances. If only a small amount of fluid was added to the clay (situation **D** in **Figure: C3-1**, in the case of a sample stored with a leachate at a fluid content equal to half of its liquid limit), the concentration of these inherited substances was automatically higher than in the case of a leachate simply added in excess (situation E in **Figure: C3-1**). In these cases the concentration present in the landfill leachates remains the same as long as the leachates are not diluted.

C 3.3 Explanation of liquid limit alterations based on changes in diffuse double layer thickness

C 3.3.1 Introduction

Tests involving various homogenised clays and various landfill leachates added in different concentrations showed changes in liquid limit (see **Part: B**). These changes will be analysed here in more detail by calculating the double layer thickness (Gouy Chapman double layer model see *e.g.* van Olphen 1963) and the liquid limit on the basis of this double layer thickness by using the relationship between the double layer thickness and the liquid limit developed by Fam and Dusseault (1999).

The assumptions are that one is dealing only with monovalent cations contained in leachates and clays and that a higher concentration in ions causes a decrease in the double layer thickness and a decrease in the liquid limit (**Table: A4-3**).

C 3.3.2 Set up of the analysis

Three different cases are discerned:

- Case A: In this case the equivalent concentration of monovalent particles is calculated for each clay-leachate combination tested on clay samples homogenised in the laboratory. The influence of the fluid phase of the clay is represented by the chemistry of the squeezed-out clay-fluid.
- Case B: In this case the equivalent concentration of monovalent particles is calculated for each clay-leachate combination tested on clay samples homogenised in the laboratory. The influence of the fluid phase of the clay is represented by the chemistry of the contact fluid of the homogenised clay.
- Case C: In this case the equivalent concentration of monovalent particles is calculated for each clay-leachate-dilution combination tested on clay samples homogenised in the laboratory. The influence of the original fluid phase of the clay is not taken into account.

Once the concentration for each case is known the conversion can be made from concentration to double layer thickness. In **Table: C3-1** the constants that were used are given.

Table: C3-1

Parameters used to make the conversion from concentration to double layer thickness.

Parameter	Symbol	Value	Unit
Valence	val	1	-
Faraday constant	F	96485.3	C/mol
Gas constant	R	8.3145	J/mol/K
Electric constant = permittivity vacuum	ε_0	$8.85419 \cdot 10^{-12}$	F/m=C²/(J·m)
Relative permittivity water = relative dielectric constant at 293K	ε'	80	-
Temperature during test	T	293	K
Density fluid	ρ_f	1000	kg/m³

Once the double layer thickness is known the liquid limit can be calculated using the method Fam and Dusseault (1999) proposed (described in paragraph **A 4.2.4.2**). Therefore the specific surface of each clay type has to be known (**see table: C3-2**):

Table: C3-2

Specific surface of the natural clays and the reference Smectite.

Clay type:	Tournai	Soignies	Kruibeke	Reference Smectite	Reference Smectite
S_a (m²/kg)	$6.60 \cdot 10^{+4}$	$1.35 \cdot 10^{+4}$	$2.02 \cdot 10^{+4}$	$5.56 \cdot 10^{+5}$	$4.70 \cdot 10^{+4}$
Method	N_2-BET (1)	N_2-BET (1)	N_2-BET (1)	EGME (2)	N_2-BET (2)

(1) Tests performed in the department of Prof. Jacobs (Katholieke Universiteit Leuven).
(2) Keijzer (2000).

C 3.3.3 Results

The method proposed by Fam and Dusseault (1999) predicts liquid limit values that are too low: For Soignies clay the predicted LL < 5% whereas the value should be around 35% (**Table: C5-1**). For Tournai clay the predicted liquid limit is around 20% whereas it should be > 100% *etc*. There is clearly a problem in estimating the base level of the liquid limit of a clay. But imagine that this base level would have been attained, could the approach give at least qualitative estimates of the modification of the liquid limit if leachates are added? The results discussed in paragraph **B 3.7.3.5** (expressions (**B3 - 2**) to (**B3 - 6**)) and their qualitative estimate using the diffuse double layer theory with the assumptions made in case A to C are shown in **Table: C3-3**.

Table: C3-3

*Estimation of the LL rules as discussed in **Part: B** by using the double layer theory.*

Observation made and discussed in paragraph B 3.7.3.5	Case		
	A	B	C
$LL_{TXXX} > LL_{KXXX} > LL_{SXXX}$	true	not true	true
$LL_{TM\geq1F} > LL_{TH\geq1F} > LL_{TO\geq1F}$	not true	not true	not true
$LL_{T\beta2F} > LL_{T\beta1F} > LL_{T\beta0.5F}$ β= E or M or H or O	true	true	true
$LL_{TEF1} > LL_{T\beta F1(1/8)} > LL_{T\beta F1(1/4)} > LL_{T\beta F1}$ β = O or H	true	true	impossible

C 3.3.4 Discussion

In case A (defined in **C 3.3.2**) nearly all observations made during the test can be predicted. Only the effect caused by the different leachates cannot be predicted correctly. Why? Simply because the amount of equivalent monovalent cations measured by chemical analyses of two landfill leachates do not reflect the measured liquid limit results. The liquid limit of clays in general cannot be predicted only on the basis of the double layer (see chapter **C 5**).

Case B suffers from the same problems as case A. In addition it cannot predict a higher liquid limit of Kruibeke clay samples with respect to the Soignies clay samples. The values of Kruibeke clay samples are too low with respect to the measured values because the concentration of equivalent monovalent cations measured is very high in the contact fluid of the Kruibeke clay samples.

Case C gives results as case A but, in addition, this method cannot of course handle the influence of diluted leachates on the concentration of cations in the reactivated fluid phase contained in the clays.

C 3.4 Conclusion

Liquid limit predictions on the basis of the double layer model like the Fam-Dusseault model used for the analyses above do not give correct (wrong order) quantitative predictions of the values of the liquid limit. This is caused by:

- The definition of the void ratio, which as will be shown in **C 6.3.4**, is only valid for clays like Smectite in which the particles contain only several and not hundreds or thousand TOT/TO-layers.
- The assumption that the liquid limit is based only on the diffuse double layer. In chapter **C 5** it will be shown that the liquid limit depends largely on the changes in the interlayer space.

Anyway this model can be used to determine changes due to leachate interaction qualitatively but of course only on the basis of differences in the concentration of cations. This can lead to some deviation to the measured results. If both, the natural fluid phase of the clay and the nature of the leachates, are taken into account the best estimates are obtained.

The composition of the natural fluid phase of a clay can be determined in several ways (squeezed-out clay-fluid and contact fluid). Depending on the extraction method other results are obtained.
It was shown that:

- The squeezed-out clay-fluid contains more substance originating from the interlayer space than the contact fluid (**Part: B**).
- For the considered clays the squeezed-out clay-fluid gave the best prediction of the liquid limit.

This underlines the fact that the characteristics of the interlayer level (in this case the chemical composition) have a profound influence on the liquid limit. This aspect and the observation that other interactions between the clay and leachates are not based on modifications on the particle level but on the interlayer level which cannot be predicted correctly with the diffuse double layer theory will be discussed more extensively in chapters **C 5**.

C 4 Correlation between various mineral species

C 4.1 Introduction

In this section correlations are sought between:

- Clay mineral species: To validate the clay mineral alteration pathways.
- Different Atterberg limits: To find relationships between the liquid limit, plastic limit and plasticity index.

An extensive analysis of the closed data can be found in Schmitz (2001a)

A correlation between clay mineral species and Atterberg limits cannot easily be interpreted. Therefore this will be discussed separately in chapter **C 5**.

This chapter is subdivided in the analyses of the:

- Open data. Atterberg limits are not closed as the clay mineral data. Thus no correction is needed (see paragraph **C 4.2**).
- “Opened” data. The original closed clay mineral data is analysed (see paragraph **C 4.3**) using Niggli numbers (correction for the dominant mineral species).

The correlation coefficient was calculated using the following formula:

$$r = \frac{n \cdot (\Sigma X \cdot Y) - (\Sigma X) \cdot (\Sigma Y)}{\sqrt{\left[n \cdot \Sigma X^2 - (\Sigma X)^2\right] \cdot \left[n \cdot \Sigma Y^2 - (\Sigma Y)^2\right]}} \qquad \textbf{(C4 - 1)}$$

r	product moment correlation coefficient, a dimensionless index that ranges from -1.0 to 1.0 inclusive and reflects the extent of a linear relationship between two data-sets
X	a value of dataset x
Y	a value of dataset y depending on X
n	number of values in data-set x or y

Why are correlations sought?

- If a correlation between α and A is known to exist and if a correlation can be found between parameter A and B (A and B are variations on the same physical parameter), the link between B and α is known. (*e.g.* EBS → LL → PI, example in chapter **C 5**).
- Correlations as *e.g.* the correlation between the liquid limit and plastic limit within one clay species are known to exist from literature. If these correlations do not (anymore) exist for the same clays treated with and without leachate this could be caused by the modifications induced by the leachates added to the clay if this clay-leachate interaction caused such changes with respect to the original clay, that a new mineral with another LL-PI relationship has been formed.

C 4.2 Open data-set: Atterberg values

Liquid limit, plasticity index, plastic limit:

Atterberg parameters are in contrast to the mineralogical data presented in terms of relative quantities thus as open data.

Atterberg parameter versus another Atterberg parameter:

The correlation between the liquid limit and the plasticity index of homogenised Tournai, Kruibeke and Soignies clay in contact with landfill leachates exists nearly on all levels[34]. A major exception is the SXXX level (see Schmitz 2001a). The correlation between the liquid and plastic limit is plotted in **Figure: C4-1**. This correlation is used in chapter **C 5** and Schmitz (2003a) to find PI - LL relationships for Tertiary clays.

It is obvious that although the correlation coefficients are close to 1, the lines are connecting three "clouds". The clay type gives the position of each "cloud". The relationship between plasticity index and liquid limit can further be analysed for each "cloud" separately. The position of the line connecting data points within one "cloud" is not given by the factor clay type but is a function of the variation within the clay combinations, due to a change in temperature during storage, initial fluid content, leachate type or the natural heterogeneity. These factors cause changes in liquid limit and plasticity index that are, however, too small to change the overall correlation. Even if the relationships between the Atterberg parameters are analysed on another level, *e.g.* XXX2 or the XOXX shown in **Figure: C4-1**, the dominance of the clay type prevails. Moreover the scatter within one clay type can be represented by a line parallel to the A-line (TXXX in **Figure: C4-1**). This is an indication that these points belong to related soils (Muir-Wood 1990). The leachates were not able to modify the nature of the soils. Some of the other correlations have been plotted in **Figure: C4-2**.

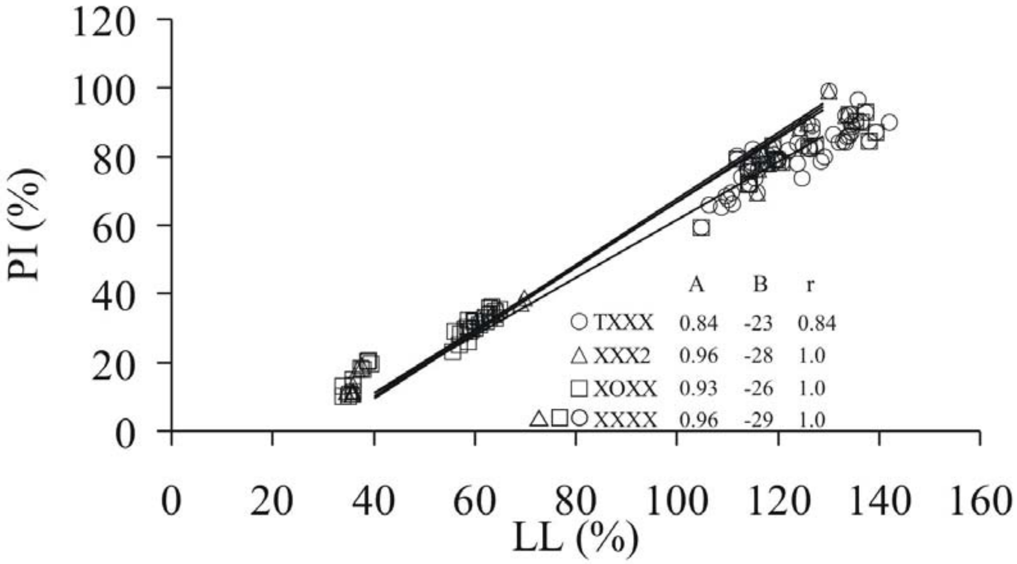

Figure: C4-1

The correlation between the Atterberg test values LL and PI. The relationships between LL and PI are given by: LL = A·LL+B and have been determined by assuming that PI and LL contribute equally to the error with respect to the correlation function (see Bolle 2000). Note that the results showing the tests with reference Smectite are outside the range of the figure.

---

[34] *The level is given by the type and number of variables that are known. Analysis at another level actually means that one takes out the effect of a certain variable like the effect of the leachates. This is the case for the analysis of the XOXX, XHXX or XMXX levels with respect to XXXX level.*

In **Figure: C4-2** it is shown once again that the addition of fluids (landfill leachates) does not change the original character of the clay: The position of each clay remains identifiable in the PI-LL, the MBA-LL and the MBA-PI field although some deviations (**Figure: C4-2-A**) are produced. These cases show that the "influence" of the leachate is low compared to the "influence" of the clay type. Especially for clays with a large liquid limit (LL), the liquid limit and plasticity index (PI) seem to be linearly related even after leachate contact.

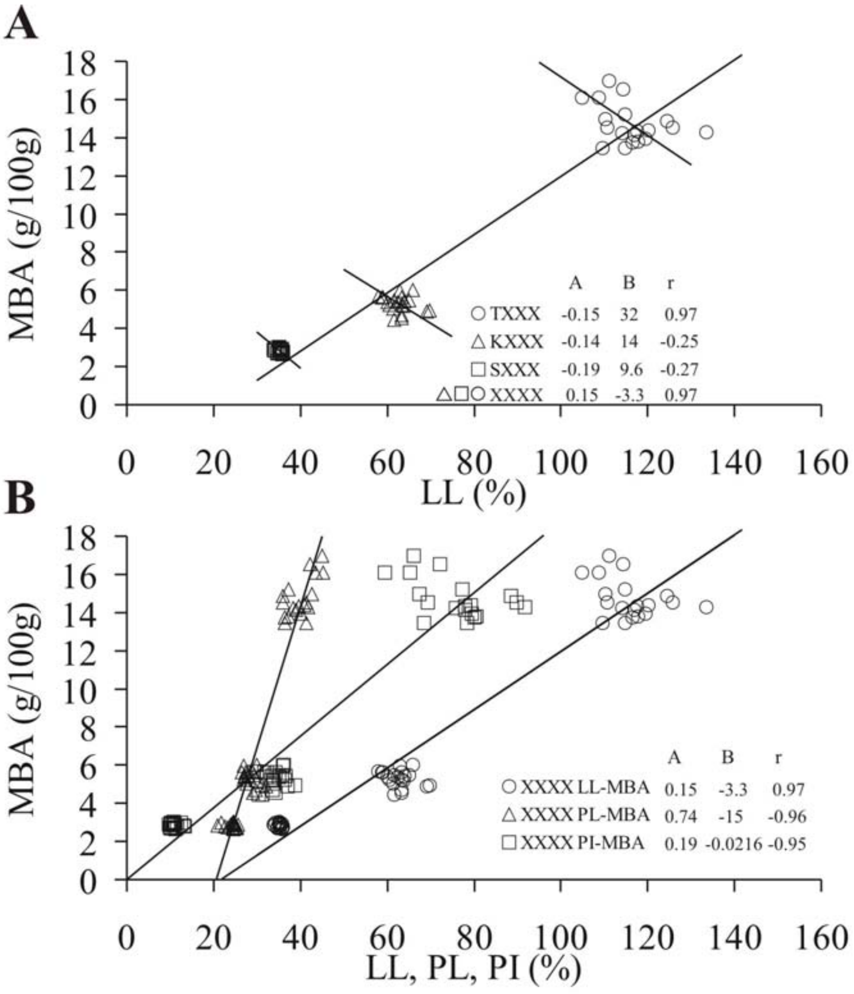

Figure: C4-2

A: The correlation between the Atterberg test values, methylene blue adsorption (MBA) and the liquid limit (LL). B: Similar observations as those that have been made for the MBA versus LL can be made for the MBA versus the plasticity index (PI) or the plastic limit (PL).

C 4.3 Opened data: Clay minerals

The relationships within the clay mineral data are analysed complementary to the theory presented in **Part: A** and the observed alteration processes in **Part: B**. In Schmitz (2001a) the clay minerals were compared to each other at the XXXX level in their closed form. In **Table: C4-1** all Niggli number correlations (see *e.g.* Swan and

Sandilands 1995) having a correlation coefficient larger or equal to 0.6 are sorted according to the appropriate clay mineral alteration process (**Figure: B3-10**). A negative correlation coefficient in **Table: C4-1** indicates that one component diminishes while the other increases. This indicates a possible transformation of one component into the other. With this number no conclusions can be drawn on the direction of the transformation or the reversibility of processes. A positive correlation coefficient indicates that both components decrease or increase (*e.g.* **Table: C4-2**). In some cases a combination of two separate steps have been observed *e.g.* 1B)+2D). This indicates that an Illite has been transformed to a mixed-layer Illite-Montmorillonite that has then been transformed to a pillared Smectite (Sm_{Al}). Other correlations that were found but not known from **Figure: B3-10** are given in **Table: C4-2**. Some of the correlations have been visualised in **Figure: C4-3**.

Table: C4-1

*Overview of known mineral alteration pathways (e.g. mineral A → B) and the measured correlation coefficient (e.g. between the quantity of mineral A and B in different tests). The numbers between brackets form an arbitrary numeration used as link between the correlations shown in this table, **Figure: C4-3** and **Table: C4-2**.*

Mineral alteration process in Figure: B3-10	Niggli numbers		
	Clay type for which the observation was made	Major constituent for which correction was made	Correlation coefficient between the clays involved in the mineral alteration process
1B) = 2A)	Soignies	(10-14c)	-0.8 (1)
	Soignies	(Kao)	-0.6 (11)
	Soignies	(Chlo)	-0.8 (14)
1B)+2B)	Kruibeke	(Kao)	-0.8 (26)
	Kruibeke	(Chlo)	-0.6 (28)
	Soignies	(10-14m)	-0.7 (3)
	Kruibeke	(10-14m)	-0.8 (22)
2B)	Kruibeke	(I)	-0.6 (24)
	Soignies	(Kao)	-0.6 (13)
	Soignies	(I)	-0.6 (10)
1B)+2D)	Kruibeke	(10-14c)	-0.6 (19)
	Tournai	(10-14m)	-0.9 (16)
2B)+2D)	Tournai	(10-14m)	-0.8 (17)
5A)	Kruibeke	(10-14c)	-0.6 (21)
	Kruibeke	(10-14m)	-0.8 (23)
	Kruibeke	(I)	-0.7 (25)

The clay mineral alteration pathways given in **Table: C4-1** (1B to 5A) show that (even) after “opening” of the clay mineral data all clay mineral alteration processes described previously in **Figure: B3-10**, can be confirmed statistically.

Figure: C4-3

In this figure some examples of correlations that were discerned by analysing the "opened" data-sets of mineral alteration processes of Tournai, Kruibeke and Soignies clay in contact with landfill leachates-C, -H2 and -M. These correlations were shown in ***Table: C4-1*** *and* ***Table: C4-2*** *and correspond to the mineral alteration processes shown in* ***Figure: B3-10****. In the different figures the following combined mineral alteration pathways are shown:*

A and B:	*1B) +2B)*	*I ↔ (10-14m)↔ (10-14c)*
C:	*2B*	*(10-14m) ↔ (10-14c)*
D and E:	*1B)+2D)*	*I ↔ (10-14m)↔* Sm_{Al}
F:	*2B)+ 2D)*	*(10-14c) ↔ (10-14m)↔* Sm_{Al}
G:	*2A), 2B), 3B) and 5A)*	*I ↔ (10-14m)↔(10-14C) → Chlo → Kao*
H:	*2D), 2B), 3B) and 5A)*	Sm_{Al} *↔ (10-14m)↔(10-14C) → Chlo → Kao*

C

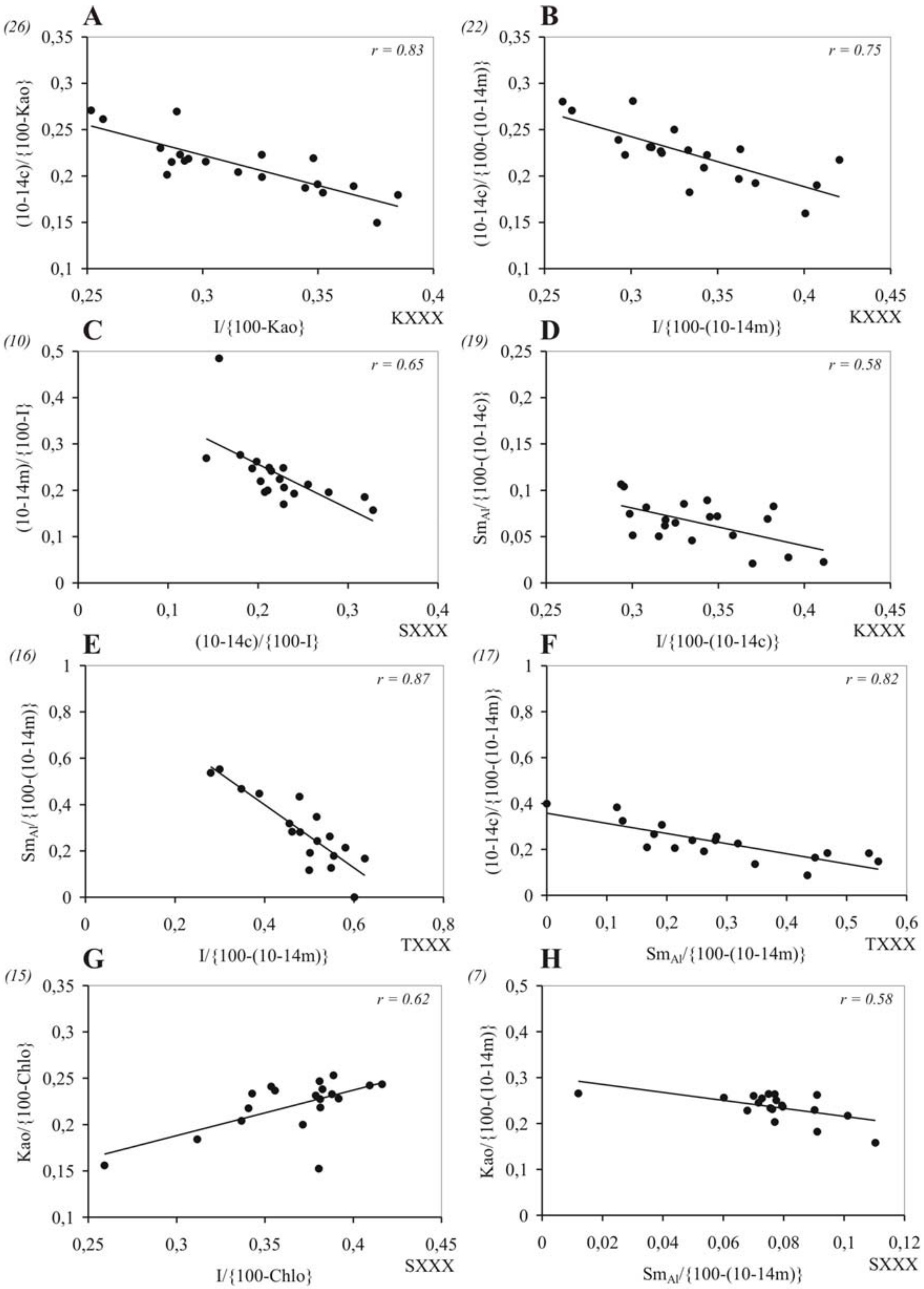
A
(26)
r = 0.83
(10-14c)/{100-Kao}
0,35
0,3
0,25
0,2
0,15
0,1
0,25
0,3
0,35
0,4
I/{100-Kao}
KXXX
B
(22)
r = 0.75
(10-14c)/{100-(10-14m)}
0,35
0,3
0,25
0,2
0,15
0,1
0,25
0,3
0,35
0,4
0,45
I/{100-(10-14m)}
KXXX
C
(10)
r = 0.65
(10-14m)/{100-I}
0,5
0,4
0,3
0,2
0,1
0
0
0,1
0,2
0,3
0,4
(10-14c)/{100-I}
SXXX
D
(19)
r = 0.58
Sm_{Al}/{100-(10-14c)}
0,25
0,2
0,15
0,1
0,05
0
0,25
0,3
0,35
0,4
0,45
I/{100-(10-14c)}
KXXX
E
(16)
r = 0.87
Sm_{Al}/{100-(10-14m)}
1
0,8
0,6
0,4
0,2
0
0
0,2
0,4
0,6
0,8
I/{100-(10-14m)}
TXXX
F
(17)
r = 0.82
(10-14c)/{100-(10-14m)}
1
0,8
0,6
0,4
0,2
0
0
0,1
0,2
0,3
0,4
0,5
0,6
Sm_{Al}/{100-(10-14m)}
TXXX
G
(15)
r = 0.62
Kao/{100-Chlo}
0,35
0,3
0,25
0,2
0,15
0,1
0,25
0,3
0,35
0,4
0,45
I/{100-Chlo}
SXXX
H
(7)
r = 0.58
Kao/{100-(10-14m)}
0,5
0,4
0,3
0,2
0,1
0
0
0,02
0,04
0,06
0,08
0,1
0,12
Sm_{Al}/{100-(10-14m)}
SXXX

Table: C4-2

Overview of additional mineral alteration pathways (e.g. mineral A → B) and the measured correlation coefficient (e.g. between the quantity of mineral A and B in different tests).

	Niggli numbers		
	Clay type for which the observation was made	Major constituent for which correction was made	Correlation coefficient between the clays involved in the mineral alteration process
I ↔ Chlo	Soignies	(10-14m)	-0.7 (5)
(10-14m) ↔ Chlo	Kruibeke	(Kao)	-0.6 (27)
X → I + Kao	Soignies	(10-14m)	+0.6 (4)
	Soignies	(Chlo)	+0.6 (15)
(10-14C) ↔ Kao	Soignies	(10-14m)	-0.8 (6)
Sm_{Al} ↔ Kao	Soignies	(10-14m)	-0.6 (7)
X → (10-14m) + Kao or (10-14m) ↔ Kao	Soignies	(10-14C)	-0.6 (2)

From **Table: C4-2** one can conclude that in addition to the mineral alteration pathways (known from **Figure: B3-10**) a new reaction should be proposed: Transformation from the Illite-Chlorite mixed-layer into secondary Chlorite (pathway designated as 3B). Thereby the link between Illite ↔ (10-14m) ↔ (10-14c) ↔ Chlorite → Kaolinite is made. This validates the measured relationship between Illite and Kaolinite, which suggests a degradation of secondary Chlorite into Illite and Kaolinite or vice versa the formation of secondary Chlorite by these two minerals.

C 4.4 Conclusion

With the opening of the data by converting the data into Niggli numbers, correlations within the clay mineral data of Tertiary clays-landfill leachate mixtures could be discerned. Thereby the clay mineral alteration pathways presented in **Figure: B3-10** were validated and an additional (path 3B) was proposed.

C 5 Equivalent basal spacing

C 5.1 Introduction

It has been thought for years that a link between the Atterberg limits and clay mineralogy exists. But apart from some vague statements that a Smectite should have a higher plasticity (without defining what was actually meant) than *e.g.* a Kaolinite, no quantitative tools were available to link clay mineralogy to geomechanical properties, up to 2002, when the equivalent basal spacing (EBS) was introduced[35] (Schmitz *et al* 2002b).

With the equivalent basal spacing concept one exactly knows what it means if the Smectite (Sm) or Illite (I) increases in terms of the liquid limit (LL). With the link between the liquid limit and other geomechanical properties, the mineralogy can be related directly to the compression index (C_c), the consolidation coefficient (C_V), the friction angle (ϕ') *etc*. as will be shown in this chapter. The data of the clays used in this chapter is summarised in **Table: C5-1**.

Table: C5-1

Average Atterberg properties (data using all information of tests on homogenised clay in contact with demineralised water and landfill leachates for which clay mineralogical data was available) and clay mineral composition. LL_{Casa} *is the liquid limit determined with the Casagrande cup, CF the amount of 1 clay mineral species expressed as % of the total amount of clay, TCF the amount of clay mineral species expressed as % of the total amount of soil.*

Clay type:	LL_{Casa} (%)	CF_{Illite}^{FOA} (%)	$CF_{(10\text{-}14c)}^{FOA}$ (%)	$CF_{(10\text{-}14m)}^{FOA}$ (%)	CF_{SmAl}^{FOA} (%)	$CF_{Kaolinite}^{FOA}$ (%)	$CF_{Chlorite}^{FOA}$ (%)	TCF^{TRP} (%)
Reference Kaolinite	59	10	0	0	0	90	0	95
Kruibeke average	63	28	18	17	5	13	19	71
Tournai average	$1.2 \cdot 10^2$	16	7.0	68	9.0	0	0	81
Soignies average	35	33	15	16	6.0	20	10	49
Reference Smectite	$6.6 \cdot 10^2$	0	0	$1.0 \cdot 10^2$	0	0	0	95

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[35] *The equivalent basal spacing was first published by the author: Schmitz (et al 2002b) as Equivalent Interlayer Distance (EID), refined in Schmitz (et al 2004a) and extended in Schmitz (et al 2003a).*

C 5.2 Derivation of the equivalent basal spacing

C 5.2.1 Introduction

When in geomechanical literature reference is made to clay mineralogy and the aspects of sample preparation for X-ray diffraction analyses (XRD) is discussed, the fact that usually only the fraction smaller than 2 micrometer is analysed is defended with the proclamation that Smectites (or Illite-Smectite mixed-layers) are:

- The most dominant clay minerals.
- Nearly entirely present in the fraction smaller than 2 micrometer.

These hypotheses are tested in the following paragraphs.

C 5.2.2 Liquid limit versus Smectite content

The relationship that the liquid limit depends only on the Smectite (or Illite-Smectite mixed-layer) content is plotted in **Figure: C5-1.**

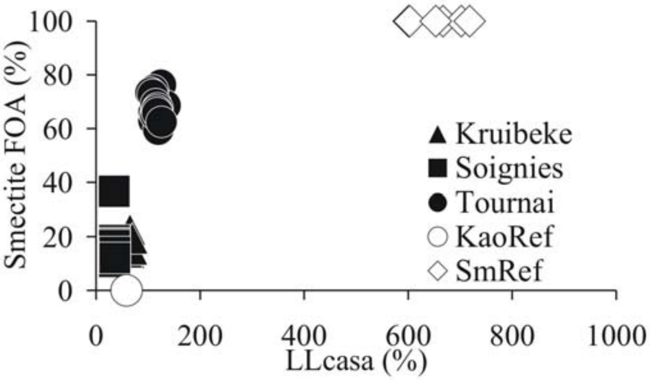

Figure: C5-1

The Smectite content alone does not account for all clay reactivity when expressed in terms of the liquid limit (LL_{Casa}).

It is obvious (**Figure: C5-1**) that this assumption is a too large generalisation for two reasons:

- The Soignies clay and Kruibeke clay are characterised by a large difference in liquid limit (30%) although their relative Smectite content is comparable.
- When the reference Kaolinite is considered one can see that the fairly large liquid limit (LL) of this clay is not represented correctly when the focus is placed on Smectite only.

Thus, not only the Smectite is a reactive clay mineral: the other clay minerals need to be considered as well.

C 5.2.3 Liquid limit versus clay content

If only the amount of clay minerals is considered - irrespective of possible differences between these minerals - one obtains a situation that exists as if the activity of the clays is determined according to Skempton (1953). This is shown in **Figure: C5-2** (considering only the liquid limit and not the plasticity index).

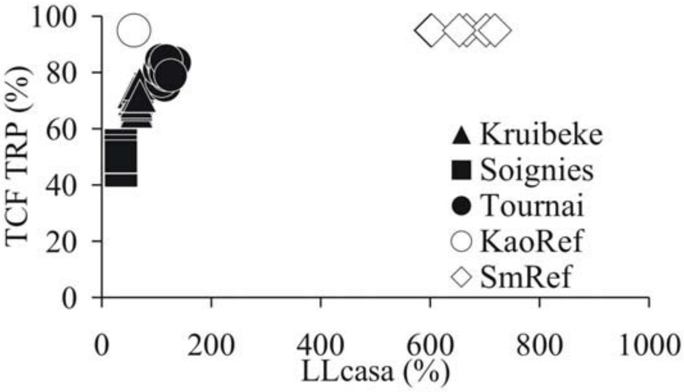

Figure: C5-2

The total amount of clay minerals (TCF) plotted versus the liquid limit (LL_{Casa}).

In this case the same liquid limit should be expected for the reference Kaolinite and Smectite, which obviously is not true.

C 5.2.4 The equivalent basal spacing

The examples illustrated in the previous sections have demonstrated that finding a correlation between geomechanical index properties and clay mineralogy is not straightforward. In chapter **A 2.2** it has been discussed that the changes in interlayer distance are important for engineering applications. This has been reflected by the analyses in this section. It was shown that it is not sufficient to consider only the Smectite content of a clay sample that contains various other clay species. Neither was it sufficient to take only the total amount of clay present in the sample into account without discrimination between individual clay species. Both observations show that the individual clay species need to be considered in terms of their relative contribution to the total available interlayer space. Thus a correct formulation linking clay mineralogy to the liquid limit needs to include information on the:

- Clay mineralogy qualitatively.
- Clay mineralogy quantitatively.

In the previous paragraph it was shown that both the amount of Smectite *and* the total amount of clay minerals need to be considered, *but* not only the amount of clay counts: Besides Smectite, other clay minerals (like Kaolinite) should be considered as well.
Thus one should take into account:

- The amount of clay in the sample.
- The type of clay minerals: Smectite but also Kaolinite and other clay minerals.

The solution to this problem is called the equivalent basal spacing (EBS).
The concept of equivalent basal spacing (EBS) was previously introduced by the author (Schmitz *et al*. 2002b) to relate the interlayer space and the basal spacing of a polymineral clay to the liquid limit:

$$EBS = TCF^{TRP} \cdot \sum_{i=1}^{n} CF_i^{FOA} \cdot BS_i^{(001)FOA} \quad \textbf{(C5 - 1)}$$

The relative amount of a clay mineral (CF_i^{FOA}) is multiplied with the basal spacing ($BS_i^{(001)FOA}$ in Å) of this mineral as known from literature (*e.g.* Mitchell 1993, overview in Schmitz 2001a or any other handbook dealing with clay mineralogy). This step is repeated for all measured clay fractions. Next, these values are summed. Subsequently this sum is corrected for the total fraction of clay minerals in the sample (TCF^{TRP})[36].
Some examples: If the sample only consists of Smectite, the $TCF^{TRP} = 1$, the $CF_{Smectite}^{FOA} = 1$ and the $BS_{Smectite}^{(001)FOA} = 14$ Å. Therefore the equivalent basal spacing will be 14 Å as well. If the sample only consists of sand, the EBS = 0 Å.
In this way the equivalent basal spacing takes into account the larger reactivity of clays with a larger interlayer distance, the larger reactivity of pure clays with respect to soils with other non-clay constituents like sand and the reactivity of interstratified clay minerals which, as Yong and Warkentin (1975) stated, have properties that are intermediate between those of the two clay components.

In **Figure: C5-3** and **C5-4** the equivalent basal spacing is plotted versus the liquid limit (the clay mineral alteration line of complex clay mixtures like the Belgian Tertiary clays) of the same samples (Casagrande cup). If the following (Boltzmann) distribution of data is assumed (coefficient of determination (r^2) is equal to 0.98) the equivalent basal spacing is related to the liquid limit as follows:

$$EBS = \frac{A_1 - A_2}{1 + e^{(LL_{Casa} - x_0)/x_d}} + A_2 \quad \textbf{(C5 - 2)}$$

$$LL_{\mathrm{Casa}} = x_d . LN\left(\frac{A_1 - A_2}{EBS - A_2} - 1\right) + x_0 \quad \textbf{(C5 - 3)}$$

with:
$A_2 = 13.2$ Å; value of equivalent basal spacing at LL → +∞. This value corresponds to the clay with the highest EBS in the database *i.e.* the reference Smectite. This parameter is changed later in paragraph **C 5.3.2** to find translations of the clay mineral alteration curve.

$x_d = 65.7$ % fluid content; the equivalent basal spacing value changes drastically within a zone with width LL = x_d. This parameter is changed later in paragraph **C 5.3.2** to find translations of the clay mineral alteration curve.

$A_1 = -127$ Å; arbitrary value of the equivalent basal spacing at LL → -∞. Note that the values, as these were published by the author (Schmitz et al 2003a) were found by a best fit of the data e.g. least square error. The physical meaningful intersection through the origin is obtained by setting this parameter to -134 Å.

$x_0 = -153$ %; arbitrary fluid content; the LL, halfway between A_1 and A_2.

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[36] *Information about the forced oriented aggregate (FOA) and the total random powder (TRP) is given in paragraph **B 3.1.2.1** and in (SP-XRD 2004).*

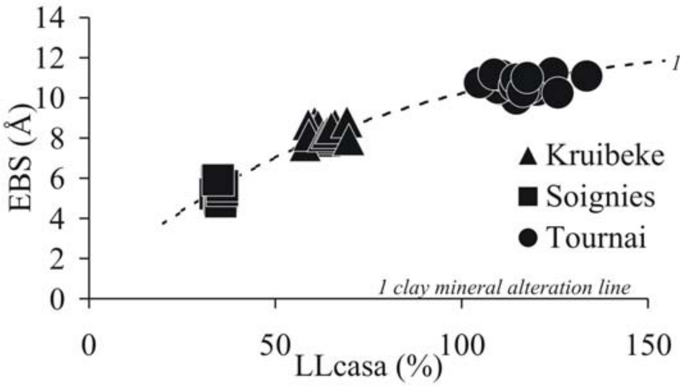

Figure: C5-3

The equivalent basal spacing (EBS) versus the liquid limit (LL_{Casa}) of three natural clays (exposed to landfill leachates). The same figure with as additionally clay the reference Smectite is given in ***Figure: C5-4.***

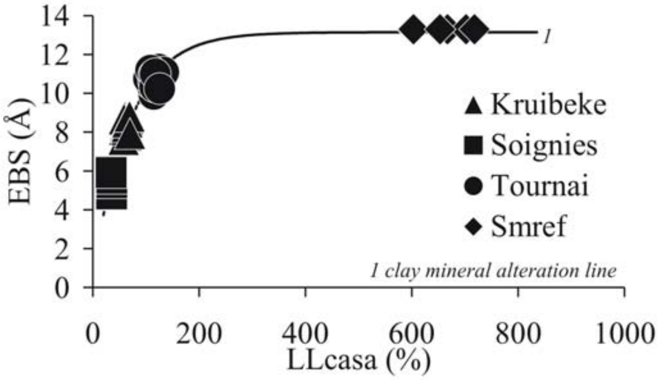

Figure: C5-4

The equivalent basal spacing (EBS) versus the liquid limit (LL_{Casa}) of three natural clays and a reference Smectite (Sm_{ref}). A zoom of the Tournai, Soignies and Kruibeke clay separately is given in ***Figure: C5-3.***

How the correlation between the equivalent basal spacing and the liquid limit can be used to predict the behaviour of clays in engineering terms[37] is shown in the examples in the following paragraphs. Therefore references are made to the following well-known correlations between the Atterberg test results and other geomechanical properties:

- Using the expression by Terzaghi and Peck (1967), a link can be made between the liquid limit (%) and the compression index (-):

$$C_C = 0.009 \cdot (LL - 10) \qquad \textbf{(C5 - 4)}$$

- Using the expression by Wetzel (1990) a link can be made between the specific surface (m^2/g dry clay) of the clay and the liquid limit (%) (if LL > 50%):

---

[37] The EBS approach replaces the need to create a clay atlas proposed by Schmitz (et al 2003c) in which different environmental strains (heat and chemicals etc.) and the effect of these strains on clay properties are described.

$$S_a = \frac{(LL - 46.5)}{1.01} \qquad \textbf{(C5 - 5)}$$

It can be confirmed that this expression fits relatively well to the data of the investigated Belgian Tertiary clays and the reference Smectite as long as the latter clay is not tested dry but with interlayers accessible to the testing fluid.

- If the results of index tests (%) on a number of samples of related soils are plotted on a plasticity chart the points tend to lie on a straight line which is often approximately parallel to the A-line (Muir-Wood 1990):

$$PI = A \cdot LL + B \qquad \textbf{(C5 - 6)}$$

The fact that this expression was valid only at large liquid limit values was shown in chapter **C 4.2**. The parameters A and B were determined for the three natural clays and the reference Smectite and are presented in **Table: C5-2**.

Table: C5-2

*Relationship between LL and PI for different clay families. All samples were dried carefully, exposed to demineralised water and different landfill leachates. Values are the average of a total of 188 tests (data using all information of tests on homogenised clay in contact with demineralised water and landfill leachates). A and B are coefficients used to correlate the plasticity index to the liquid limit in expression (**C5 - 6**) determined by minimising the error (to the correlation line) with respect to PI (values outside square brackets) and by assuming that PI and LL contribute equally to this error (values inside square brackets). For explications concerning the latter method see Bolle (2000).*

Clay type:	A (-)	B (% fluid content)	r (-)
Kruibeke average	0.94 [1.1]	-26 [-33]	0.88
Tournai average	0.71 [0.84]	-6.6 [-23]	0.84
Soignies average	2.0 [2.2]	-57 [-64]	0.91
Reference Smectite average	1.0 [1.0]	-62 [-63]	0.99

With the relationship between the liquid limit and the plasticity index for each clay (Tournai, Kruibeke, Soignies or one of the reference clays), the change in plasticity index can be estimated if a change in equivalent basal spacing is known.

- The plasticity index (%) of a clay can be related to the peak value of ϕ’ (°) (Mitchell 1993):

$$\phi = -6.6 \cdot Ln(PI) + 50.4 \qquad \textbf{(C5 - 7)}$$

C 5.3 Applications of the equivalent basal spacing

In the following paragraphs examples are shown in which the equivalent basal spacing as derived above can be used to predict changes in geomechanical properties when the clay is subjected to different conditions like heat or chemicals. Other examples show how the equivalent basal spacing can be used to understand which chemical or physical processes are important in such cases.

C 5.3.1 Application of EBS: Clay exposed to heat, example I

What will happen to the clay in a barrier once it is exposed to heat, as in the case of storage of radioactive waste? From clay mineralogy it is known that heating to *e.g.* 500°C during several hours causes a collapse of Smectite to 10 Å and the disappearance of the 7 Å (001) Kaolinite peak. How these processes can be described in terms of equivalent basal spacing is shown below.

For the reference Smectite the initial EBS = 0.95·14 = 13.3 Å according to (**C5 - 1**). This value corresponds using relationships (**C5 - 3**) - (**C5 - 6**) to:
LL >> 300%
PI >> 300%
Cc >> 3.2
$S_a > 300\ m^2/g$

These values were validated as is evidenced by the following measured values: LL = 660%, PI = 610%, Cc = 5.3 (van Paassen 2002) and $S_a = 556\ m^2/g$ (Keijzer 2000).

After heating to 500°C: EBS = 0.95·10 = 9.5 Å. This corresponds using relationship (**C5 - 3**), (**C5 - 4**), (**C5 - 6**) to:
LL = 85%, PI = 25% and Cc - 0.7.
The clay has changed enormously but still, its properties are those of a high plastic clay (type: TA DIN18196 or CH BS1377). This liquid limit value is thus representative of a Smectite after collapse of its interlayer spaces without rehydration.

Atterberg tests cannot, however, be performed without re-exposure of the sample to water. Tests were performed to analyse the reversibility of the collapse of the interlayer space. After renewed exposure to water part of the collapsed Smectite (43%) reopens while another part remains at 10 Å (57%). This corresponds to an EBS = 0.95·(0.57·10+0.43·14)= 11.7 Å and using relationships (**C5 - 3)**, (**C5 - 4**) to a liquid limit near $1.5 \cdot 10^2\%$ and Cc near 1.2.

The measured liquid limit varied between $1.6 \cdot 10^2$ % and $1.9 \cdot 10^2$ %, which is close to the predicted value (see **Figure: C5-5**). The variability is due to the difficult rehydrating of the clay after heating. The same observation is valid for the plasticity index. Due to the heating the Cc also decreased from 5.3 to 1.9, an order of magnitude predicted correctly by the equivalent basal spacing concept.

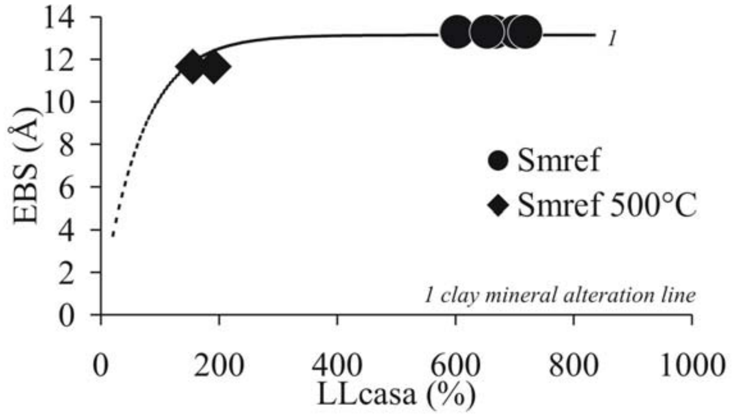

Figure: C5-5

The equivalent basal spacing (EBS) versus the liquid limit (LL_{Casa}) of the reference Smectite (Sm_{ref}) and the same clay after heating to 500°C (Sm_{ref} 500°C).

Tournai clay has an initial $EBS = 0.81\cdot(0.16\cdot 10+0.07\cdot 12+0.68\cdot 14+0.09\cdot 14) = 10.7$ Å corresponding to, using relationship (**C5 - 3**), (**C5 - 4**), (**C5- 6**), (**C5 - 7**):

A liquid limit near $1.1\cdot 10^2$%, plasticity index near $7.3\cdot 10^1$%, Cc near 0.9, $S_a = 65$ m²/g and ϕ' near 22°.

The measured values are close to the ones predicted with the EBS; measured was:
$LL = 1.2\cdot 10^2$%, $PI = 7.6\cdot 10^1$%, $Cc = 0.9$ and a $S_a = 66$ m²/g only the ϕ' was higher than expected being equal to 27°.

When Tournai clay was exposed to 500°C heat it was impossible to determine the liquid limit afterwards. The clay did not rehydrate, and did not show the typical clayey stickiness. Therefore it is assumed that this material had a liquid limit just below the test limit of about 28% (Wendehorst 1996). If it is assumed that the loss of its "plasticity" indicates destruction of the Smectite, this fraction has to be added to the fraction of non-clay minerals. This results in an $EBS = 0.26\cdot(0.49\cdot 10+0.23\cdot 12+0.28\cdot 14) = 3.0$ Å and a $LL = 15$ %, indeed a value below the test limit of the liquid limit test. This indicates that the assumption was correct. The transition of the equivalent basal spacing and liquid limit properties of the Tournai clay due to heating are shown in **Figure: C5-6**. The apparition of an enlarged non-clay fraction could be a reason for the additional increase of the friction angle.

These examples show that although heating has a tremendous effect on the liquid limit, the impact of heating is different, depending on the relative composition of the clay minerals. The reference Smectite resists the effect of heating fairly well and can still be classified as a plastic clay (type TA DIN18196 or CH BS1377) after heating, whereas the Tournai clay changes from a plastic clay (TA or CH) to a clay-silt mixture (ST). This behaviour was predicted for different clays using the equivalent basal spacing concept and validated by performing laboratory tests.

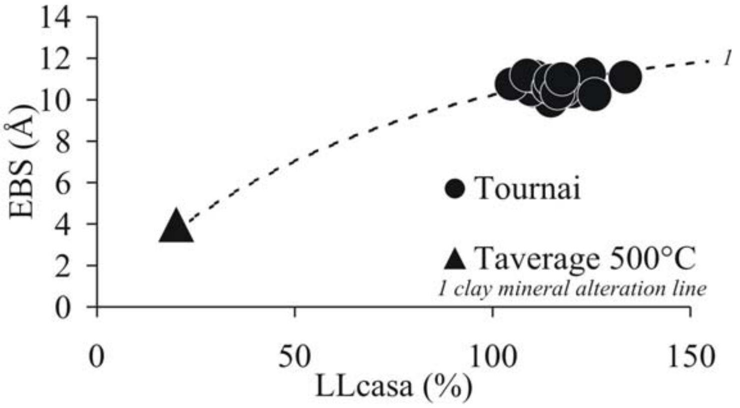

Figure: C5-6

The equivalent basal spacing (EBS) versus the liquid limit (LL_{Casa}) of the Tournai clay after heating to 500°C ($T_{average}$ 500°C).

C 5.3.2 Application of EBS: Clay mixtures

C 5.3.2.1 Inert mixtures: Sand, Kaolinite and Smectite

How does the liquid limit change if sand is mixed to clay? It probably will decrease but how much? Can one quantify this? To answer these unknown questions several clays were mixed with various amounts of sand[38] in Liège. Additionally the data by Seed (*et al* 1964) was reanalysed and plotted next to the Liège results. As a result the liquid limit did not only decrease linearly with the amount of sand, the relationship was 1:1 (see **Figure: C5-7**).

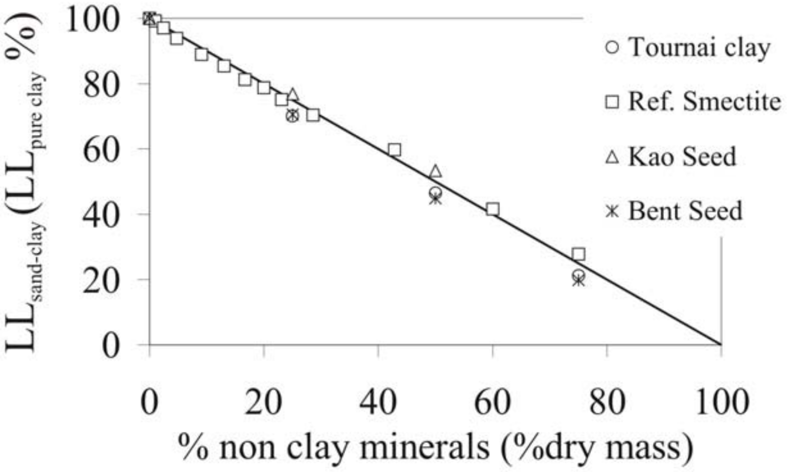

Figure: C5-7

The decrease of the liquid limit ($LL_{sand-clay}$) is related 1:1 to the amount of sand (% non-clay minerals) added to the clay (with an initial $LL_{pure\ clay}$).

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[38] *The sand has a grain size < 0.425mm. Rounded quartz grains (rolled) constitute >90% of the volume. Other grains are Fe-oxides. The sand shows practically no reaction with 0.25M HCl (PC Darimont).*

How these mixtures look like in the EBS-LL diagram is shown in **Figure: C5-8**. From the starting point of the clay without sand (determined using either relationship (**C5 - 1**) or (**C5 - 2**) the sand-clay mixture follows a line from this initial point to the origin.

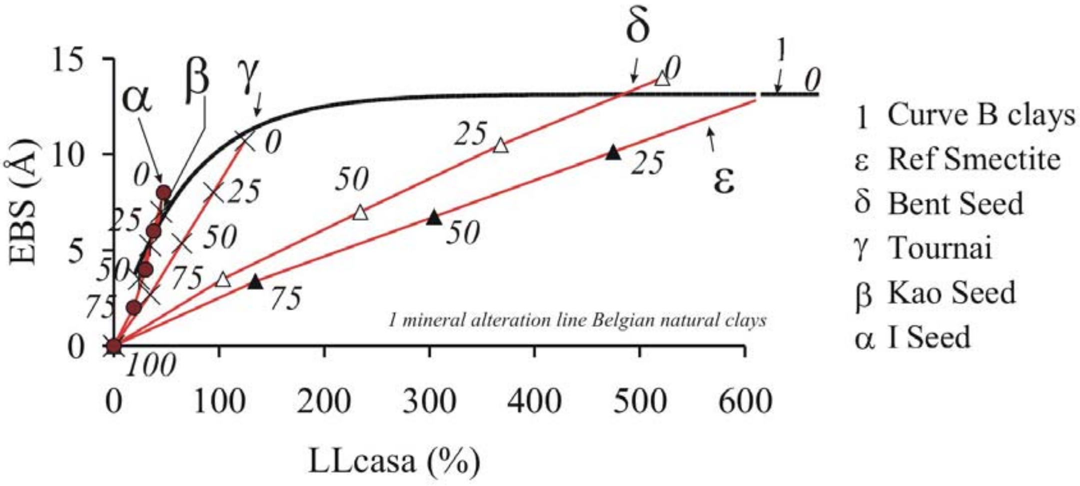

Figure: C5-8

Mixtures of clays with inert materials. The numbers indicate the amount of sand (weight percentage) in the clay-sand mixture; the liquid limit (LL_{Casa}) was measured; Equivalent basal spacing (EBS) was determined using relationship ***(C5 - 1)****.*

But what happens if the clay is mixed with another clay like Kaolinite? To answer this question one can have a look at the data provided by Seed (*et al*. 1964) and interpret these results in terms of the new EBS-LL relationship (see **Figure: C5-9**).

The starting point in terms of EBS and liquid limit can be calculated using the measured liquid limit and the mineralogy in terms of the equivalent basal spacing (relation (**C5 - 1**)). These equivalent basal spacing and liquid limit values were plotted for the Smectite and Kaolinite in **Figure: C5-9** (marked Bentonite and Kaolinite). As shown in **Figure: C5-8**, equivalent basal spacing and liquid limit for sand mixtures starting from the "pure" clays can be found by connecting these points to the origin. Inert clay-clay mixtures behave similarly: Bentonite-Kaolinite mixtures are located on a line connecting the (LL,EBS) coordinates of the pure clays.

Since one knows now how inert clay mixtures and clay sand mixtures behave one can construct a nomogramme (**Figure: C5-10**) to find the LL-EBS relationship for any inert clay-clay-sand mixture. These results have been validated by testing them on the database provided by Seed (et al. 1964) with the assumption: Smectite, pure, EBS = 14 Å; Kaolinite, pure, EBS = 7 Å[39] (*e.g.* Thorez 1976 or Mitchell 1993).

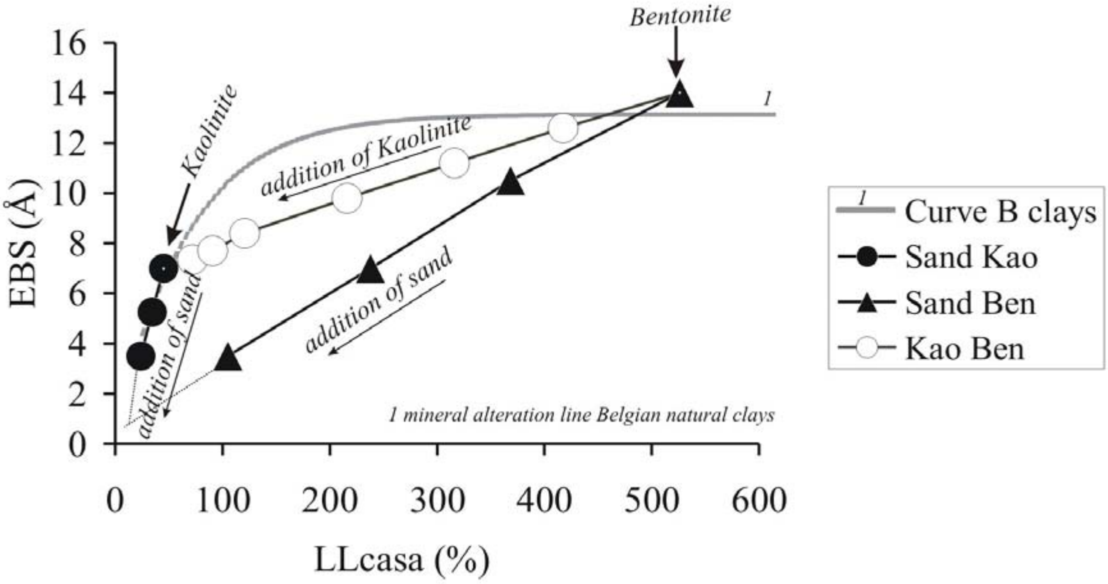

Figure: C5-9

If Smectite (marked as Bentonite) is mixed with increasing amounts of Kaolinite, the mixtures will not follow the mineral alteration curve but a direct line connects the "pure" Smectite to the "pure" Kaolinite. EBS is the equivalent basal spacing. LL_{Casa} is the liquid limit.

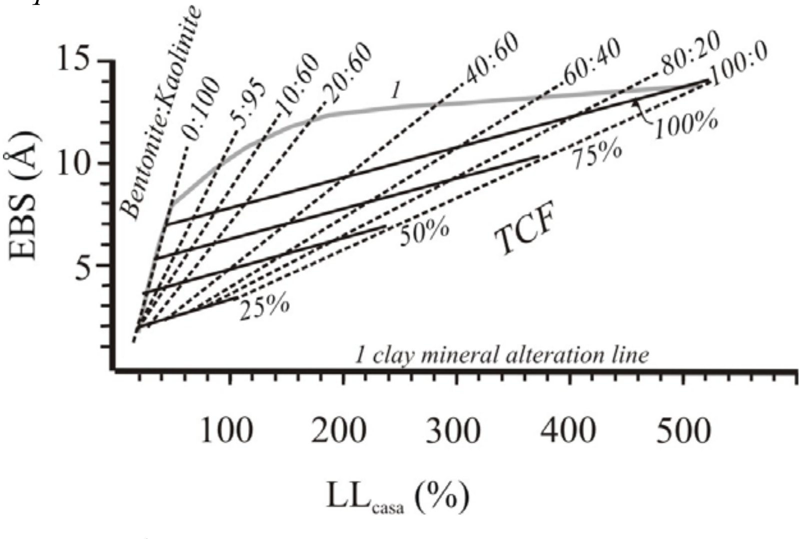

Figure: C5-10

Nomogramme to determine the liquid limit (LL_{Casa}) - equivalent basal spacing (EBS) relationship for any sand:Kaolinite:Bentonite (Smectite) mixture.

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[39] *Note that the calculated EBS of Kaolinite (using **Table: C5-1** and expression **(C5 - 3)**) is larger than 7 Å which points to intercalations in the interlayer space of Kaolinite missed by XRD analysis.*

C 5.3.2.2 Active mixtures: Illite and Smectite

In the previous paragraph it has been shown that inert mixtures do not follow the clay mineral alteration line determined for Belgian natural clays and that the liquid limit values can be determined by linear interpolation. This is not the case for clay mineral mixtures in which clay mineral alteration has occurred by the mixture (natural or artificial) of different active clay species.

Figure: C5-11 resembles **Figure: C5-9** but there is one major difference: The Illite-Smectite mixtures are not located on a straight line but they follow the clay mineral alteration curve determined for the Belgian clays! In **Figure: C5-11** it is assumed that the Illite was pure (*i.e.* EBS = 10 Å). In **Figure: C5-12** it is assumed that the Illite clay consisted of 80% Illite and 20% inert materials (*i.e.* EBS = 8 Å).

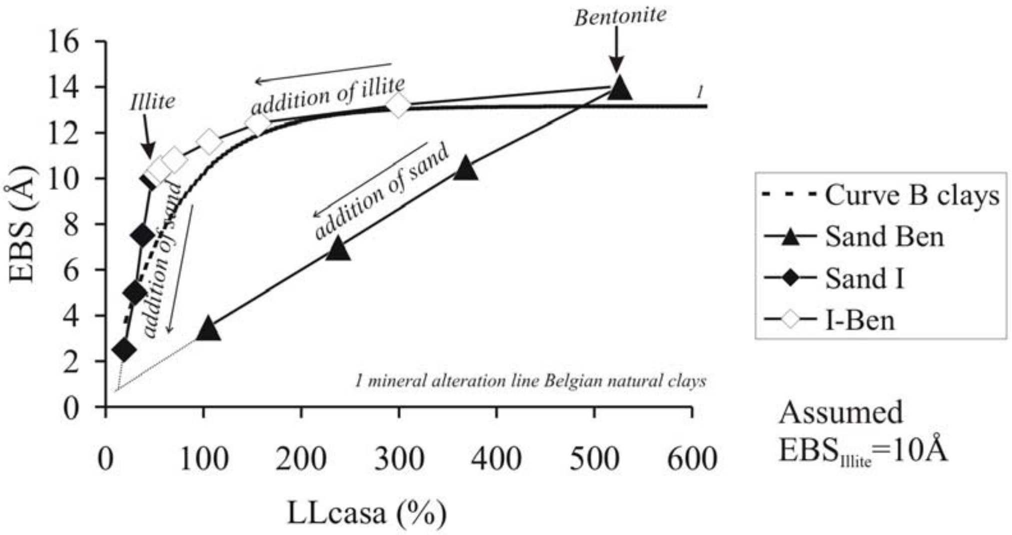


Figure: C5-11

Illite - Smectite mixtures follow the mineral alteration curve. In this figure it is assumed that the Smectite as well as the Illite were pure. Furthermore it was assumed that the EBS of the "pure" Illite was 10 Å. EBS is the equivalent basal spacing. LL_{Casa} *is the liquid limit.*

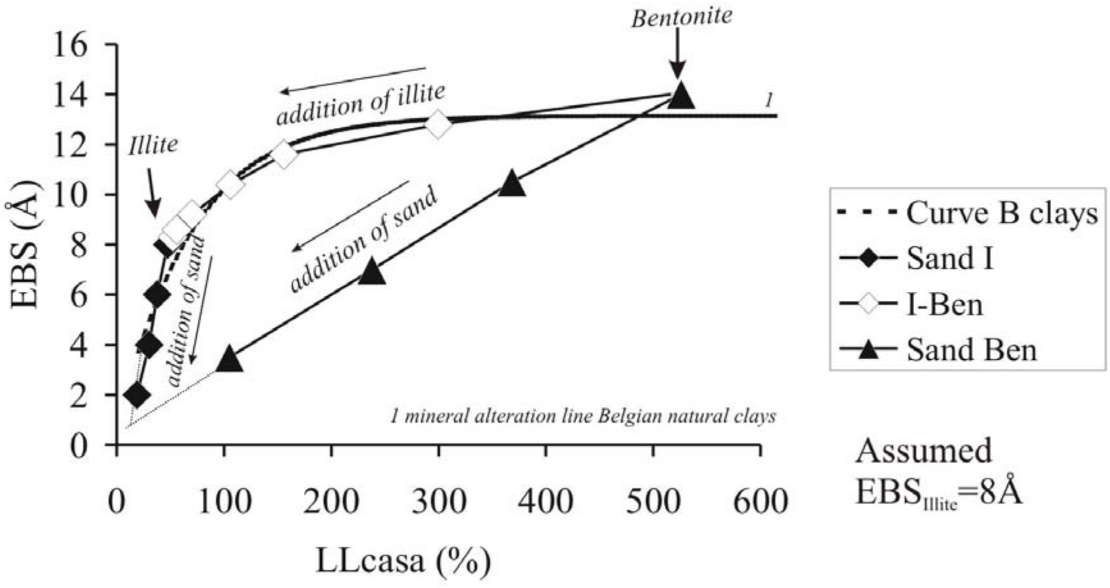


Figure: C5-12

Illite - Smectite mixtures follow the mineral alteration curve. In this figure it is assumed that the Smectite was pure. Illite is never pure in contrast to Kaolinite and Smectite (in Bentonite). In this figure it was assumed that the Illite clay consisted of 80% Illite and 20% inert materials leading to an EBS of 8 Å. EBS is the equivalent basal spacing. LL_{Casa} *is the liquid limit.*

For Illite-Bentonite-sand mixtures the mineral alteration curve and translations of this curve are followed as is shown in **Figure: C5-13**.

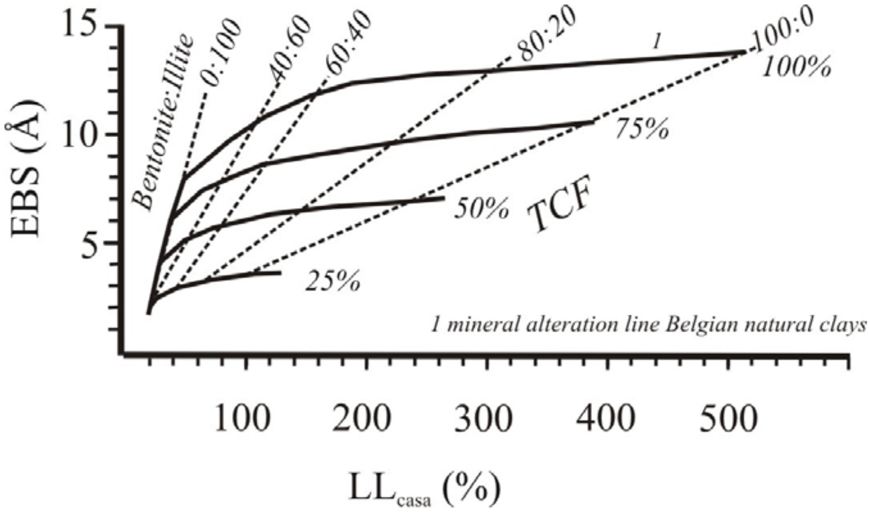


Figure: C5-13

This nomogramme shows how the Atterberg properties and the clay mineralogy can be determined for any Illite:Smectite:sand mixture, with Illite-Smectite mixed-layers formation. EBS is the equivalent basal spacing. LL_{Casa} *is the liquid limit.*

C 5.3.2.3 Summary about clay mixtures

The method used to construct nomogrammes and to determine the liquid limit (and equivalent basal spacing) of any clay-clay-sand mixture is shown in **Figure: C5-14**.

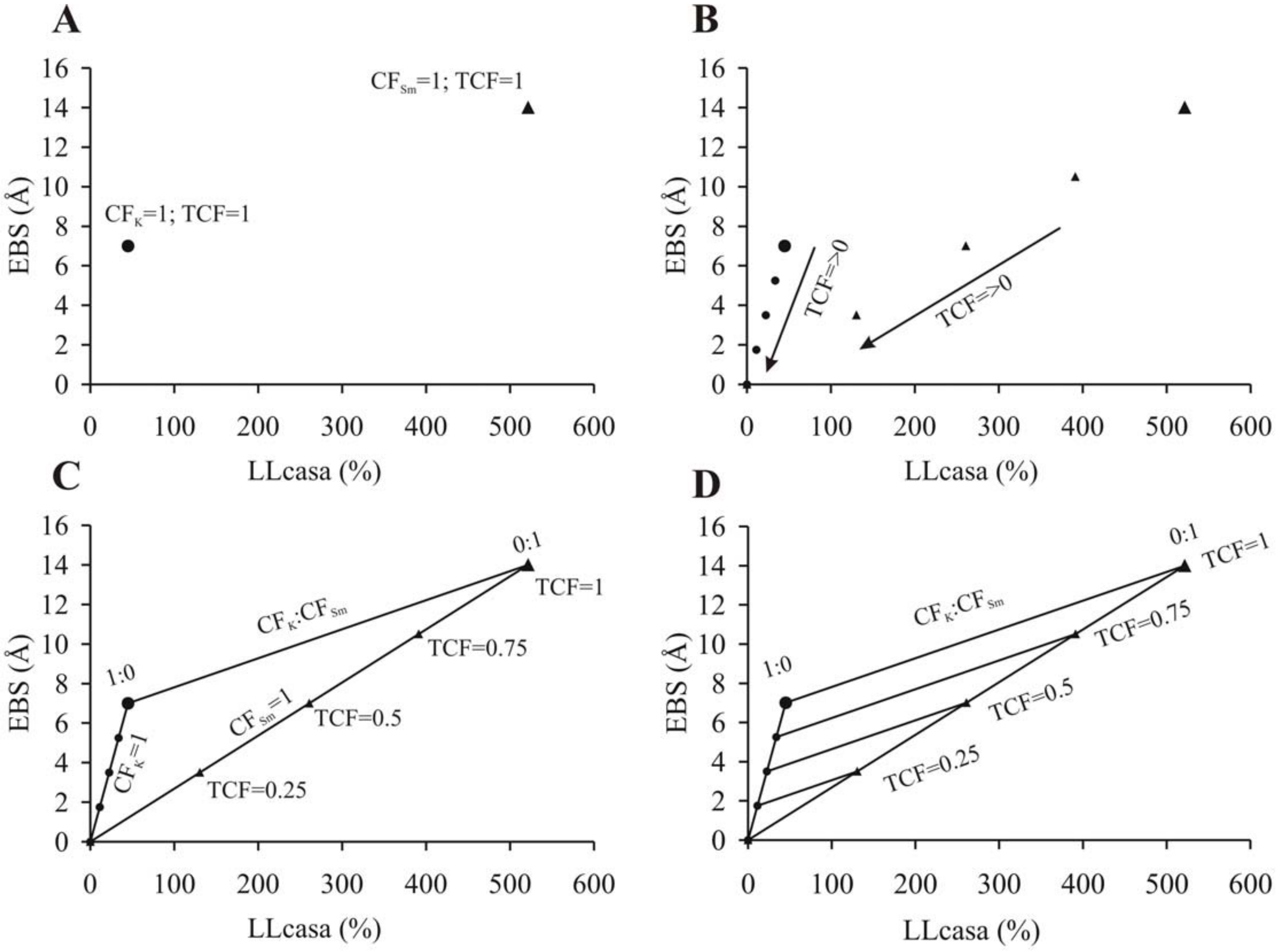
On the next page:

Figure: C5-14.

A - H. Construction of nomogrammes of inactive mixtures.
A) The liquid limit (LL) and equivalent basal spacing (EBS) of the clays that will be mixed must be known to provide the initial (LL,EBS) coordinates.
B) From the initial (LL,EBS) coordinates the line towards the origin (sand - clay mixture line) is followed if these clays are mixed with sand (see ***Figure: C5-7****). Each dot marks an increase in steps of 25% of the non-clay fraction from 0% to 100%.*
C) The line connecting the (LL,EBS) of the pure clays is followed if the clays are mixed together at a clay fraction equal to 1. This is the clay - clay mixture line.
D) The lines, representative of mixtures of the clays at clay fractions lower than 1, can be found by connecting the points on the respective individual sand - clay mixture lines.
E) The EBS of each clay - clay - sand mixture can be calculated according to expression (C5 - 1). These values are marked as crosses on the EBS axis.
F + G) From each marker on the vertical axis a line parallel to the LL axis will provide the LL value of the specific mixture at the intersection with the clay - clay mixture line.
H) The theoretical nomogramme to determine the LL of any inert clay - clay - sand mixture is ready for use if the clay-clay proportion lines are connected with the clay - clay - sand mixture lines.

I - P. Construction of nomogrammes of active mixtures.
I) The LL and EBS of the clays that will be mixed must be known to provide the initial (LL,EBS) coordinates.
J) From the initial (LL,EBS) coordinates the line towards the origin (sand-clay mixture line) is followed if these clays are mixed with sand. Each dot marks an increase of the non-clay fraction from 0% to 100% in steps of 25%.
K + L) The clay - clay mixture line follows a curve parallel to the clay mineral alteration line.
M) The clay-clay mixture lines for each considered clay fraction can be found by setting A_2 *in expression (C5 - 2) to the EBS of the pure clay with the highest EBS and LL and by changing* x_d *to such a value that the clay-sand mixture line of the clay with the lowest EBS and LL is intersected in the appropriate point.*
N) The EBS of each clay - clay - sand mixture can be calculated according to expression (C5 - 1). These values are marked as crosses on the EBS axis.
O) From each cross on the EBS axis, a line parallel to the LL axis will provide the LL value of the specific mixture at the intersection with the clay - clay mixture line.
P) If the intersection with the clay - clay mixture line of the same clay - clay proportion is connected the theoretical nomogramme to determine the LL of any active clay - clay - sand mixture is ready for use.

C


A
B
C
D
EBS (Å)
LLcasa (%)
0
2
4
6
8
10
12
14
16
0
100
200
300
400
500
600
CF_{Sm}=1; TCF=1
CF_K=1; TCF=1
TCF=>0
TCF=>0
1:0
0:1
TCF=1
$CF_K:CF_{Sm}$
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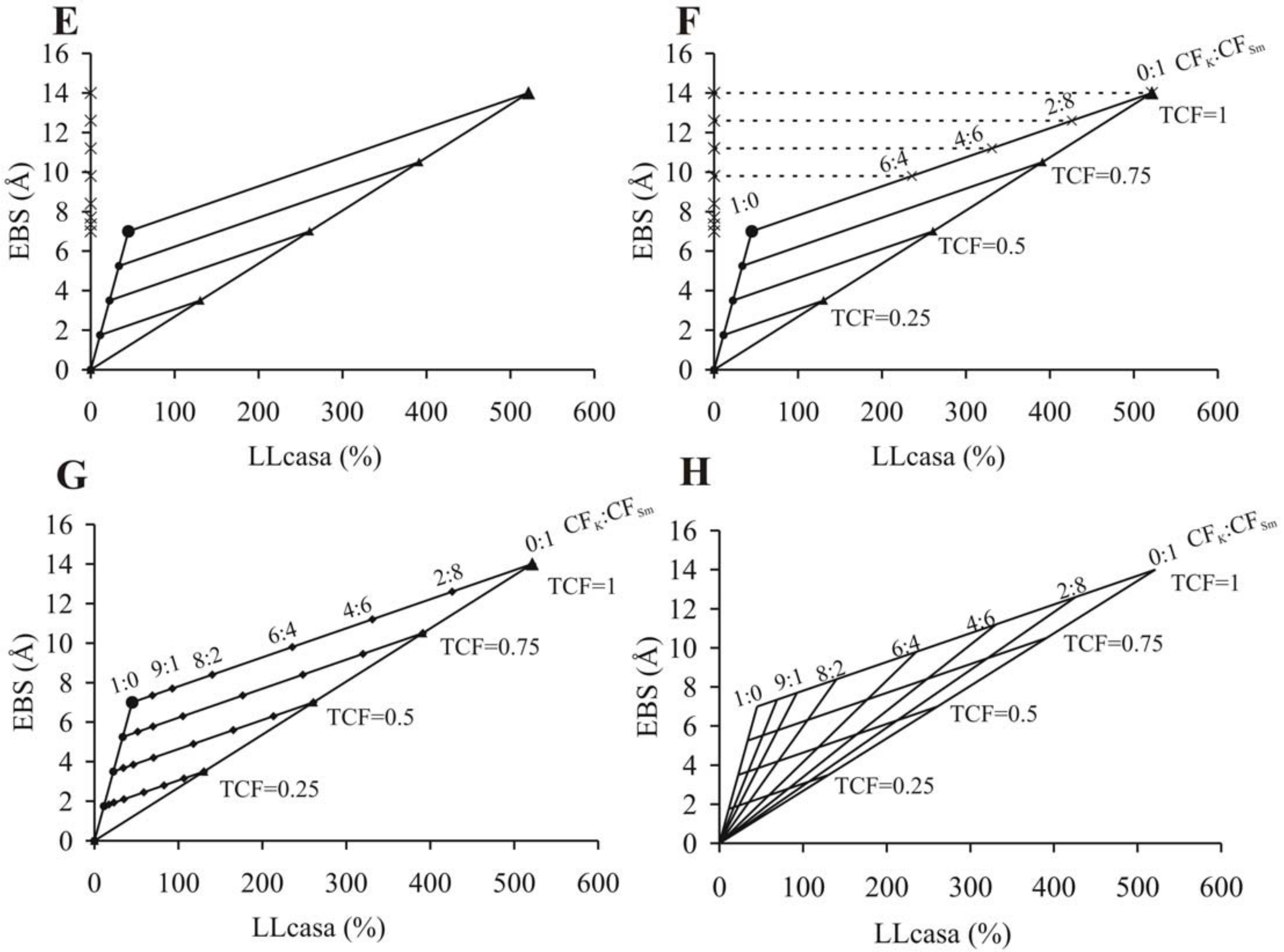
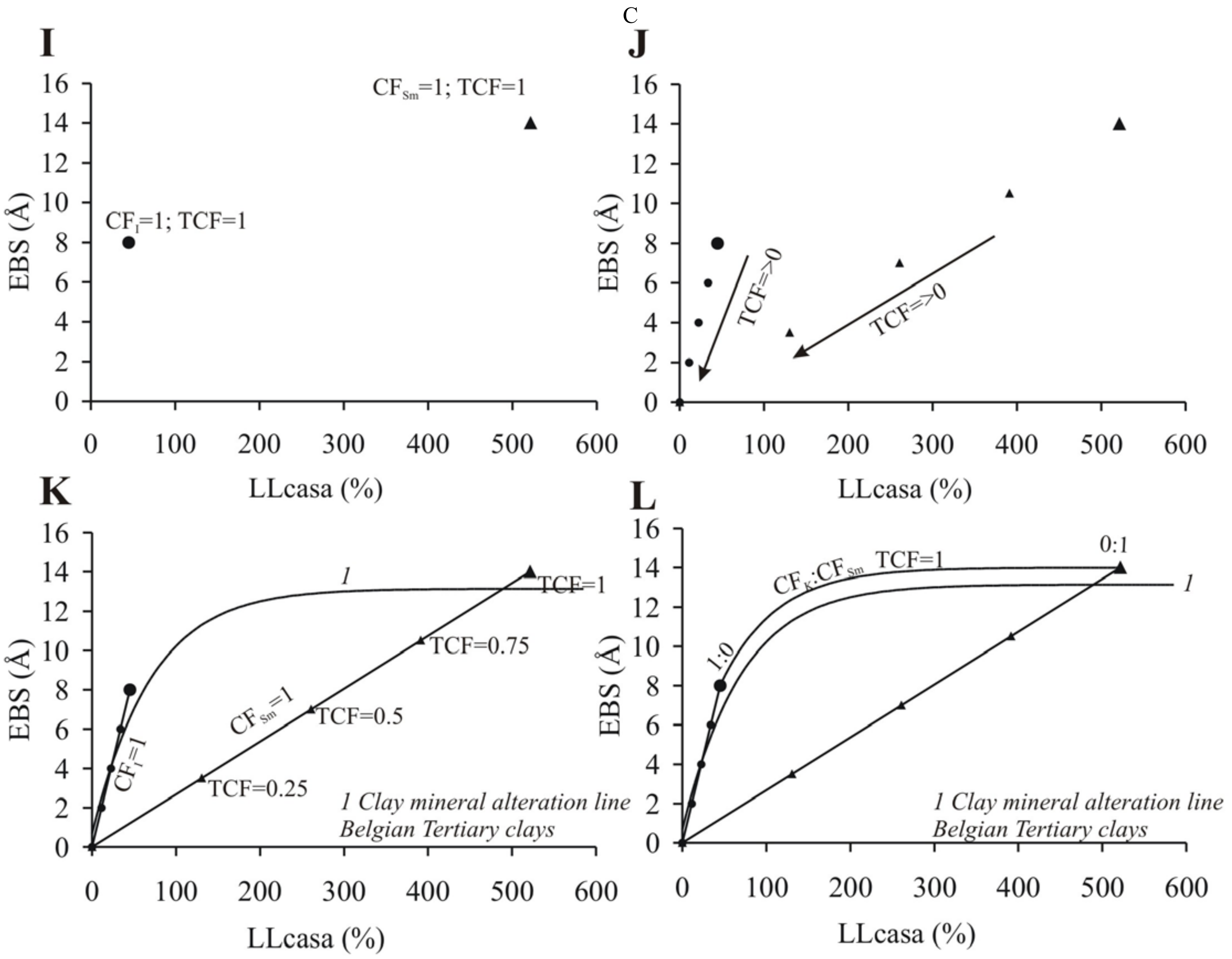
CF_{Sm}=1
TCF=0.5
CF_K=1
TCF=0.25

C


E
F
G
H
EBS (Å)
LLcasa (%)
0
2
4
6
8
10
12
14
16
0
100
200
300
400
500
600
0:1 CF$_K$:CF$_{Sm}$
2:8
4:6
6:4
8:2
9:1
1:0
TCF=1
TCF=0.75
TCF=0.5
TCF=0.25


C
I
CF$_{Sm}$=1; TCF=1
CF$_I$=1; TCF=1
EBS (Å)
LLcasa (%)
J
TCF=>0
TCF=>0
EBS (Å)
LLcasa (%)
K
1
TCF=1
TCF=0.75
CF$_{Sm}$=1
TCF=0.5
CF$_I$=1
TCF=0.25
1 Clay mineral alteration line
Belgian Tertiary clays
EBS (Å)
LLcasa (%)
L
0:1
CF$_K$:CF$_{Sm}$ TCF=1
1
1:0
1 Clay mineral alteration line
Belgian Tertiary clays
EBS (Å)
LLcasa (%)
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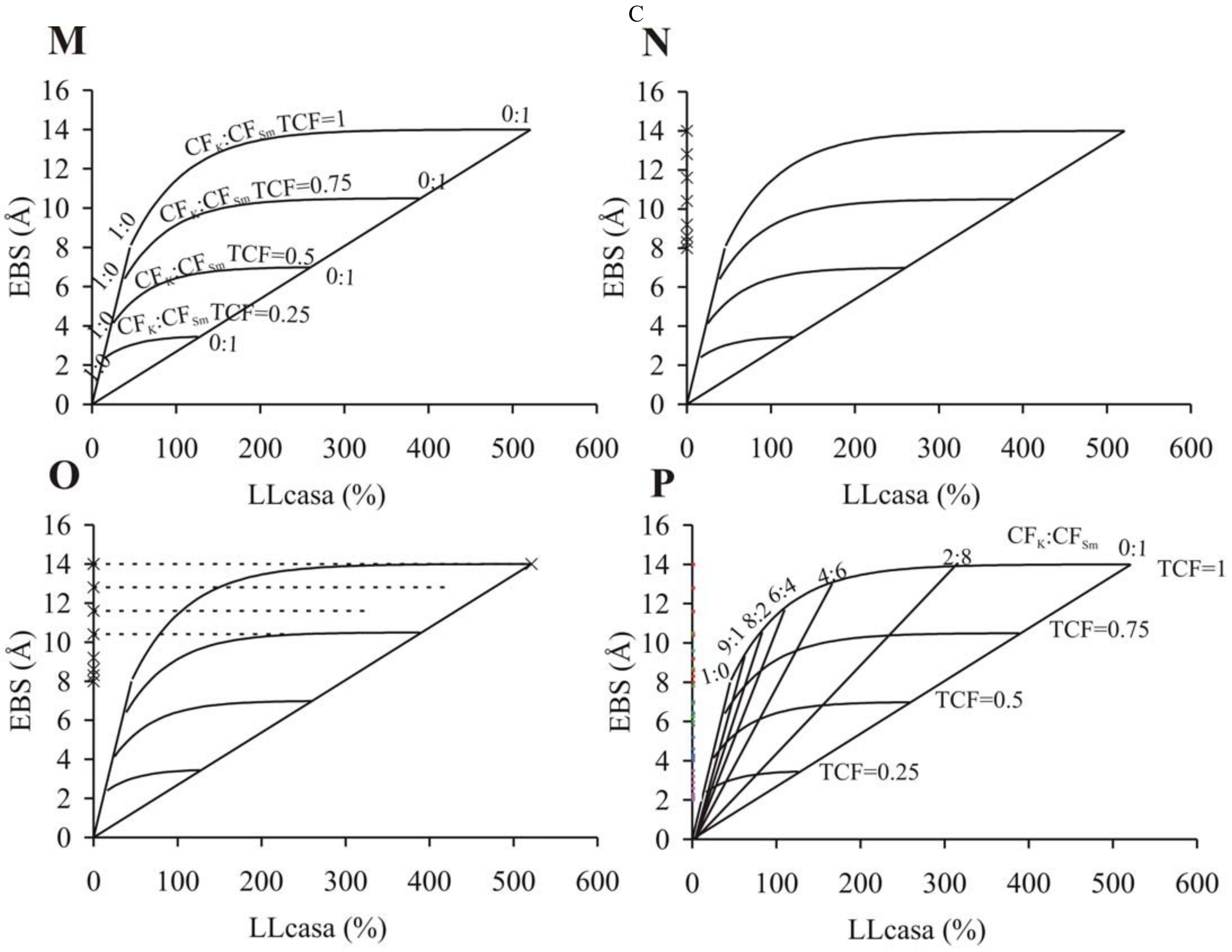
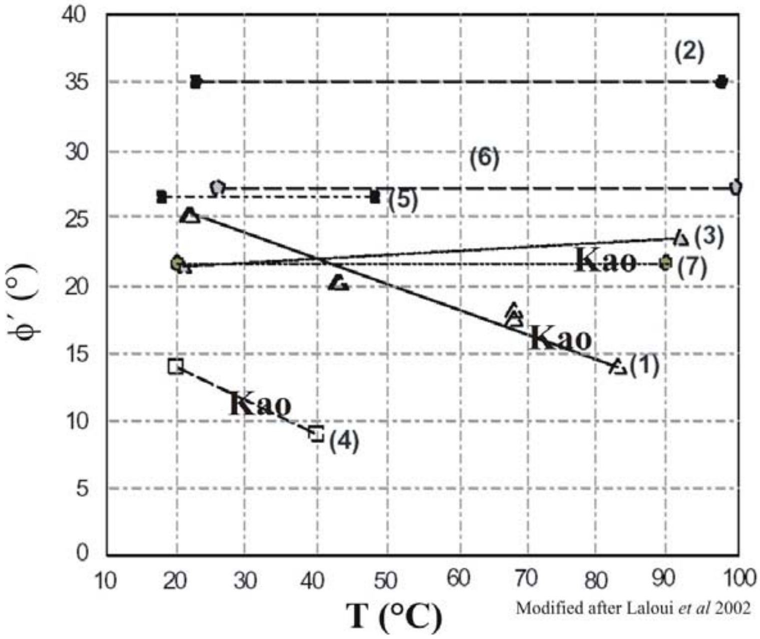
2
4
6
8
10
12
14
16
0
100
200
300
400
500
600


C
M
EBS (Å)
LLcasa (%)
$CF_K:CF_{Sm}$ TCF=1
$CF_K:CF_{Sm}$ TCF=0.75
$CF_K:CF_{Sm}$ TCF=0.5
$CF_K:CF_{Sm}$ TCF=0.25
1:0
1:0
1:0
1:0
0:1
0:1
0:1
0:1
N
EBS (Å)
LLcasa (%)
O
EBS (Å)
LLcasa (%)
P
EBS (Å)
LLcasa (%)
$CF_K:CF_{Sm}$
1:0
9:1
8:2
6:4
4:6
2:8
0:1
TCF=1
TCF=0.75
TCF=0.5
TCF=0.25
0
2
4
6
8
10
12
14
16
0
100
200
300
400
500
600

C 5.3.3 Application of EBS: Clay exposed to heat, example II

Another example that shows the “value” of the equivalent basal spacing concept is related to the investigations by Cekerevac (2003) about the thermal modification of strength of Kaolinites.

Hypothesis:
In one of the publication of Cekerevac (Laloui *et al* 2002) it is stated: “The friction angle at critical state can either increase or decrease (or remain independent) with temperature (**Figure: C5-15**). In some cases, thermal dependency can be quite pronounced (Kaolinite). It seems that the friction angle variation with temperature depends on the nature (note: mineralogy?) of the soil…”.



Modified after Laloui *et al* 2002

Figure: C5-15

Temperature (T) affects the friction angle (at critical state, ϕ’). The samples consisting of Kaolinite have been indicated as such. Each number refers to another test programme. Lines 1, 4 and 7 represent Kaolinites, the other lines other clays.

Problem:
Figure: C5-15 shows that two out of three tested Kaolinites showed a strong dependency on temperature, but not the third Kaolinite (marked by 7). The latter was tested by Cekerevac. Who is right? Does the friction angle change with temperature?

The approach:
If the “nature” of the soil is represented by its mineralogical fingerprint this means that:
If the friction angle of a Kaolinite would change with temperature (see **Figure: C5-15**) the mineralogy should change as well because:

i) The friction angle is related to the Atterberg limits (relationship (**C5 - 6**) and (**C5 - 7**))

ii) The Atterberg limits are related to the equivalent basal spacing (relationship (**C5 -2**))

iii) The equivalent basal spacing is related to the clay mineralogy (relationship (**C5 - 1**)).

Thus if the clay mineralogy changes with temperature the friction angle will change as well.

Does the mineralogy of Kaolinite change if heated to 500°C?
From standard X-ray diffraction analyses it is known that heating to 500°C will destroy Kaolinite (*e.g.* overview in Schmitz 2001a). According to relationship (**C5 - 1**) a decrease of the clay content (TCF) will reduce the equivalent basal spacing. According to relationship (**C5 - 2**) and (**C5 - 3**) a reduced equivalent basal spacing indicates a reduced liquid limit. A reduced liquid limit corresponds to an increase of ϕ. Thus temperature clearly influences the shear strength of clays.

Does the mineralogy of Kaolinite change if heated to 90°C?
Will the Kaolinite change at a much lower temperature level of 90°C? To answer this question the Lausanne Kaolinite samples were tested in Liège before and after heating to 90°C.

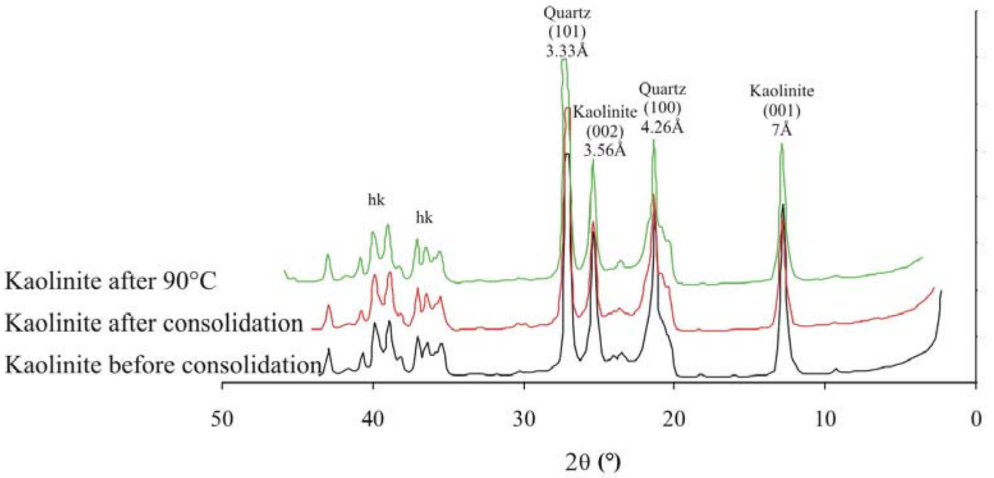


Figure: C5-16

The heating to 90°C did not change the mineralogical composition of the Kaolinite samples. θ is the angle of incidence of the X-ray beam (°).

The solution:
In **Figure: C5-16** the mineralogical analysis of the Kaolinite clay is shown before and after heating to 90°C. The heating did not cause any modification of the clay mineralogy. If the mineralogy does not change, the liquid limit does not change and neither does the friction angle. This result corresponds to the analysis performed by Cekerevac (line N° 7) in **Figure: C5-15** showing that the friction angle of the Kaolinite did not change in the trajectory from 20°C to 90°C. Contrary to the statement cited above the “nature” of the soil *i.e.* the mineralogy does not change, thus the equivalent basal spacing does not change, therefore there is no reason for the ϕ’ to change on the

basis of the mineralogy. This was confirmed by the test performed in Lausanne (**Figure: C5-15** line 7).

C 5.3.4 Application of EBS: Clays exposed to salt solutions

Salt solutions tend to change the behaviour of clays (Schmitz and van Paassen 2003) according to the following processes:

- Osmotic effects
  - on a large scale (sample level): If the entire clay sample is considered as a semi-permeable membrane the presence of salts induces fluids to migrate outwards from the sample, producing a decrease of volume an increase of shear strength, *etc*.
  - on a small scale (particle level): If salts enter the clay sample by advection or diffusion, the thickness of the double layer is decreased, the clay particles approach each other, resulting in a decrease of the liquid limit, a decrease of volume, an increase of hydraulic conductivity, *etc*.
- Crystallisation of salt crystals (particle level)

  By increasing the concentrations of ions in the clay-fluid by *e.g.* evaporation salts start to crystallise. This modifies the clay in two ways:
  - Due to the hygroscopic nature of salt, water is drawn from the clays; this loss of water is accompanied by a decrease of volume, reorientation of clay particles (if cinematically admissible), *etc*.
  - The presence of salt crystals in solid form increases the grain size of the total sample; the silt-sized fraction increases with respect to the clay fraction which results in a decrease of the liquid and plastic limit, an increase in the internal angle of friction, *etc*.
- Mineral alteration (interlayer level):

  Cations, like potassium, can enter into the pseudohexagonal voids in the O-sheet of the interlayers of Smectites. This causes to some degree an irreversible collapse of the interlayer space. The properties of this collapsed material will correspond to that of an Illitic clay or to an Illite-Smectite mixed-layer clay, which generally have a lower liquid limit and a higher shear strength.

For “ pure” clays the decrease of the liquid limit with increasing salt concentration is well documented:

i) Di Maio (1996) tested the liquid limit of Ponza Bentonite exposed to several salt solutions.

ii) Van Paassen (2002) did the same tests but used the same Sm_{ref} as the one used for this thesis.

iii) The author merged these databases and discovered that these different Smectites behave similarly. If a correction for the amount of positive charges for each cation was made it turned out that the different salt solutions had the same influence on the liquid limit.

iv) The author and van Paassen (Schmitz and van Paassen 2003) introduced an empirical formulation, which can be used to determine the liquid limit of any clay, having only knowledge of the liquid limit with demineralised water and the clay content of the sample.

v) The empirical formulation mentioned under 4) was based on the cone penetrometer data by Di Maio (1996) and van Paassen (2002). To convert these measurements to

LL_{Casa} the expression (**A4 - 2**) developed in **Part: A** can be used. Now a diagram can be made relating the LL_{Casa} to salt concentrations (**Figure C5-17-A**).
vi) With expression (**C5 - 2**) relating the liquid limit to the equivalent basal spacing (EBS), the EBS can be related to the salt concentration (**Figure C5-17-B)**.[40]

In **Figure: C5-17-A** it can be seen that the addition of salt causes a significant decrease in liquid limit. This observation holds true for NaCl, KCl and $CaCl_2$. The empirical relationship between the liquid limit and the salt concentration cannot only be used to obtain a prediction of the evolution of a mechanical parameter as for example the compression index (Schmitz and van Paassen 2003), but additionally (using the concept of the equivalent basal spacing (EBS) introduced previously in this contribution) one can have a look at the evolution of the interlayer distance with increasing salt (*e.g.* KCl) concentration (see **Figure: C5-17-B**).

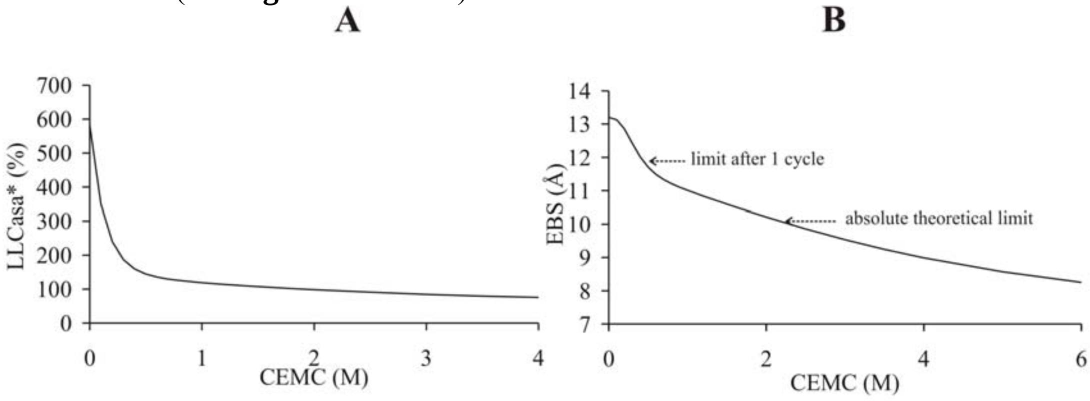


Figure: C5-17

A: The evolution of the liquid limit (LL_{cone}, based on figure from Schmitz and van Paassen 2003) for Smectites (reference Smectite = Natural Na-Montmorillonite) and Ponza Bentonite (=Na-Montmorillonite). B: The evolution of the equivalent basal spacing (EBS).

Reference Smectite

The decrease of the liquid limit with increasing salt concentration can be described for the reference Smectite in terms of equivalent basal spacing as follows:
Initial EBS = 0.95·14 = 13.3 Å corresponding to (confirmed by measurements) a LL larger than 580% and a Cc > 5.
After addition of a KCl solution and air-drying the samples during only one cycle, the basal spacing collapsed to 12 Å. The equivalent basal spacing becomes:
EBS = 0.95·12 = 11.4 Å corresponding to a LL = 135%. The measured liquid limit, however, was much lower, smaller than 50% (see **Figure: C5-18**).

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[40] *If parameter A_2 in expression (**C5 - 2**) is set to 20 Å (the BS of moist Smectite) and parameter A_1 is set to -93 (to guarantee that the LL-EBS line intersect the origin) then the BS-h_{TOT} - salt concentration diagram - established by Lagaly (1993) on the basis of sophisticated XRD measurements - can be confirmed (dashed line in F**igure: C7-10**) on the basis of the EBS and the EBS-LL relationship introduced in this chapter.*

During the determination of the Atterberg properties it was reported that the clay sample felt silt-like. This fact plus the overestimation of the liquid limit showed that a important factor during the test had been missed. Therefore additional XRD analyses were performed. The results showed that these “silt” particles were sylvite (KCl salt) crystals. After a standard had been created to determine accurately the amount of KCl, it was found that the sample consisted up to an average of 40 % sylvite. The equivalent basal spacing in this case was:

$EBS = 0.6\cdot(1\cdot 11.4) = 6.8$ Å corresponding to a LL = 47 %, the value measured in the laboratory. The original value of the reference Smectite, the correlation line between the liquid limit, the equivalent basal spacing and the actual measured data points are given in **Figure: C5-19**.

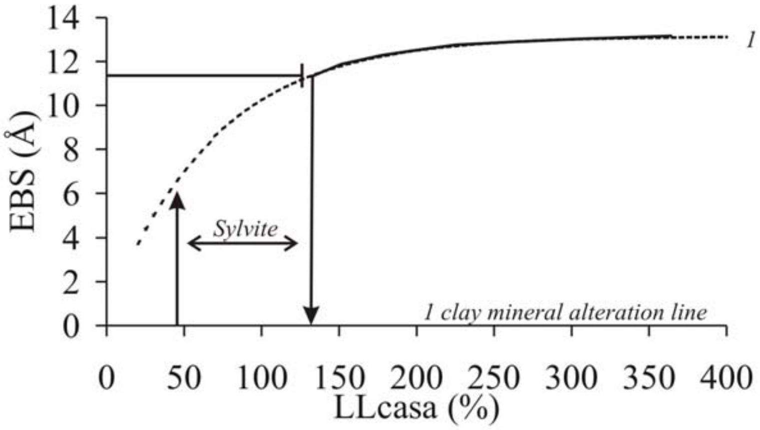

Figure: C5-18

Clay mineralogy related to the liquid limit to explain the effect of salt solutions on the liquid limit. After one cycle of exposure to a saturated KCl solution the expected EBS = 11.4 Å, the corresponding LL should be 135%. The measured LL was however much lower. Why? Because Sylvite precipitated and reduced the TCF of the sample.

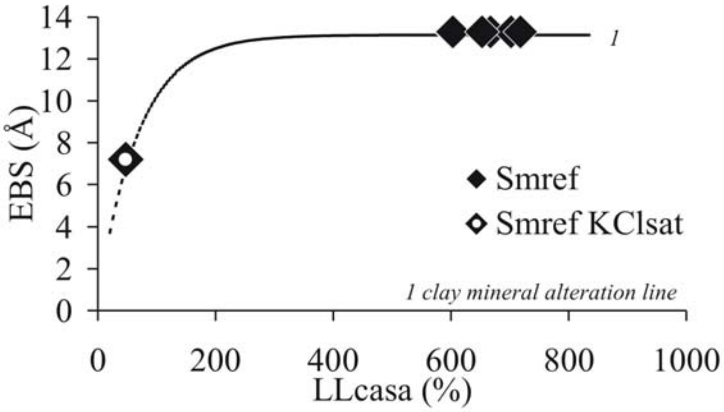

Figure: C5-19

The equivalent basal spacing (EBS) versus the liquid limit (LL_{Casa}) of the reference Smectite (Sm_{ref}) and the same clay after exposure to a saturated salt solution (Sm_{ref} KClsat).

It must be noted that this important feature - the formation of salt crystals - would have been missed, had the equivalent basal spacing not been analysed.

Natural Tournai clay
The friction angle of a remoulded Tournai clay sample tested during consolidated undrained (CU) triaxial tests was 27°. If the sample is exposed to a saturated NaCl solution, remoulded and tested, will the salt change the friction angle? From the experiment with the reference Smectite and salt described above one knows that the clay fraction decreases from 95% to 60%, thus by a factor 1.58. If it is assumed that this same factor applies to the Tournai clay - NaCl combinations, the initial clay fraction of 81% will decrease to 51%, additionally the basal spacing of the 68% (10-14m) will decrease from 14 Å to 12 Å. This will result in an:
$EBS = 0.51\cdot(0.16\cdot10+0.07\cdot12+0.68\cdot12+0.09\cdot14) = 6$ Å, LL = 40% and $\phi' = 30°$.
The salt increased the relative friction angle by 4°. Laboratory results were able to confirm these changes. The measured value was 31°.

C 5.3.5 Application of EBS: Podzolisation

Clays are often used as engineered barriers to contain hazardous waste because clays:

- Are available in large quantities in low lying areas, former basins near the sea or lakes, where the population density is highest and thus, the need for these industrial materials is the largest.
- Are cheap.
- Have a low hydraulic conductivity.
- Can be easily handled and reworked/formed.
- Are quite stable because they are at the end of the weathering chain.

As discussed in **Part: B4**, a Tournai clay sample, consisting of a core of compacted natural clay, was permeated during months with a young landfill leachate. At the end, thin sections of this clay sample were examined. The analyses showed that the processes observed such as Smectitisation and secondary Chloritisation strongly resembled the process of Podzolisation observed in nature. This indicates that if the laboratory test is representative for the conditions present at the base of a landfill the clay used in the clay barrier will slowly transform into Kaolinite at the end.
What does this mean for the changes in terms of geomechanical properties?
In **Figure: C5-20** the position of the three natural clays is shown as well as the position of a “pure” Kaolinite. The process of Kaolinisation will have the largest impact on the Tournai and Soignies clays. Kruibeke clay will not change that much. Although the process is beneficial for the Tournai clay in terms of gaining shear strength (higher ϕ’) and decreasing the compression index, the Soignies clay will be affected the other way around. Next to the gain in “strength” the Tournai clay will show a decrease of the specific surface and of cation exchange capacity *etc*. For the Soignies clay it will be the opposite effect.

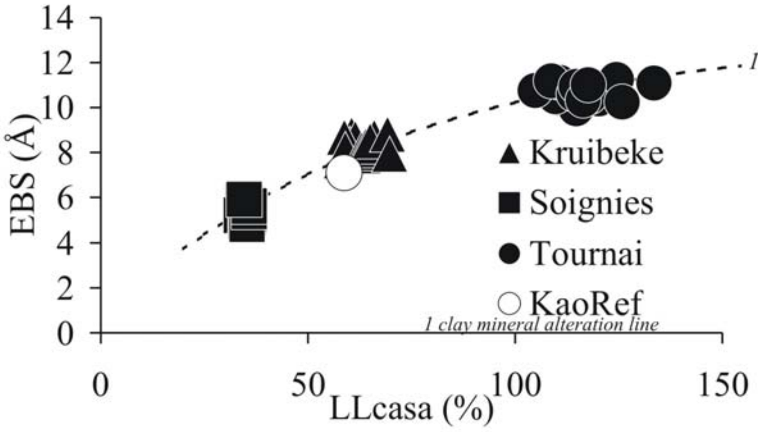

Figure: C5-20

The equivalent basal spacing (EBS) versus the liquid limit (LL_{Casa}) of three natural clays and of a reference Kaolinite (Kao ref).

C 5.4 Modification EBS of moist samples

The basal spacing of clay minerals can be determined on air-dried samples. This is the most common applied method used as well in the clay laboratory of the University of Liège. More sophisticated XRD equipment is able to test the basal spacing of moist samples. With the latter, the basal spacing can be determined in diverse fluids as will be shown in **Figure: C7-10** in paragraph **C 7.3.4**. Of course the definition of the equivalent basal spacing remains identical to the definition given in expression **(C5 - 1)**. A simulation of the equivalent basal spacing in this case is given in **Figure: C5-21**. Only the value of the Smectite fraction (in the different clays) will be modified from 14 Å to 17 Å.

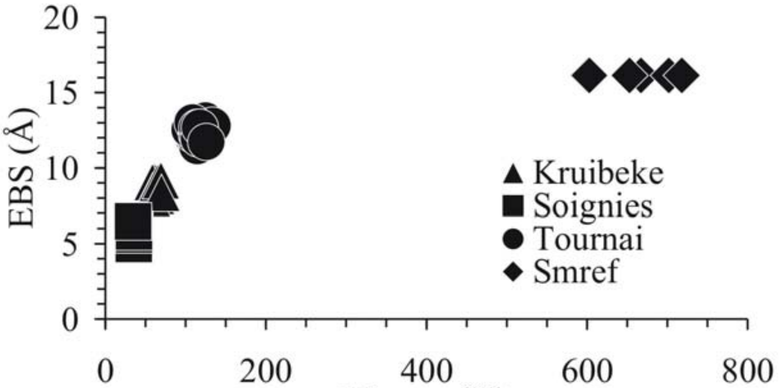

Figure: C5-21

In this figure the equivalent basal spacing (EBS) is given as a function of the liquid limit (LL_{Casa}) for the Tournai, Kruibeke and Soignies clay and additionally for the reference Smectite. The EBS has been determined on the basis of the basal spacing of moist samples.

C 5.5 Summary

The behaviour of clayey soils is related to the microstructure and to the mineralogy of clays. The clay mineralogy changes if clays are used in various engineering applications. In environmental engineering clays are frequently used as a barrier to contain hazardous waste. If clays are used as a seal they will be exposed to *e.g.* brines and heat. The effect of this exposure was analysed for three natural soils with a complex mineralogy, representative of the common natural clay with which an engineer will work in practise. The microstructure on the interlayer level of clays can be studied in various ways but only if all clay minerals are analysed and not only the fraction smaller than 2 micrometer (modifications in sample preparation) the X-ray diffraction technique is a very suitable method.

A link between the result obtained by X-ray diffraction analyses and geomechanical properties can be made using the equivalent basal spacing (EBS) concept.

With the equivalent basal spacing the changes of clays, if exposed to different environmental ordeals, can be predicted on the basis of its mineralogy. With the link between the equivalent basal spacing and the liquid limit these changes can be expressed in geomechanical terms. Several examples were shown, like the exposure to heat and brines. These processes caused a collapse of the interlayer spaces. A quantifiable decrease in Atterberg limits and compressibility can be given with the equivalent basal spacing. It was shown that if the reaction of clay minerals if exposed to certain conditions is known from clay mineralogical literature, quantitative predictions of the changes in various geomechanical properties can be given. Finally, it was shown that once the mineralogical alteration process during permeation of domestic landfill leachate through the clay barrier is recognised, comparison to natural analogues can be made. Based on this knowledge, suitable clay deposits can be chosen to limit the changes in geomechanical properties during the technical life of the clay seal.

The behaviour of mixtures of clays can be predicted in terms of clay mineralogy (equivalent basal spacing) and Atterberg limits. Different rules have to be applied depending if the mixtures are reactive (new clay minerals are formed like mixed-layered clay minerals) or inert.

With the concept of equivalent basal spacing a new tool has been created which provides a direct link between clay mineralogy and geomechanical properties. Once, in future, the mineralogical composition of a clay is available, a quick assessment of its engineering properties can be made. In addition it is possible to quantify the engineering significance of any known clay mineral alteration process. Thus: Clay mineral characterisation can be useful in engineering practise not only qualitatively but quantitatively as well.

C 6 Identification of the clay particle geometry, size and arrangement

C 6.1 Introduction

This chapter forms a bridge between chapter **C5** which discussed reactions - between fluids or substances contained in fluids and clays - on the interlayer level of clays, and chapter **C7** which will discuss reactions between the same components but on the particle level.

The different chemical-mineralogical-physical reactions occurring during clay - fluid contact analysed up to this point are:
- Reactions on a TOT/TO level, these reactions can be described using natural analogues (chapter **B 4**).
- Reactions within the clay particles, the interlayer level, these reactions can be described with the developed tools as the mineral alteration pathways (**Figure: B3-10**) and the equivalent basal spacing (chapter **C 5**).
- Reactions that play a role between the clay particles - particle level - these reactions can be described using the double layer theory (see chapter **A 3.1.2**).

The aim of this chapter concerns the reactions of the latter two types. In chapter **A 3.1** it has been discussed that for engineering applications the changes in the interlayer distance are important clay mineral features that have to be taken into account. This led to the definition of the equivalent basal spacing (EBS) in chapter **C 5**. But clay particles are not alone, they are social “beings”. In contrast to clay mineralogists, geomechanical engineers should have an interest in the “social” behaviour of clays: How does the alteration of one clay mineral particle affect another clay mineral particle, possibly of another clay mineral species? The “social” behaviour of clay minerals depends to a large extent on repulsive forces that arise from the presence and size (location of the centre of mass) of the double layers and on all factors that influence the “thickness” of the double layer like temperature, available cations, the relative permittivity of the permeate *etc*.

To use the information contained in this double layer theory one needs to know the general set up of the assembly of clay particles. If clay samples are considered as being build-up of a homogeneous anisotropic assembly of discrete clay particles, the general set-up of a part of such a clay sample is given by the model presented in **Figure: C6-1**. In fact the model consists of an assembly of several blocks, each block representing one clay particle. A clay particle is composed of TOT/TO-layers. Likewise each block is formed by a series of parallel TOT-layers.

The dimensions (this is the first aspect of this chapter) of this model in terms of:
- Number of clay particles.
- Size of clay particles.
- Orientation of clay particles.
- Morphology of clay particles.

Can be determined using information from:
- Thin sections (petrographs).
- Oedometer tests with brines.
- The build-up of the interlayer level.

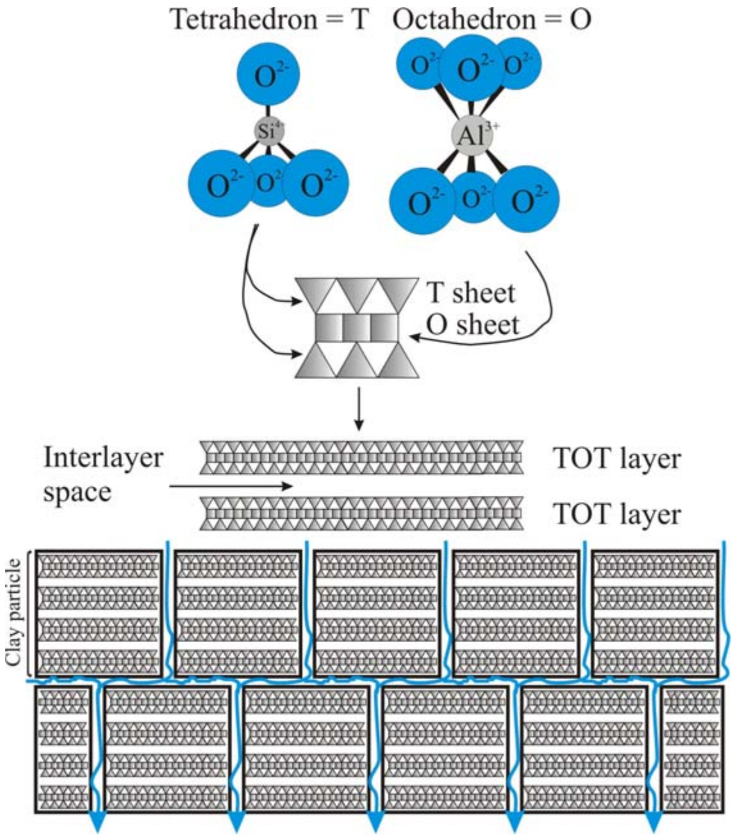

Figure: C6-1

Si-O tetrahedrons and Al-O octahedrons form long TOT-layers. Between two layers an interlayer is formed. Several TOT-layers form a clay particle.

The model presented in **Figure: C6-1** can not only incorporate changes on the particle level but changes on the interlayer distance as well. These changes will result in a strain of the clay block. Depending on the mineral alteration process that is active, the magnitude and orientation of the strain change. In chapter **C 5** changes on the interlayer level were discussed. It was shown how clay mineralogists measure these changes and how these results can be interpreted in geomechanical terms. Changes on the particle level will occur more easily than on the lower levels because leachates and the substances they carry will contact the larger voids, like interparticle voids first. Contrary the changes in geomechanical terms on the particle level due to interaction of the clay with leachates are less important than changes on the interlayer level (changes on a lower level may even mask the changes on a higher level). As will be shown in this chapter under some circumstances *e.g.* during the initial phase of leaching of a clay barrier on which a mechanical stress is exerted the interlayers are not accessible at all. In this case all leachate-clay interactions will occur on a particle level. This accessibility forms the second aspect of this chapter.

First the build-up of clay particles constituting clay samples and clay barriers is discussed on the basis of several geomechanical tests. Then the second aspect, in extension to the discussion started in **Part: A**, the interlayer accessibility of clays is discussed under hydro-mechanical conditions resembling those of clay liners used for waste containment in *e.g.* domestic landfill sites.

C 6.2 Identification of the overall orientation of clay particle assemblages

Clay minerals are part of the layer silicates mineral group and are formed by long TOT/TO-layers *i.e.* starting from their smallest building stone clay minerals are anisotropic. This anisotropy is reflected in the form of the clay particles (*e.g.* **Table: A4-1**). The anisotropy influences the mechanical and hydraulic properties of clays. Information about the orientation of minerals or particles within a rock or a soil other than clays are generally analysed by preparing and studying thin sections of this geomaterial by using a polarising (or electron) microscope. With such a microscope it is impossible to see details smaller than the wavelength of visible light (PT 1994). The wavelength of visible light varies between $4\cdot10^{-7}$m violet and $7\cdot10^{-7}$m red (Binas 1986). Thus only the largest clay particles (see **Table: A4-1**) can be seen. Therefore it is stated in general that thin sections of clays do not provide much information. The author has shown (Schmitz 2000) that nevertheless, a thin section of a clay mineral can reveal important (thus geomechanical) properties of a clay using a light microscope. The advantage of thin sections over today's (non-environmental) scanning electron microscopic analyses of clays is that the structure is solidified before and not after sectioning. The solidification of clays requires however some modification of the standard equipment used for thin sectioning *e.g.* plastic instead of metal laps for polishing and hydrocarbon instead of water cooled saw (Carmuti and Guire 1999). These changes were made in the geology department of the University of Liège. An example of a thin section of Tournai clay is given in **Figure: C6-2**.

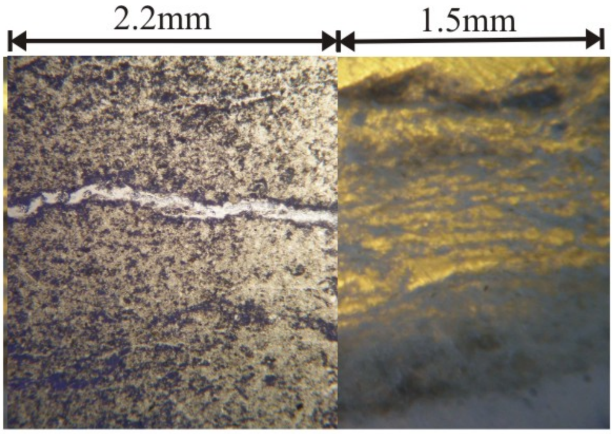

Figure: C6-2

A: Thin section of the natural Tournai clay. The clay matrix is isotropic (except for the drying crack in situ?) and nonhomogeneous. B: Thin section of homogenised Tournai clay after oedometric loading to 100kPa. This clay matrix is anisotropic (layered) and homogeneous [41]*.*

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[41] *Note that isotropic and homogenous are used in a geomechanical sense. In mineralogical terms:*

- *Isotropic means that crystal remains black if looked with crossed nichols.*
- *Homogeneous refers to a sample without layering, while non-homogeneous corresponds to a sample exhibiting a layer (stratified) texture.*

From **Figure: C6-2** one can see that thin sections reveal important geomechanical properties of the micro build-up of clays: In these cases the reorientation of the clay particles upon homogenisation and oedometric compression is an important feature. The observed reorientation of Tournai clay particles perpendicular to the principle stress as shown in the example in **Figure: C6-2** occurs under stress conditions near to those in a clay barrier. In the literature reorientation of clay particles were observed at similar stress levels *e.g.* Morgenstern and Tchalenko (1967) and Schmitz (2000) on other clay types. It can therefore be supposed that a certain degree of reorientation will occur in a clay barrier confining *e.g.* domestic landfill waste. In the remainder of this chapter it is therefore supposed that the clay particles (and the TOT/TO-layers) are orientated perpendicular to the principle (vertical stress).

C 6.3 Identification of the number of TOT-layers in a clay particle and the number of clay particles in a clay sample

C 6.3.1 Introduction

In the previous paragraphs the general concept of clay samples being build-up of a homogeneous anisotropic assembly of discrete clay particles oriented perpendicular to the largest principle stress were discussed. In this paragraph the dimensions of the clay particles and their number are deduced from a series of tests.

In **Figure: C6-3** the steps needed to determine the set up (*e.g.* the dimension) of the clay particle model are illustrated. With the physical model (repulsion law) that was presented briefly in paragraph **A 4.2.4.2** and which will be discussed extensively in chapter **C 7**, the observations made in paragraph **C 6.2,** the assumption that the sample is loaded to a stress high enough to cause parallel arrangement of particles perpendicular to the principle stress, the correct set-up of size and orientation of the clay blocks can be determined.

If the sample is percolated by a salt solution and if the flow takes place around the clay particles, the double layer will contract and the clay particles can approach each other (see chapter **C 7** or explanation type 4 in paragraph **3.1.3.1**). This will macroscopically result in a settlement of the sample at constant stress (**Figure: C6-3-B**). With this information the number of particle interfaces can be determined in the settlement direction. The number of clay particles is equal to the number of interfaces plus one. With additional information of the void ratio (**Figure: C6-3-C**), which is normally tested during an oedometer test, the ratio between the number of clay particle interfaces and the number of interlayers can be determined. In this case it is assumed that the void ratio, determined in geomechanical engineering at 100°C, is able to remove the water from the interparticle voids and the water from the interlayer spaces. With all this information the number of clay particles and their size (in terms of number of TOT-layers) can be determined. This will be highlighted in the example discussed in the following paragraph.

C 6.3.2 Procedure to determine the number of TOT-layers in a clay particle and the number of clay particles in a clay sample

The approach that is followed is shown in **Figure: C6-3**. The distance between clay particles is a function of the double layer thickness and varies *e.g.* with the concentration of cations in the fluid (**Figure: C6-3-A**). A clay sample percolated under oedometer condition will settle if percolated by salt solutions (**Figure: C6-3-B**). The stress deformation relationship measured during an oedometer test provides a void ratio stress relationship (**Figure: C6-3-C**). The different curves shown in **Figure: C6-3-A, B** and **C** allow the determination of the dimensions of clay particles and particle interfaces shown in **Figure: C6-3-D**.

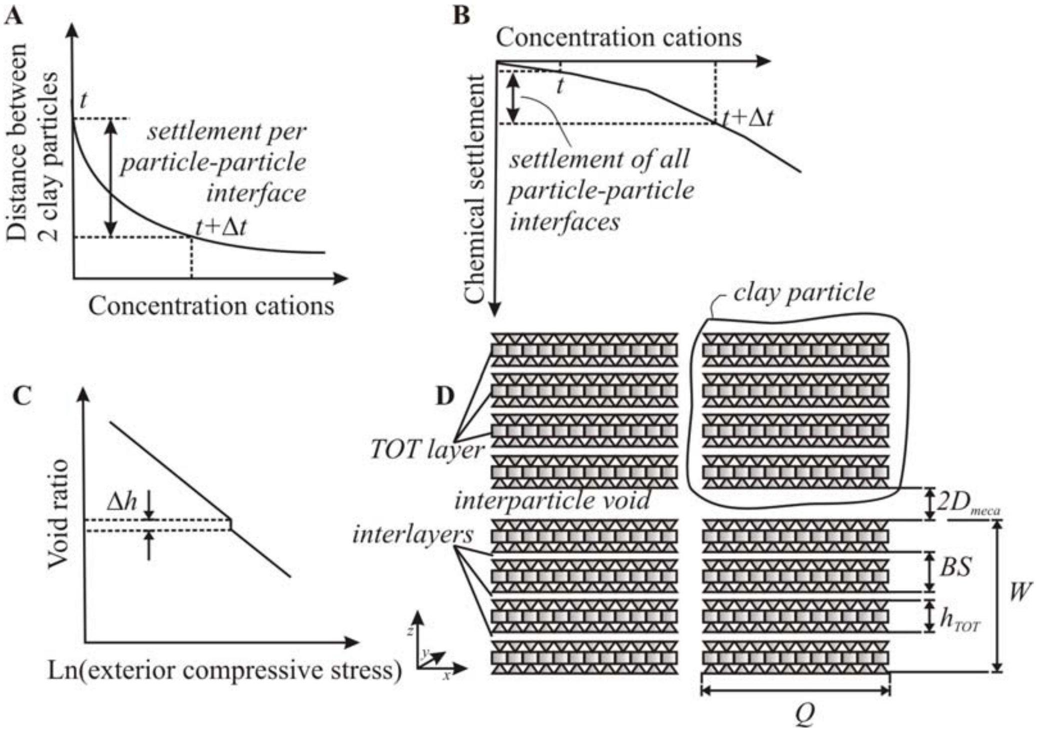

Figure: C6-3

A: Interparticle distance as a function of the interparticle chemistry according to the theory introduced in chapter ***C 7****. B and C: Oedometer tests of a clay sample during percolation with brines. D: The dimensions of clay particles that have to be determined.*

The following variables need to be determined:

$2D_{BSBH}$ = distance between clay particles before heating or percolation with salt:
To calculate $2D_{BSBH}$ one needs to know the concentration of ions in the space between the clay particles. With this concentration $2D_{BSBH}$ can be calculated using the theory presented in chapter **C 7**.

$2D_{AS}$ = distance between clay particles after percolation with salt solution.
This value is determined in the same way as $2D_{BSBH}$ except that the concentration of salts *etc.* corresponds to the concentration of the percolating fluid. Intuitively one could think that the permeate does not enter all voids between the particles within a short test

duration (amount leached equal to void volume), thus that the chemical settlement would increase as a function of time *i.e.* amount of permeate leached through the sample. Long-term tests (amount leached larger than several times the void ratio) have shown that this does not happen. Therefore one can assume that the permeate arrives in the void between the particles within a relative short time delay.

$2D_{AH}$ = distance between clay particles after heating to 500°C.
Note that this value does not express a distance between particles *s.s.* but represents the volume of evaporated fluid. $2D_{AH} = 0$ Å.

BS_{BSBH} = Basal spacing before heating and before percolation.
The basal spacing before heating and before percolation at atmospheric pressure can be calculated using the results of X-ray diffraction analysis of the clay under consideration and the EBS theory presented in paragraph **C 5.4**.

BS_{AS} = Basal spacing after percolation of permeate.
The basal spacing after percolation at atmospheric pressure can be determined by performing X-ray diffraction analysis on a:

- Clay sample after percolation.
- Batch test by mixing the clay with the leachate.

In the latter case it must be guaranteed however that the interlayer is accessible for the leachates during permeation under oedometer conditions. If the interlayer is not accessible for substances during percolation at an external stress, the initial BS is identical to the one after permeation: $BS_{AS} = BS_{BSBH}$.

BS_{AH} = Basal spacing after heating.
The basal spacing after heating can be determined by performing:

- X-ray diffraction analysis of a clay sample after heating.
- Calculating the EBS (chapter **C 5**) using values from literature.

h_{TOT} = thickness of a TOT/TO-layer
The thickness of TOT-layers is approximately 10 Å. The thickness of TO-layers is approximately 7 Å. The average thickness of a layer can be calculated as: $TCF^{TRP} \cdot h_{TOT}$.

Δh = settlement due to the interaction clay - leachate
If a clay is permeated with a leachate that decreases the double layer thickness, this will be noticeable macroscopically as a settlement.

V = breadth clay particle (y direction **Figure: C6-3**) and **Q** = width clay particle (x direction **Figure: C6-3**).
This value is not measured but will be varied to test which particle form fits the best to the results *e.g.* an elongated block or a cube *etc.* In an initial approach V and Q are assumed to be equal to W.

With the variables mentioned above, the following clay particle dimensions can be deduced:

N$_{int}$ = number of clay - clay interfaces.
The number of clay-clay interfaces can be determined after a percolation test with *e.g.* a salt solution. The salt will cause a collapse of the clay-clay interfaces resulting in a macroscopically observable settlement of the sample (Δh). As long as the salt does not enter the interlayer space (see paragraph **C 6.4**) the settlement is the result of a particle move-together, thus a decrease of the $2D_{meca}$ from $2D_{BSBH}$ to $2D_{AS}$:

$$N_{\text{int}} = \frac{\Delta h}{2D_{BSBH} - 2D_{AS}} \qquad \textbf{(C6 - 1)}$$

W = height of clay particle.
The height of a clay particle can be calculated once the number of clay - clay interfaces N_{int} has been determined. The total height of the sample is composed of N_{int} + 1 particles with height W and N_{int} clay-clay interfaces with height $2D_{BSBH}$:

$$W = \frac{h - \left(N_{\text{int}} \cdot 2D_{BSBH}\right)}{N_{\text{int}} + 1} \qquad \textbf{(C6 -2)}$$

N$_{layers}$ = the number of TOT-layers per clay particle.
If it is assumed that the TOT-layers are oriented parallel to each other and perpendicular to the principle stress (thus perpendicular to the z axis like the arrangement of clay particles themselves see F**igure: C6-2**) the number of TOT-layers per particle can be determined if the particle height W and the basal spacing BS_{BSBH} are known.

$$N_{layers} = \frac{W}{BS_{BSBH}} = \frac{W}{BS_{AS}} \qquad \textbf{(C6 - 3)}$$

Now all relevant clay block model dimensions can be determined.

e = the void ratio.
This value has been measured and can be calculated to test which particle form (ratio of width: V, to height: W and breadth: Q) should be selected.

The volume of voids is composed of the part inside the particles (the interlayer space) and the part outside the particles (the voids between different clay particles or interparticle voids). The void volume in a particle depends on the ratio between the decrease of the BS upon heating. The void volume between the particles depends on the change in distance between the particles upon heating.

An expression on the basis of the void volume of one clay particle is given below:

$$e = \frac{V_{voids}}{V_{solids}} = \frac{V_{in\ clay\ particle} + V_{between\ clay\ particles} + V_{other\ voids}}{V_{solids}} \qquad \textbf{(C6 - 4)}$$

$$e = \frac{\left\{\left(2 \cdot \frac{2D_{BSBH}}{2} + V\right) \cdot \left(2 \cdot \frac{2D_{BSBH}}{2} + Q\right) \cdot \left(2 \cdot \frac{2D_{BSBH}}{2} + W\right) - V \cdot Q \cdot W\right\} + N_{layers} \cdot V \cdot Q \cdot (BS_{BSBH} - BS_{AH}) + V_{other\ voids}}{N_{layers} \cdot V \cdot Q \cdot h_{TOT}}$$

(C6 - 5)

C 6.3.3 Example: Tournai clay

During oedometer tests with homogenised Tournai clay (h = the initial height is 20 mm), the clay sample was first loaded to 100kPa. At 100kPa the void ratio was 2. As can be seen in **Figure: B3-12**, a void ratio of 2 is within the range of other Tournai clay samples tested at 100 kPa. After the settlement came to a halt, the sample was percolated by 1.7 Mol/l KCl. This caused an additional settlement (Δh) of average[42] 0.07 mm.

$2D_{BSBH}$ = distance between clay particles before heating or percolation with salt.
To calculate $2D_{BSBH}$ one needs to know the concentration of ions in the space between the clay particles. In paragraph **B 3.4.3** (Geochemistry part II) it was shown that the composition of this fluid can be determined by a chemical analysis of the fluid called contact fluid. The composition of this fluid is given in **Table: B3-19**. Depending if a correction for dilution is made or not, the CEMC varies between 10 mol/m³ and 41 mol/m³.
Using this value, following the theory presented in chapter **C 7**, the distance between the clay particles can be calculated and equals 62.4 Å.

$2D_{AS}$ = distance between clay particles after percolation with salt solution.
This value is determined in the same way as $2D_{BSBH}$ except that the concentration of salts *etc.* corresponds to the concentration of the percolating fluid. In this way the calculated distance between the particles is 18.4 Å. (Note that in **Figure: C7-2**, it is shown that double layers cease to exist at these concentrations, an interlayer is formed; this was not confirmed under oedometer test conditions, therefore the value 18.4 Å is retained.)

$2D_{AH}$ = distance between clay particles after heating to 500°C.
Note that this value does not express a distance between particles *s.s.* but represents the volume of evaporated fluid. $2D_{AH}$ = 0 Å.

BS_{BSBH} = basal spacing before heating.
The basal spacing before heating at atmospheric pressure can be calculated using the data in **Table: C5-1,** and the consideration in paragraph **C 5.4**. The BS_{BSBH} amounts to 10.7 Å in the air-dried state. In the moist state the BS_{BSBH} = EBS = 14 Å, calculated in **Table: C6-1**.

Note that this value represents the equivalent basal spacing at atmospheric pressure. When a larger mechanical stress is applied, the actual EBS is equal or smaller than the calculated in **Table: C6-1**.

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[42] *Homogenised Tournai clay powder was cured with demineralised water during at least 1 month at a fluid content equal to the liquid limit. Then the slurry was consolidated in an oedometer (area 40 cm², 20 mm high) at 100 kPa. Next the sample was percolated by demineralised water and salt solutions. At 100 kPa and a 1.7M KCl solution two Tournai clay samples were percolated. This resulted in a "chemical" settlement of (average) 0.07 mm.*

Table: C6-1

The BS_{BSBH} of Tournai clay in the moist state.

	CF_i^{FOA} (-)	$BS_i^{(001)FOA}$ (Å)
Illite	0.16	10
(10-14c)	0.07	12
(10-14m) (not air-dried)	0.68	20
Sm_{Al}	0.09	14

$\Sigma CF_i^{FOA} \cdot BS_i^{(001)FOA} = 17.3$
TCF^{TRP} (-) = 0.81
EBS (Å) = 14

BS_{AS} = basal spacing after percolation of permeate.
There are several indications that at an external stress of several 100kPa the interlayer is not easily accessible. This accessibility is discussed in paragraph **C 6.4**. If the interlayer is not accessible for substances during percolation at an external stress, the initial BS is identical to the one after permeation: $BS_{AS} = BS_{BSBH}$.

BS_{AH} = basal spacing after heating.
The BS_{AH} = EBS = 8.5 Å is calculated with the information given in **Table: C6-2**.

Table: C6-2

The BS_{AH} of Tournai clay.

	CF_i^{FOA} (-)	$BS_i^{(001)FOA}$ (Å)
Illite	0.16	10
(10-14c)	0.07	12
(10-14m)	0.68	10
Sm_{Al}	0.09	14

$\Sigma CF_i^{FOA} \cdot BS_i^{(001)FOA} = 10.5$
TCF^{TRP} (-) = 0.81
EBS (Å) = 8.5

h_{TOT} = thickness of a TOT-layers.
In the absence of Kaolinite or other TO-layer clay minerals, the average thickness of a TOT-layers is = $TCF^{TRP} \cdot 10$ Å. In this case it is 8.1 Å.

Δh = settlement due to the interaction clay-leachate.
If a clay is permeated with a leachate that decreases the double layer thickness, this will be noticeable macroscopically as a settlement. This settlement is called Δh and is in this case 0.07mm for an initial height of 20mm.

V = breadth clay particle (y direction **Figure: C6-3**) and **Q** = width clay particle (x direction **Figure: C6-3**).

In an initial approach V and Q are assumed to be equal to W, the height of the clay particle.

With the variables mentioned above, the following clay particle dimensions can be deduced:
N_{int} = number of clay - clay interfaces.
As long as the salt does not enter the interlayer space (see paragraph **C 6.4**) the settlement can be calculated according to (**C6 - 1**). For a sample with an initial height of 20 mm this gives:

$$N_{\text{int}} = \frac{\Delta h}{2D_{BSBH} - 2D_{AS}} = \frac{0.07 \cdot 10^{-3}}{(62.4 - 18.4) \cdot 10^{-10}} = 1.6 \cdot 10^{4}$$

W = height clay particle.
The height of a clay particle can be calculated with expression (**C6 - 2**):

$$W = \frac{h - (N_{\text{int}} \cdot 2D_{BSBH})}{N_{\text{int}} + 1} = \frac{20 \cdot 10^{-3} - (1.6 \cdot 10^{-4} \cdot 62.4 \cdot 10^{-10})}{1.6 \cdot 10^{4}} = 1.3 \cdot 10^{-6} m$$

N_{layers} = the number of TOT-layers per clay particle.
The number of TOT-layers per particle can be determined according to expression (**C6 - 3**) once the particle height W and the basal spacing BS_{BSBH} are known.

$$N_{layers} = \frac{W}{BS_{BSBH}} = \frac{W}{BS_{AS}} = \frac{1.3 \cdot 10^{-6}}{14 \cdot 10^{-10}} = 8.9 \cdot 10^{2}$$

Now all relevant clay block model dimensions have been determined for Tournai clay.

e = the void ratio
The void ratio can be determined according to expression (**C6 - 4**):

$$e = \frac{\left\{(62.4 \cdot 10^{-10} + 1.3 \cdot 10^{-6})^{3} - (1.3 \cdot 10^{-6})^{3}\right\} + 8.9 \cdot 10^{2} \cdot (1.3 \cdot 10^{-6})^{2} \cdot (14 \cdot 10^{-10} - 8.5 \cdot 10^{-10}) + 0}{8.9 \cdot 10^{2} \cdot (1.3 \cdot 10^{-6})^{2} \cdot 8.1 \cdot 10^{-10}} = 0.71$$

Without considering additional voids the calculated e = 0.71.

In the remainder of the chapter the particle form of a block will be retained because, as it will be shown, the results are close to reality and very illustrative.

Remark that the dimension of the clay particle inferred from theoretical considerations and laboratory tests corresponds well to the results summarised from literature and presented in **Table: A4-1**.

C 6.3.4 Comparison of void ratio determination

The void ratio can be determined according to expression (**C6 - 5**) as discussed above or according to the expression (**A4 - 8**), as shown below:

$e_d = S_a \cdot \rho_s \cdot D_{meca}$ **(A4 - 8)**

$2 \cdot D_{BSBH} = 62.4$ *Å*

$S_a = 6.60 \cdot 10^{+4}$ *m²/kg (**Table: C3-2,** in the S_a the EBS is hidden.)*

$\rho_s = 2700\ kg/m^3$ ([43])
$e_d = 0.56$

Both void ratios, determined either according to ((**C6 - 5)**; e = 0.71) or to ((**A4 - 8**); e_d = 0.56) give similar results but are too low with respect to the measured void ratio (e = 2). In this paragraph it will be explained why the void ratio determined according to (**A4 - 8**) gives too low values for clays other than Smectites. In the next paragraph the consequences of the low void ratio determined according to expression (**C6 - 5**) will be explained.

The e_d, as calculated with the formula above which was derived in paragraph **A 4.2.4.2**, is too low (and practically independent of V and Q) and changes too much as a function of the change in particle to particle distance (Δe_d is directly related to ΔD_{meca}). This is due to the fact that the e_d was derived with the hypothesis that all specific surface (S_a) is exposed to the permeate. This is only true in the case that clay particles consist of one to a few TOT-layers[44]. This is the case for Smectites in which W approaches the BS ($N_{layers} \rightarrow 1$). This is the reason why Bolt (1956) found the best fit for the expression based on e_d for Na-Montmorillonite in low electrolyte solutions. Why at low electrolyte concentration? Because at high concentrations some double layers become interlayers and the particle size increases (see discussion paragraph **C 5.3.4**).

C 6.3.5 The volume of voids between the clay particles.

The void volume (calculated with expression (**C6 - 5**)) between the Tournai clay particles (*i.e.* the volume of the flow paths affected by changes in interparticle fluid

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[43] *Tournai: $\rho_s = 2700\ kg/m^3$; Soignies: $\rho_s = 2703\ kg/m^3$; Kruibeke: $\rho_s = 2725\ kg/m^3$*

[44] *Back calculation of the number of TOT-layers in Ponza Bentonite exposed to a saturated NaCl solution with the method presented in this chapter (raw data by di Maio and Fenelli 1994) shows that for the clay samples in which alignment perpendicular to the principle stress direction can be assumed (σ>100 kPa) only 16 (at σ=125 kPa) to 19 (at σ=330 kPa) TOT layers constitute a Bentonite particle (i.e. N_{layers} = 16 - 19). Assumptions were:*

*$2D_{BSBH}$ = Calculated according to relationship (**A4 - 15**) and (**A4 - 16**), assuming that the initial CEMC is very low (somewhere between $1 \cdot 10^{-4}$ and 1 mol/m³). Why such a low CEMC? Because it was shown that Ponza Bentonite is in geomechanical sense comparable to the reference Bentonite (see Schmitz and van Paassen 2003) and the latter is treated industrially.*

$2D_{AS}$ = Like $2D_{BSBH}$ but at CEMC = $6.15 \cdot 10^3$ mol/m³ corresponding to a saturated NaCl solution (Binas 1986).

BS_{BSBH} = at maximum 20Å. At higher values interlayers are transformed into double layers (Lagally 1993).

BS_{AH} = 10 Å because the Smectite contained in Ponza Bentonite is a TOT layer mineral.

Δh = determined from figure 8 in di Maio and Fenelli (1994).

h = 20mm.

h_{tot} = 10 Å.

*With a V and Q to W ratio of 2.5 the void ratio according to expression (**C6 - 5**) corresponds closely to the reported one.*

composition) amounts to only 3% of the volume inside the clay particles. The consequence is that:

- The form of the clay particle within reasonable variations (**Table: A4-1**) *e.g.* height to width ratios up to a factor 100 does not change the void ratio value.
- Changes in interparticle fluid composition do not influence the void ratio and all related geomechanical parameters as long as the chemicals do not enter the interlayer space except for those geomechanical properties that are influenced by local modifications like the hydraulic conductivity as for instance due to choking of the flow paths. Such effects that do not change other macroscopic parameters are therefore not easily detectible (see Schmitz *et al* 2002a).

C 6.3.6 Other voids

The measured void ratio (e = 2) is much higher than the void ratio calculated with the two methods shown above (e = 0.56 to 0.71). These two methods were based on the assumption of a regular arrangement of clay blocks without additional voids. Where are these other voids?

- Other clay particle arrangements, spheres, cones *etc.* can be considered and will increase the calculated void ratio. There are several disadvantages of using these forms:
  i) The double layer theory in the form presented in this thesis and the repulsion law derived from it are only valid for plate-to-plate contacts.
  ii) The maximum void ratio will be obtained if spheres are considered but the increase in void ratio is still relative small and the influence of particle-to-particle contact is negligible with this arrangement.
  iii) Cone shapes in general and solemnly spherical particles in a clay matrix do not correspond to the form of clay particles in nature (see *e.g.* O'Brien and Slatt 1990).

- Other voids are formed by the irregular arrangement of clay particles with respect to each other. An increase of the vertical stress leads to an increase in the regularity of the particle arrangement. This leads to a decrease of these voids.

- Other voids can incorporate conduits that are not influenced by clay-leachate interactions on double layer basis, like isolated pockets of fluid or pores filled with stagnant fluid. The worst-case scenario for a barrier is the interconnection of all these additional voids to form separate flow conduits. If these conduits are wide enough (larger than several hundred Å) they will not be influenced by changes in pore fluid composition on double layer basis. The more "inert" large conduits are present the more flow will pass through them. This will decrease the amount of flow through the smaller interparticle spaces. As a result the overall hydraulic conductivity will be less influenced by changes in double layer thickness.

  This can be quantified: If the flow conduits influenced by clay-permeate interaction constitute a combined flow (Q_I) and the "inert" large pores not influenced by clay-permeate interaction constitute a combined flow (Q_{II}) the influence of the clay-permeate interaction on the total flow Q_{tot} in a sample or barrier will be (see **Figure: C6 - 4**):

$$\frac{Q_{tot\ ini}}{Q_{tot\ fin}} = \frac{Q_{I\ ini} + Q_{II\ ini}}{Q_{I\ fin} + Q_{II\ fin}} = \frac{Q_{I\ ini} + Q_{II}}{Q_{I\ fin} + Q_{II}} \tag{C6 - 6}$$

Note that laws describing the influence of physico-chemical reactions on the geomechanical properties of clays (*e.g.* hydraulic conductivity) in chapter **C 7** are valid only for the flow marked Q_I. If Q_{II} is much larger than Q_I (because a construction worker pierced through the entire liner with a shovel) the influence of physico-chemical reactions will be nil. If however Q_{II} is small with respect to Q_I *i.e.* there are no "inert" flow paths unhindered by changes in pore fluid composition the effect of clay - permeate interaction will be large (see **Figure: C6-4** and expression (**C6 - 7**)):

$$\frac{Q_{tot\ ini}}{Q_{tot\ fin}} \approx \frac{Q_{I\ ini}}{Q_{I\ fin}} \tag{C6 - 7}$$

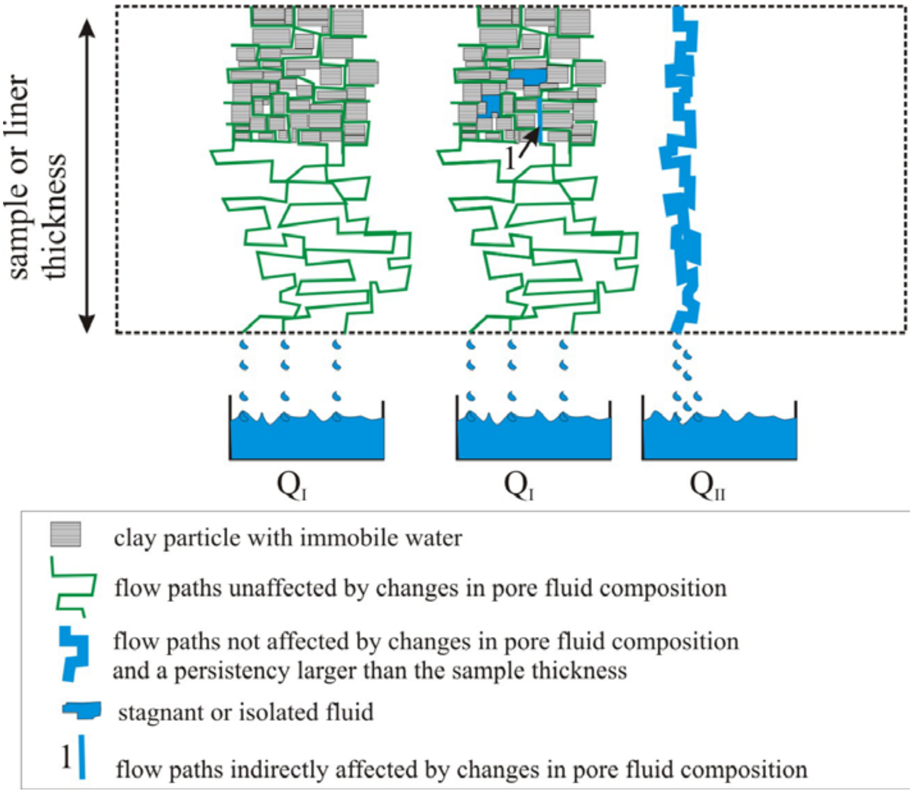

Figure: C6-4

The total amount of voids in a sample consist of voids between the TOT- or TO-layers, voids between the particles in flow paths (either inert or affected by clay-permeate interaction), voids between the particles in stagnant fluid pockets etc.

C 6.4 Interlayer accessibility part II

Several considerations shown in this paragraph can be used to interpret the accessibility of the interlayer space towards permeates during leaching. This matter was discussed previously in paragraph **A 3.2.2**.

A) The measured settlement (Δh) of Tournai clay upon percolation with salt solutions was explained by the decrease of the spacing between particles: 2D. If *e.g.* salts enter the interlayer space of clays like Smectite this will cause a decrease of the TOT to TOT distance, *i.e.* an increase of ΔBS. The BS_{BSBH} of the Tournai clay before leaching amounts to 14 Å (see **Table: C6-1**). If a saturated KCl solution enters the interlayer space of a Smectite it was shown that after one cycle of exposure to KCl solution and subsequent drying (see paragraph **C 5.3.4**) this caused a collapse to 12 Å. The equivalent basal spacing of Tournai clay after KCl entered the interlayer space has been calculated in **Table: C6-3**.

Table: C6-3

The equivalent basal spacing of Tournai clay after KCl entered the interlayer space (BS_{AS}).

Clay species	CF_i^{FOA} (-)	$BS_i^{(001)FOA}$ (Å)
Illite	0.16	10
(10-14c)	0.07	12
(10-14m)	0.68	12
Sm_{Al}	0.09	14

$\Sigma CF_i^{FOA} \cdot BS_i^{(001)FOA}$	11.9
TCF^{TRP} (-)	0.81
EBS (Å)	9.6

The combined collapse caused by the addition of the ΔBS is given by:

$$\Delta h = (BS_{BSBH} - BS_{AS}) \cdot N_{layers} \cdot (N_{int} + 1) \qquad \textbf{(C6 - 8)}$$

$$\Delta h = (14-9.6) \cdot 10 \cdot 10^{-10} \cdot 8.9 \cdot 10^{2} \cdot 1.6 \cdot 10^{4} = 6.3 \cdot 10^{-3} \mathrm{m}$$

This shows that if the observed collapse was produced only by a collapse of the basal spacing (thus not by a decrease of the interparticle distance) on the interlayer level from 14 Å to 9.6 Å this would have caused in the case tested here (*e.g.* initial height sample 20 mm) a collapse on the clay sample level 100 times higher than the measured collapse. Such a large settlement was not measured. Could it be that only some interlayers collapsed? Sure, in this case only 1.1% of the available interlayers needed to collapse to produce the observed settlement. Now one has two choices to interpret the observed settlement:

i) All interparticle spaces easily accessible for flow collapsed nearly instantaneous upon percolation.

ii) 1.1% of the more difficult to access interlayers collapsed instantaneously; even with time the other interlayers remain closed. Interparticle distances were not affected.

As will be shown in argument C and D, option ii will have to be discarded.

B) The expressions for the void ratio used above show that for realistic values of particle-particle distance, the space in-between the TOT-layers dominates the value of the void ratio rather than the void between the particles.
If it is assumed that the space between the TOT-layers is not accessible and thus only the space between the particles changes during permeation, the void ratio will remain constant. This is exactly what was measured by performing tests on Tournai clay *e.g.* Delvaux (2003): During permeation with *e.g.* brines the void ratio did not change in contrast to the situation in which the clay was remoulded with brines before the oedometer test. In the latter case the void ratio of samples at the same pressure but mixed with different brines varied a lot. These examples show that it is important to know the order in which brines are added to the clay, before or after consolidation (= *BOAC*, introduced by Schmitz et al. 2004b). Thus: clay remoulded with brines and subsequently consolidated, has a much lower liquid limit (factor 10-100 %fluid content) and much higher hydraulic conductivity (factor 10-100) *etc.* than the same clay tested with demineralised water. The same clay remoulded with demineralised water subsequently consolidated has a lower hydraulic conductivity (~factor 10) with brines as leachate than with demineralised water.

C) In this third example discussing the interlayer accessibility of clays the interaction of salt solutions with Tournai clay is compared to that of ethylene glycol and Tournai clay on the interlayer level and the particle level.

Interlayer level:
Reactions between fluids and clays and substances contained in fluids and clays on the interlayer level can be analysed referring to the equivalent basal spacing.
Ethylene glycol affects clays on the interlayer level differently than salt solutions. The latter cause a decrease of the EBS (see paragraph **C 5.3.4**). Ethylene glycol causes an increase (see paragraph **A 3.2.2**).

Particle level:
Reactions between fluids and clays and substances contained in fluids and clays on the particle level can be analysed referring to the diffuse double layer theory. In chapter **C 7** it will be shown that changes in hydraulic conductivity due to permeation with a leachate can be related to changes of the location of the centre of mass of the diffuse double layer.
The location of the centre of mass of the diffuse double layer is given for monovalent cations by expression (**A3 - 1**):

$$\theta_{ddl} = \sqrt{\frac{R \cdot T \cdot \varepsilon_0 \cdot \varepsilon'}{2 \cdot F^2 \cdot CEMC}} \qquad \textbf{(A3 - 1)}$$

The difference in double layer thickness before (θ_{ini}) and after (θ_{fin}) permeation with a leachate is given by expression (**C6 - 9**):

$$\frac{\theta_{ddl\ ini}}{\theta_{ddl\ fin}} = \frac{\sqrt{\dfrac{R\cdot T\cdot \varepsilon_0 \cdot \varepsilon'_{ini}}{2\cdot F^2 \cdot CEMC_{ini}}}}{\sqrt{\dfrac{R\cdot T\cdot \varepsilon_0 \cdot \varepsilon'_{fin}}{2\cdot F^2 \cdot CEMC_{fin}}}} = \sqrt{\frac{\varepsilon'_{ini}\cdot CEMC_{fin}}{\varepsilon'_{fin}\cdot CEMC_{ini}}} \qquad \textbf{(C6 - 9)}$$

According to this expression the permeation of Tournai clay with both:
- Ethylene glycol: $\varepsilon'_{ini} = 80$, $\varepsilon'_{fin} = 30$
- Salt solution *e.g.* 1.7M KCl: $CEMC_{fin} = 1700$ mol/m^3, $CEMC_{ini} = 10 - 41$ mol/m^3

causes a decrease of the double layer thickness. Therefore the influence of ethylene glycol and salt solutions is comparable (less remarked for ethylene glycol than for salt solutions of 1.7 M) on the particle level.

Permeation tests of Tournai clay at 30 kPa and 100 kPa vertical stress under oedometer conditions showed that permeation of the same type of clay with ethylene glycol and with salt solutions decreases the hydraulic conductivity and causes a minute settlement of the clay sample, in the two cases.
If reactions on the interlayer level would have occurred the permeation of the Tournai clay with ethylene glycol and salt solutions would have provided opposite results: Swelling and settlement, respectively. Because reactions on the interlayer level take place at a smaller level than reactions on the larger particle level these expected opposite reactions on the interlayer level would even have masked expected similar behaviour on the particle level. Contrary, both tests gave approximately the same results: Both minute settlement. Only reactions on the particle level were measurable. The interlayer did not react in Tournai clay samples under oedometer conditions at 30-100 kPa vertical stress and a hydraulic gradient of maximal 50.

D) The fact that ions contained in a leachate percolating a clay sample under oedometer conditions enter the interparticle space and not the interlayer space is shown by the following example:
- Sample material: Homogenised Tournai clay cured with demineralised water. Inserted into the oedometer. Applied a vertical stress of 30 kPa.
- Leaching test with: 0.67 M KCl (1.1 times pore volume) and 1.7 M KCl (0.2 times pore volume)
- Chemical analyses (based on method ii, paragraph **B 3.4.3.1**): Clay material was carefully scratched from the centre of the Tournai clay sample, air-dried, mixed with a large amount of demineralised water and handed to the chemistry department for chemical analyses.
- Expected results: If it is assumed that the KCl leached through the sample is retained in the interparticle space, then the leaching with 0.67 M KCl could have increased the KCl concentration to 0.67 M at maximum (assuming that all former interparticle fluids would have been chased away). The second percolation step with 1.7 M could have increased this concentration at maximum to: $(0.2 \cdot x\ l \cdot 1.7\ mol/l + 0.67\cdot x\ mol)/\ x\ l = 1.0$ M.
- Results of the chemical analyses: The measured KCl concentration was 0.9 M. The reason that the measured concentration is lower than the expected one is related to the assumption that the 1.7 M front was distributed uniformly over the sample. Logically

the front will be located nearer to the place where leachates enter the clay sample (top or bottom but not the middle of the sample). The measured concentration of K^+ cations is larger than the concentration of Cl^- anions (0.8 M).

Observations that can be made on the basis of these measurements are:

- Cations and anions enter the interparticle space, *i.e.* the zone controlled by the double layer forces, together with the percolating fluid.
- K^+ cations are held back by electrostatic forces; the Cl^- anions less.
- K^+ cations leached into the sample under oedometer conditions, are not captured by the interlayers: one was able to remove all inserted KCl from the samples during the chemical analyses based on method ii (paragraph **B 3.4.3.1**).

C 6.5 Summary

Using information from oedometer tests and theoretical considerations on the basis of clay mineralogy and double layer theory the particle size and particle form can be deduced. This information can be used to construct a suitable clay particle mesh. This can be implemented into a numerical simulation as will be shown in the next paragraph.

It can be concluded that during this type of permeation (oedometer conditions; 100 kPa vertical stress; homogenised Tournai clay; hydraulic gradient of max. 50; 1.7 M KCl or ethylene glycol as permeate) the permeate does not enter the interlayer space: The $BS_{AS} = BS_{BSBH}$.

In this paragraph it has been shown, for several clays and several fluids - that pollutants do not necessarily enter the interlayer space during permeation under barrier conditions. In *e.g.* chapter **C 3** it has been shown that the liquid limit depends on changes in double layer thickness and more on changes on the interlayer level. With this knowledge the following observation by Oweis and Khera (1998) can be refined: "The effect of pollutants on Atterberg limits has not yielded any reliable results for predicting their effect on hydraulic conductivity of soils used in liners and containment structures". The - not yielded - has to be replaced by cannot, not because insufficient tests results are available but because such a relationship is physically not possible as long as the interlayers of clays are not accessed during permeation under the prevailing boundary conditions. These statements are valid as long as the "pollutant" is not mixed with the clay before consolidation (see BOAC introduced above or Schmitz *et al* 2004b).

C 7 The clay particle model

C 7.1 Introduction

The aim of this chapter is to study changes in clay particle geometry on the particle level during permeation with chemical active landfill leachates using the numerical finite element method and the *LAGAMINE* code developed at the University of Liège.

First theoretical considerations on the interparticle distance will be given: A constitutive model for interfaces will be proposed, displaying its mechanical and chemical aspects.

Next the development of an interface element will be shown, with a recall of the general concept of a contact or interface problem, and the description of the interface finite element itself, as it has been introduced in the *LAGAMINE* finite element code.

After that the simulation of a 2d cross section of two different assemblies of clay particles under oedometer conditions will be presented in detail: All the initial data used will be provided and a synthesis of the results of several simulations will be given and discussed.

It has to be noted that the model does not aim to reproduce a complete (oedometer cell with a clay) sample subjected to leaching. The model serves only to understand:
- What happens during the percolation of leachates.
- How geomechanical parameters, especially the hydraulic conductivity, change and in which "direction" the changes will occur during percolation of leachates.
- How much geomechanical parameters change, *i.e.* if the order of change is negligible or not.

In this chapter, the parameters given in **Table: C3-1** and **Table: C7-1** were used if locally not specified differently.

Table: C7-1

Parameters used if not stated differently.

Parameter	Symbol	Value	Unit
Specific surface clay	S_a	$5.00\cdot10^{+4}$	m²/kg
Density solid	ρ_s	$2.70\cdot10^{+3}$	kg/m³

The fluid between the clay particles can be the original fluid found in the clay at the time of excavation or it can be the leachate permeating through the clay. This fluid is called interparticle fluid throughout this chapter.

C 7.2 Theoretical considerations on interparticle aspects

C 7.2.1 Interface constitutive model

C 7.2.1.1 Chemo-mechanical law

In chapter **A** it was explained why clays are negatively charged, that this charge deficiency is neutralised by attracting cations in suspension and that thereby a diffuse double layer is formed. Double layers of opposing clay particles repel each other. In diluted suspensions the distance between clay particles is such that the repulsion force is near zero. In soils however the clay particle spacing is not only governed by the repulsion of double layers but additionally by external stresses. The relationship between repulsion *i.e.* swelling pressure and external stress has been described by Bolt (1956) and more recently by Mitchell (1993) and mentioned by Fam and Dusseault (1999). The latter description in contemporary (SI) units is followed here.

The relation, given by the authors mentioned above, showed that with pure mechanical loading the distance between clay particles (2D) changes under increasing normal stress

(σ_l or σ_s), in a non-linear way resembling a hyperbola. A characteristic example is illustrated in **Figure: C7-1** (path A). The non-linearity in the σ-2D_{meca} relation was also recognised by other authors. When the chemistry changes (*e.g.* change in concentration of cations) or the relative dielectric constant of the interparticle fluid changes the distance between the clay particles decreases at constant vertical stress (see **Figure: C7-1**, path B). When in reaction to chemical loading equilibrium is reached and renewed pure mechanical loading takes place, another stress-displacement curve is followed (see **Figure: C7-1**, path C).

The curve describing the mechanical behaviour of a fracture under normal stress is obtained from different observations:

- In the beginning large displacements occur for a small level of applied stress.
- Changes in concentration cause the shift from one to another normal stress - deformation line.
- Progressively applied stresses induce a small amount of deformation.

From a physical point of view this non-linear behaviour can be explained by the progressive mobilisation of the electrostatic repulsion forces at short distances. Changes in concentration of cations or the relative dielectric constant of the interparticle fluid change the electrostatic repulsion.

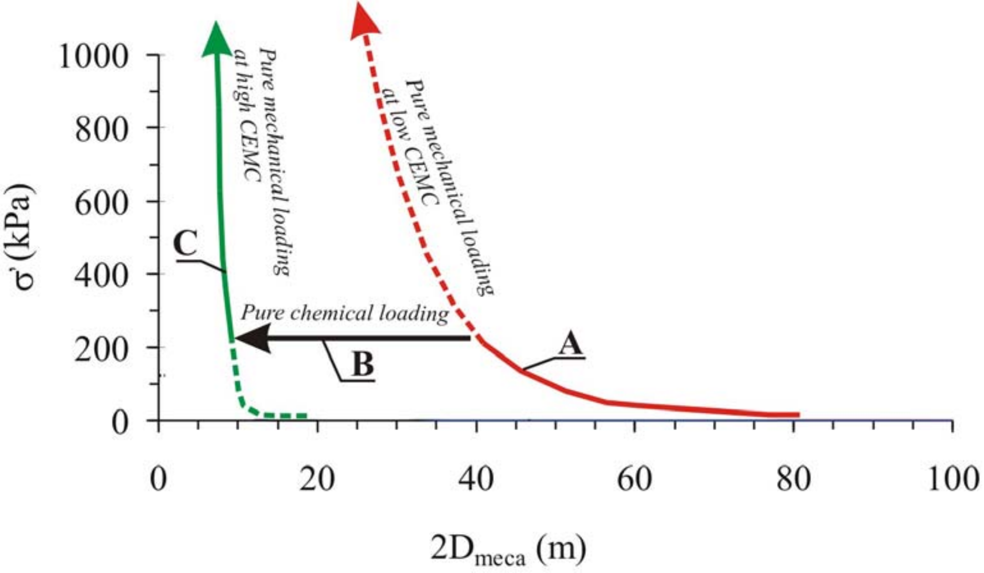

Figure: C7-1

Normal stress (σ) versus distance (2D_{meca}) between two clay particles as a function of the concentration of cations in the interparticle fluid (CEMC). As long as the CEMC remains constant the vertical stress causes purely mechanical loading following the stress-deformation curve belonging to the initial CEMC (A). If the CEMC is increased e.g. by the permeation of leachates, the distance (2D_{meca}) decreases at the same normal stress (B). If after permeation the normal stress is increased the stress-displacement curve belonging to the new CEMC values is followed (C).

At the considered stress levels it is assumed that the clay particles themselves are incompressible.

Formulations have been proposed in different literature sources. Most of these sources make a distinction between the normal stress (in equilibrium with the repulsive stress between the clay particles) - deformation characteristic at large (σ_l - 2D_{meca}) and small (σ_s - 2D_{meca}) interparticle distances. Large and small are defined differently in literature. In the simulations presented here, the largest values, either from the formulas for small or large interparticle distances are considered to be the appropriate ones. According to Fam and Dusseault (1999) the following normal stress or repulsive stress - deformation relationships are obtained (first mentioned in **Part: A** of this thesis and **Figure: C7-3**):

$$\sigma_s' = \frac{\pi^2 \cdot \lambda_{ddl}^{\ 2} \cdot R \cdot T \cdot CEMC}{e_d^{\ 2}} - 2 \cdot R \cdot T \cdot CEMC \quad \textbf{(A4 - 15)}$$

$$\sigma_l' = 64 \cdot R \cdot T \cdot CEMC \cdot e^{-\frac{2 \cdot e_d}{\lambda_{ddl}}} \quad \textbf{(A4 - 16)}$$

In which:

σ_s'	=	*Effective repulsive force at small particle to particle distance*	*(Pa)*
σ_l'	=	*Effective repulsive force at large particle to particle distance*	*(Pa)*
R	=	*Gas constant*	*(J/mol/K)*
T	=	*Temperature*	*(K)*
$CEMC$	=	*Concentration of an equivalent amount of monovalent cations*	*(mol/l)*
λ_{ddl}	=	*Reactivity coefficient*	*(-)*
e_d	=	*Void ratio based on the interparticle voids only*	*(-)*

The origin of these relationships is not discussed in detail in geomechanical literature but several papers (Fam and Dusseault (1999), Fam and Santamarina 1996 and Romero 1999) refer to the same source: Santamarina and Fam (1995). In this source it is stated that the expression for σ_l can be found in Israelachvili (1998) and the expression for σ_s in Yong and Warkentin (1975). Based on the colloidal theory summarised by Israelachvili (1998) and a simplification by Yong and Warkentin (1975) the derivation of (**A4 - 15**) and (**A4 - 16**) can be analysed. These formulas are not complementary to each other but derived on different basis:

The derivation of σ_s is based on the following simplifications:

- Only cations are taken into account (near the clay surface).
- The repulsive stress (σ) is infinitely large at the clay particle surface.

The derivation of σ_l is based mainly on the following simplifications:

- The electrostatic potential in the midplane between two clay particles (Ψ_m) is the sum of potentials from each clay particle surface.
- The electrostatic potential in the midplane between two clay particles (Ψ_m) is low (far from the surface).
- Only monovalent cations are present.

Both laws are based on the thought-model of bringing two plates with the same electric charge from infinity to a distance 2D_{meca}.

A fact that is often overlooked is that the laws based on one or the other way on the double layer are only valid up to the concentration where a double layer ceases to exist (**Figure: C7-2**).

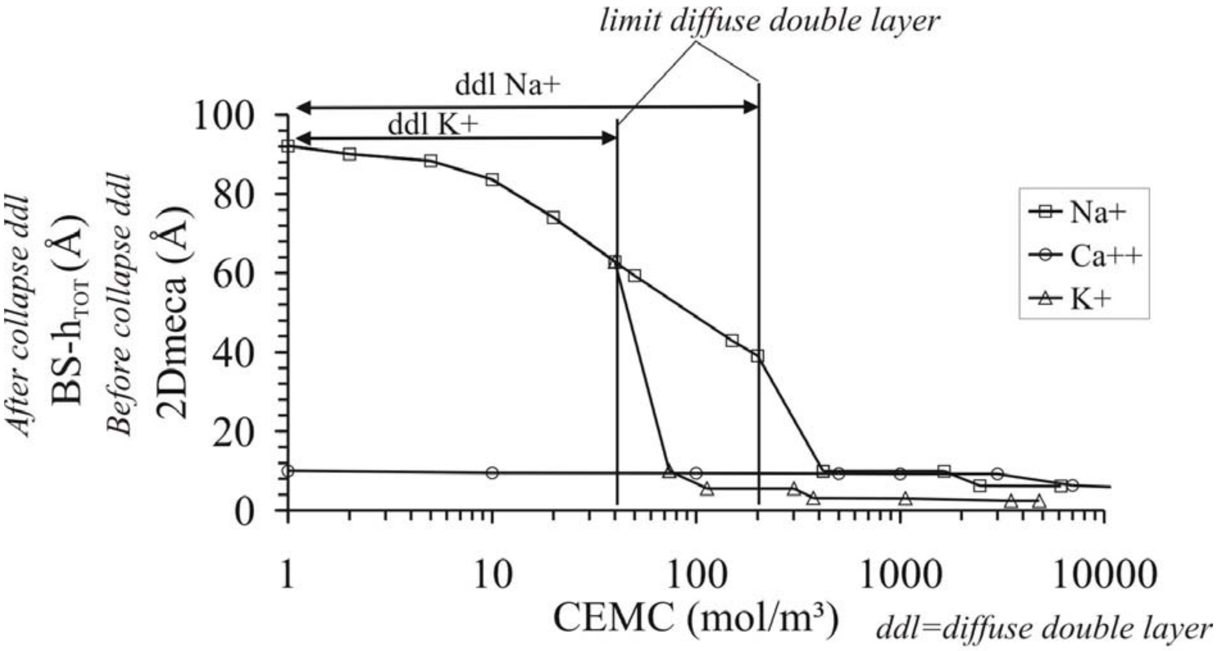

Figure: C7-2

Depending on the concentration and the type of cations the distance between the clay particles will vary as a function of the concentration. From a certain concentration onwards the double layer ceases to exist: The interparticle contact converts into an interlayer (see ***Figure: C7-10****).*

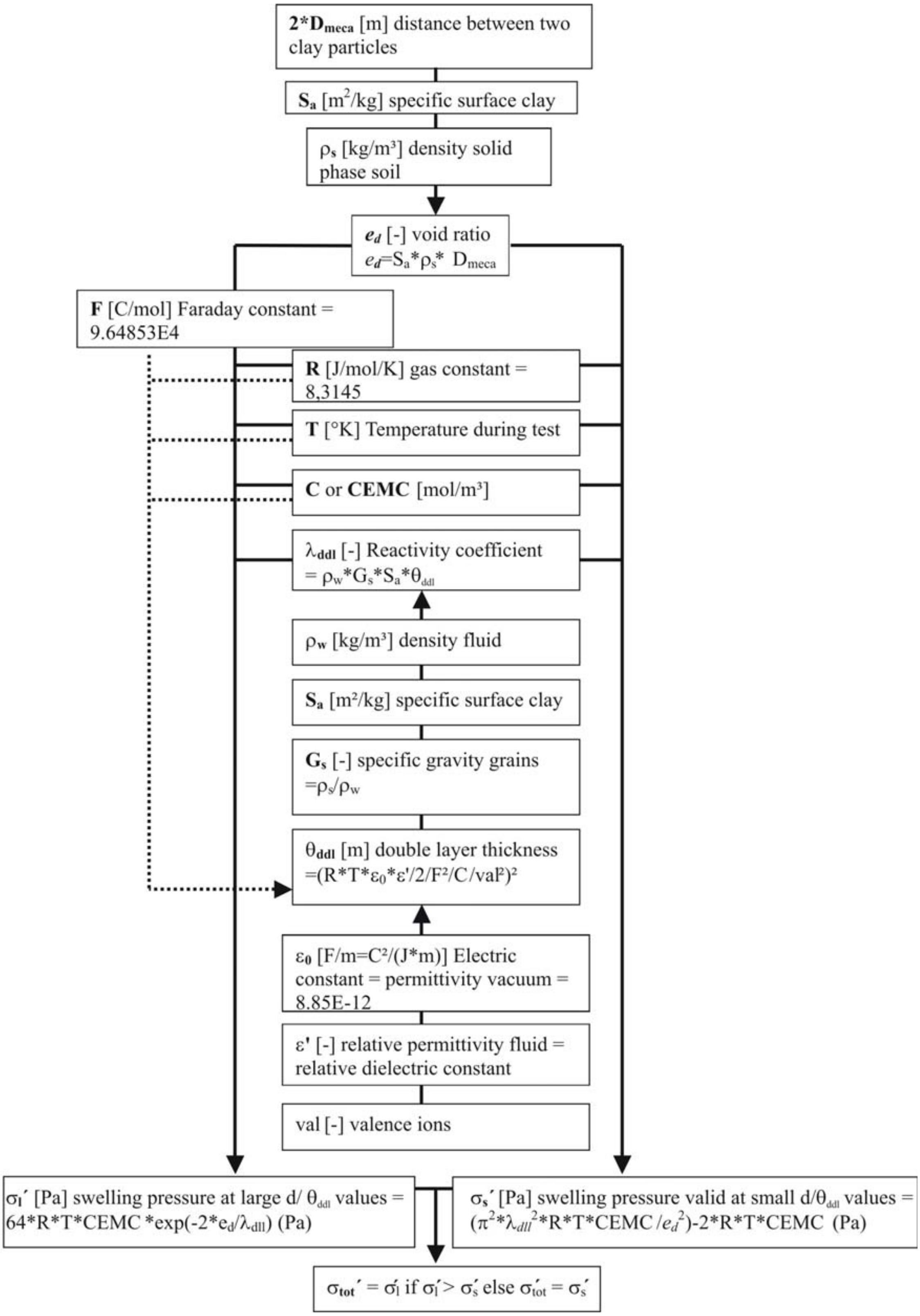

Figure: C7-3

This figure shows that the repulsive stress between two clay particles depends on the diffuse double layer.

Guiducci (*et al.* 2002) described the introduction of a constitutive law relating fracture closure ΔV under increasing normal stress into *LAGAMINE*. The same approach was followed here. Therefore a few parameters are introduced in addition to the ones shown in **Figure: C7-3**.

With the following relationship:

$$e_d = S_a \cdot \rho_s \cdot D_{meca} \tag{A4 - 8}$$

In which:

S_a = Specific surface (m²/kg)
ρ_s = Density of the solid fraction in a soil (kg/m³)
D_{meca} = Half distance between two clay particles (m)

The relationships (**A4 - 15**) and (**A4 - 16**) can be simplified to:

$$\sigma_l' = 64 \cdot R \cdot T \cdot CEMC \cdot e^{\frac{-2 \cdot S_a \cdot \rho_s}{\lambda_{ddl}} \cdot D_{meca\,l}} \tag{C7 - 1}$$

$$\sigma_S' = \left(\frac{\pi^2 \cdot \lambda_{ddl}{}^2 \cdot R \cdot T \cdot CEMC}{(S_a \cdot \rho_s)^2} \right) \cdot \frac{1}{(D_{meca\,s})^2} - 2 \cdot R \cdot T \cdot CEMC \tag{C7 - 2}$$

With the definition of the following variables:

$$A_1 = 64 \cdot R \cdot T \cdot CEMC \tag{C7 - 3}$$

$$B_1 = \frac{-2 \cdot S_a \cdot \rho_S}{\lambda_{ddl}} \tag{C7 - 4}$$

$$A_2 = \left(\frac{\pi^2 \cdot \lambda_{dll}{}^2 \cdot R \cdot T \cdot CEMC}{(S_a \cdot \rho_s)^2} \right) \tag{C7 - 5}$$

$$B_2 = 2 \cdot R \cdot T \cdot CEMC \tag{C7 - 6}$$

The expressions for the repulsive stress can be written as:

$$\sigma_l' = A_1 \cdot e^{B_1 \cdot (D_{meca\,l})} \tag{C7 - 7}$$

$$\sigma_s' = \left(\frac{A_2}{(D_{meca_s})^2} \right) - B_2 \tag{C7 - 8}$$

In terms of D_{meca} this results in:

$$(D_{meca\ l}) = \frac{\ln\left(\frac{\sigma_l'}{A_1} \right)}{B_1} \tag{C7 - 9}$$

$$\left(D_{meca\ s}\right)=\sqrt{\frac{A_2}{\sigma_s{}'+B_2}} \qquad \textbf{(C7 - 10)}$$

The closure of a discontinuity (*e.g.* the interparticle void) (V) is defined as:

$$V=-2\cdot D_{meca\,0}+2\cdot D_{meca} \qquad \textbf{(C7 - 11)}$$

In which:

$2{\bullet}D_{meca\ 0}$ = The distance between two clay particles at the initial concentration and mechanical stress → 0 (m)

$D_{meca\ 0}$ can be expressed using expression (**C7 - 9**) and (**C7 - 10**) as:

$$\left(D_{meca\ s\ 0}\right)=\sqrt{\frac{A_2}{B_2}} \qquad \textbf{(C7 - 12)}$$

$$\left(D_{meca\ l\ 0}\right)=\frac{\ln\left(\dfrac{\sigma'_l\rightarrow 0}{A_1}\right)}{B_1} \qquad \textbf{(C7 - 13)}$$

The problem is that the expression for $D_{meca\ l\ 0}$ does not approach an asymptotic value as $\sigma_l \rightarrow 0$, therefore the value of σ_l was determined $D_{meca\ l\ 0}$ arbitrarily at $\sigma'_l = 0.0001$ Pa.

With the formulations given above the stiffness can be expressed as:

$$\frac{\partial\sigma_l{}'}{\partial V}=\left(A_1\cdot B_1/2\right)\cdot\left(e^{B_1\cdot\left(V/2+D_{meca\,0}\right)}\right) \qquad \textbf{(C7 - 14)}$$

$$\frac{\partial\sigma_s{}'}{\partial V}=\frac{-A_2}{\left(V/2+D_{meca\,0}\right)^3} \qquad \textbf{(C7 - 15)}$$

All results will be given in terms of effective stress.

For interfaces the Coulomb's frictional law can be written as:

$$f=\tau-(c+\mu p) \qquad \textbf{(C7 - 16)}$$

In which:

μ = $\tan\phi$; the friction coefficient (-)
f = A yield surface in the (p, τ) plane which defines three zones:
$f<0$ the domain of sticking contact
$f=0$ the domain of sliding contact
$f>0$ impossible
τ = Stress normal to the interface element (Pa)
p = Stress tangential to the interface element (Pa)
c = Cohesion (Pa)

When no sliding occurs (*$f<0$*), the interface deformation remains elastic. The elastic contact stress rate can be computed from:

C

$$\underline{\dot{\sigma}}_C = \underline{K}_C \underline{\dot{\varepsilon}}_C \quad \text{or} \quad \begin{Bmatrix} \dot{p} \\ \dot{\tau} \end{Bmatrix} = \begin{bmatrix} K_p & 0 \\ 0 & K_\tau \end{bmatrix} \begin{Bmatrix} \dot{\varepsilon}_{C1} \\ \dot{\varepsilon}_{C2} \end{Bmatrix} \qquad \textbf{(C7 - 17)}$$

In which:

$\underline{K}_C$ = *The penalty coefficient matrix* *(-)*

$\underline{\sigma}_C = \begin{pmatrix} \sigma_1 \\ \sigma_2 \end{pmatrix}$ *Contact stress matrix (*$\underline{\dot{\sigma}}_C$ *derived with respect to time)* *(-)*

$\underline{\varepsilon}_C = \begin{pmatrix} \varepsilon_{c1} \\ \varepsilon_{c2} \end{pmatrix}$ *Contact strain matrix.* *(-)*

σ_1 = *p, Stress normal to the interface element* *(Pa)*

σ_2 = *τ, Stress tangential to the interface element* *(Pa)*

ε_{c1} = *Strain normal to the interface element* *(-)*

ε_{c2} = *Strain tangential to the interface element* *(-)*

K_p = *Rigidity normal to the interface element* *(Pa/m)*

K_τ = *Rigidity tangential to the interface element* *(Pa/m)*

If there is sliding contact ($f = 0$), a classical elastoplastic development can be applied. Here a non-associated flow surface $g = \tau$ is used, which correspond to isochoric plasticity, *i.e.* with dilatancy $\psi = 0$.
The penalty coefficient K_p is expressed as (see expressions **C7 - 14** and **C7 - 15**):

$$K_{p\ l} = \frac{\partial \sigma_l'}{\partial V} = \left(A_1 \cdot B_1 / 2\right) \cdot \left(e^{B_1 \cdot (V/2 + D_0)}\right) \qquad \textbf{(C7 - 18)}$$

$$K_{p\ s} = \frac{\partial \sigma_s'}{\partial V} = \frac{-A_2}{\left(V/2 + D_0\right)^3} \qquad \textbf{(C7 - 19)}$$

The mechanical characteristics of the interface elements used during the simulations are shown in **Table: C7-2**.

The tangential rigidity (K_τ**)** has not been determined on experimental basis but on modelling know-how.

Table: C7-2

Properties of the mechanical law of the interface elements.

K_τ (N/m^3)	2D$_{\text{meca 0}}$ (m)	Cohesion (Pa)	Friction angle (°)
$1 \cdot 10^{13}$	248 Å (1)	$1 \cdot 10^{4}$	25

(1) *The initial* $D_{meca\ 0}$ *value was calculated with expressions (***C7 - 12***) and (***C7 - 13***) and the constants given in* ***Table: C7-3.***

Table: C7-3

Constants and variables needed to calculate $2D_{meca\ 0}$ (m).

Variable	Name of variable	Value	Unit
$\lambda=\rho s \cdot Sa \cdot \theta$	Reactivity coefficient	1.45	-
θ_{ddl}	Double layer thickness	$9.63 \cdot 10^{-10}$	m
σ'	Vertical stress	$1 \cdot 10^{5}$	Pa
val	Valence	1	-
F	Faraday constant	$9.65 \cdot 10^{4}$	C/mol
R	Gas constant	8.31	J/mol/K
ε_0	Electric constant = Permittivity vacuum	$8.85 \cdot 10^{-12}$	$F/m=C^2/(J \cdot m)$
ε'	Relative permittivity water = relative dielectric constant at 293K	80	-
T	Temperature during test	$2.93 \cdot 10^{2}$	K
CEMC	Concentration of an equivalent amount of monovalent cations in bulk solution	100	mol/m^3
S_a	Specific surface clay	$5.56 \cdot 10^{5}$	m^2/kg
ρ_s	Density solid phase	$2.70 \cdot 10^{3}$	kg/m^3
A_1	Intermediate variable	$1.56 \cdot 10^{7}$	x
B_1	Intermediate variable	$-2.08 \cdot 10^{9}$	x
A_2	Intermediate variable	$2.23 \cdot 10^{-12}$	x
B_2	Intermediate variable	$4.87 \cdot 10^{5}$	x
$D_{meca\ 0}$ (m)	D_{meca} at starting concentration value e.g. CEMC 0.1M and 0.0001Pa	$1.24 \cdot 10^{-8}$	m

The chemo-physical behaviour $\sigma' = f(V)$ is given by expression (**C7-14**) and (**C7-15**) with parameters of **Table: C7-1** and **Table: C3-1**. Examples are given in **Figure: C7-11**.

Table: C7-4 gives the used hydraulic characteristics of the interface elements. The values for density and dynamic viscosity are those of water.

Table: C7-4

Hydraulic constants: properties of the hydraulic law of the interface elements.

Transversal transmissivity (m/(s·Pa))	Density of fluid (kg /m³)	Porosity (-)	Dynamic viscosity (Pa·s)
$1 \cdot 10^{-10}$	1000	0.3	$1 \cdot 10^{-3}$

C 7.2.1.2 Flow law

Water flow through the interface element is described in an anisotropic way. Transverse transmissivity T_t, can be divided into two separate expressions for flow, f_{t1} and f_{t2}, which can be described as follows:

$$f_{t1} = T_t \cdot \left(p_f^F - p_f^I\right) \cdot \rho_f \text{ and } f_{t2} = T_t \cdot \left(p_f^I - p_f^S\right) \cdot \rho_f \qquad \textbf{(C7 - 20)}$$

$$\frac{m}{Pa \cdot s} \cdot (Pa) \cdot \frac{kg}{m^3} = \frac{m}{s} \cdot \frac{kg}{m^3} = \frac{kg}{m^2 \cdot s}$$

where p_f^F, p_f^S and p_f^I are respectively: the pressures on the two sides of the clay particles and the pressure inside the interface and ρ_f is the fluid density.

If the interface longitudinal hydraulic conductivity k_l is not nil, the longitudinal fluid mass flow f_l is assumed analogous to laminar flow between two perfectly smooth parallel plates. This leads to the so-called "cubic law":

$$f_l = -\frac{(2 \cdot D_{meca})^3}{12 \cdot \eta} \cdot \left(\nabla p_f + \rho_f \cdot g \cdot \nabla H \right) \cdot \rho_f \qquad \textbf{(C7 - 21)}$$

$$\frac{m^2}{Pa \cdot s} \cdot \left(\frac{Pa}{m} + \frac{kg}{m^3} \cdot \frac{m}{s^2} \cdot \frac{m}{m} \right) \cdot \frac{kg}{m^3} = \frac{kg}{m^2 \cdot s}$$

where the volume flow rate f_l varies as the cube of separation $2D_{meca}$ between the two plates; η is the dynamic viscosity (Pa·s) of the fluid and ∇p_f is the fluid pressure gradient along the fracture.

Intrinsic longitudinal permeability is calculated according to Darcy's cubic law as:

$$K_{\text{int}\,rinsic} = \frac{(2 \cdot D_{meca})^2}{12} \qquad \textbf{(C7 - 22)}$$

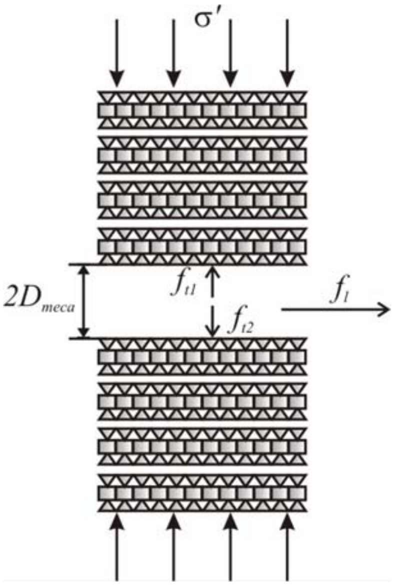

Figure: C7-4

Flow law

C 7.2.2 Interface finite element

C 7.2.2.1 General concept of a contact problem

The general concept of a contact problem is highlighted in **Figure: C7 - 5** where two deformable solids (representing in this case two clay particles) Ω^U and Ω^D are shown with boundaries $\partial\Omega^U$ and $\partial\Omega^D$.

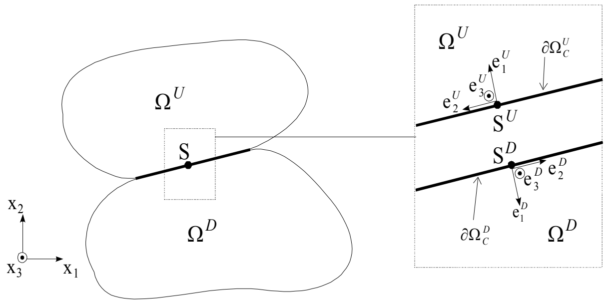

Figure: C7-5

Contact between 2 deformable solid, 2 clay particles..

In the local referential plane (e_1,e_2,e_3) (**Figure: C7 - 5**), for a plane problem, the stress tensor in each solid reduces to a contact stress vector $\underline{\sigma}_C$ defined by two components:

$$\underline{\sigma}_C = \begin{bmatrix}\sigma_1\\ \sigma_2\end{bmatrix} = \begin{bmatrix}-p\\ \tau\end{bmatrix} \qquad \textbf{(C7 - 23)}$$

where p and τ are the pressure and the shear objective stress vector (Charlier and Cescotto 1988).

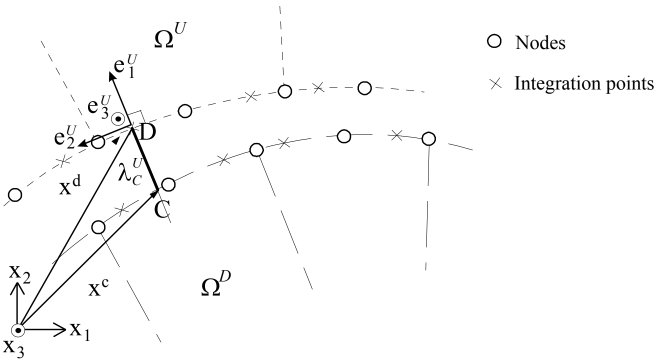

Figure: C7-6

Parabolic interface finite elements (λ^U<0, i.e. no contact).

The contact stress vector $\underline{\sigma}_C$ is associated with the relative displacement velocity $\dot{\underline{\varepsilon}}_C$ (through the interface mechanical constitutive law) defined as the time derivative of the distance vector $\underline{u}$ ($\dot{\underline{\varepsilon}}_c = \dfrac{du}{dt}$) between $\partial\Omega_C^U$ and $\partial\Omega_C^D$ (**Figure: C7 - 6**).

The contact side of each body Ω^U and Ω^D can be discretised with interface isoparametric elements which are compatible (same degree and common nodes) with the solid finite elements used to discretise the corresponding body (**Figure: C7 - 6**).

The frictional interface elements used here are based on mixed variational principle (Cescotto and Charlier 1993): Contact stresses are computed at contact element integration points whereas displacements of the solid boundary are computed at nodal points.

In the *LAGAMINE* code, the reference side $\partial\Omega_C$ on which contact stresses are computed is always referred as the *contact element side* and is discretised using interface elements; the other side on which intersections are looked for is always referred to as the *foundation side* and is discretised using foundation elements.

C 7.2.2.2 Description of the interface element

A 2-D large strain finite element has been implemented in the *LAGAMINE* code. This element consists of two isoparametric elements (**Figure: C7 - 7**), with 2 (linear) or 3 (parabolic) nodes describing the interface element, the foundation side and with 3 degrees of freedom (d.o.f) per node (2 mechanical displacements u and v, and the fluid pressure on the structure side p_f^S).

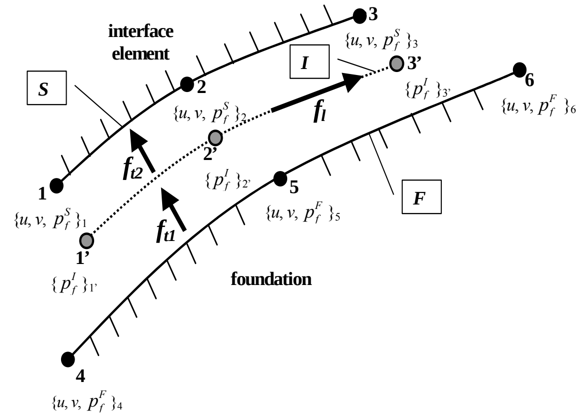

Figure: C7-7

Description of a 2-D parabolic interface element.

To describe the seepage flow inside the interface p_f^I, 2 or 3 further nodes are added with only 1 degree of freedom per node, the fluid pressure inside the interface. These nodes have thus the same co-ordinates as the corresponding nodes on the interface element.
With this element formulation, the equivalent nodal forces and the stiffness matrix in the Newton-Raphson sense will have, for a parabolic element, the following expressions ((**C7 - 24i**) and (**C7 - 24ii**)):

$$\underline{F}^T = \left(\langle \underline{F}_S \rangle_{1x9} \quad \langle \underline{F}_I \rangle_{1x3} \quad \langle \underline{F}_F \rangle_{1x9} \right)^T \qquad \textbf{(C7 - 24i)}$$

$$\underline{\underline{K}} = \begin{bmatrix} \left[\underline{\underline{K}}_{SS}\right]_{9x9} & \left[\underline{\underline{K}}_{SI}\right]_{9x3} & \left[\underline{\underline{K}}_{SF}\right]_{9x9} \\ \left[\underline{\underline{K}}_{IS}\right]_{3x9} & \left[\underline{\underline{K}}_{II}\right]_{3x3} & \left[\underline{\underline{K}}_{IF}\right]_{3x9} \\ \left[\underline{\underline{K}}_{FS}\right]_{9x9} & \left[\underline{\underline{K}}_{FI}\right]_{9x3} & \left[\underline{\underline{K}}_{FF}\right]_{9x9} \end{bmatrix} \qquad \textbf{(C7 - 24ii)}$$

where the indexes $_S$, $_I$ and $_F$ refer to the solid side, the interior interface and the foundation side respectively.

C 7.3 Simulation of the leaching of a 2D assembly of clay particles under oedometer conditions

C 7.3.1 Model

General set-up:
A network of clay particles is formed by arranging the interface/contact elements as shown in **Figure: C7-8**. Each clay particle is bounded from another clay particle by two interface/contact elements. The continuum elements representing the particles follow one of the modes described in paragraph **C 7.3.4**. Following the discussion of the interlayer reactivity under oedometer conditions (paragraph **A 3.2.2** and **C 6.4**) representative of the boundary conditions in a landfill barrier, the clay particles elements, can be considered as inaccessible under the stress levels used. Therefore, the mode 0 (see paragraph **C 7.3.4**) is followed in the remainder of the chapter.

Type of mesh:
Different orientations of flow paths or bottlenecks (**Figure: C7-8-A** to **D**) with respect to the external compressive stress (**Figure: C7-8-C**) can be analysed with the block model (**Figure: C7-8-E**) and the hexagonal model (**Figure: C7-8-F**).

As will be discussed in paragraph **C 7.3.6**, analyses showed that the different orientations of the interfaces between two particles can be grouped into two leagues, namely interfaces representing flow paths which:
i) Behave independently of the composition of the fluid. The aperture along the interface remains the same during permeation.
ii) Depend on the interparticle fluid composition. The aperture varies as a function of the chemical composition of the permeate.

With this method more complicated particle set ups of clays studied *e.g.* in thin section or in future with environmental scanning electron microscopes can easily be decomposed and a qualitative and quantitative estimate of the chemical sensitivity of the hydraulic conductivity can be given.

Two types of mesh were used, one with hexagonal clay particles and one with rectangular clay particles. The clay blocks have a diameter of 2 micrometer. This value is larger than the determined 1.3 micrometer in paragraph **C 6.3.3** but of the same order.

The total length of the cross section is 10 micrometer. The height of the section amounts to: 8 (block model) or 6 micrometers (hexagonal model).

The entire mesh of the numerical model consists of:

- Block model: 286 nodes, 78 8-node quadrangles elements and **28** foundation and interface elements (**Figure: C7-8-E**).

- Hexagonal model: 1050 nodes, 374 8-node quadrangles elements and **98** foundation and interface elements (**Figure: C7-8-F**).

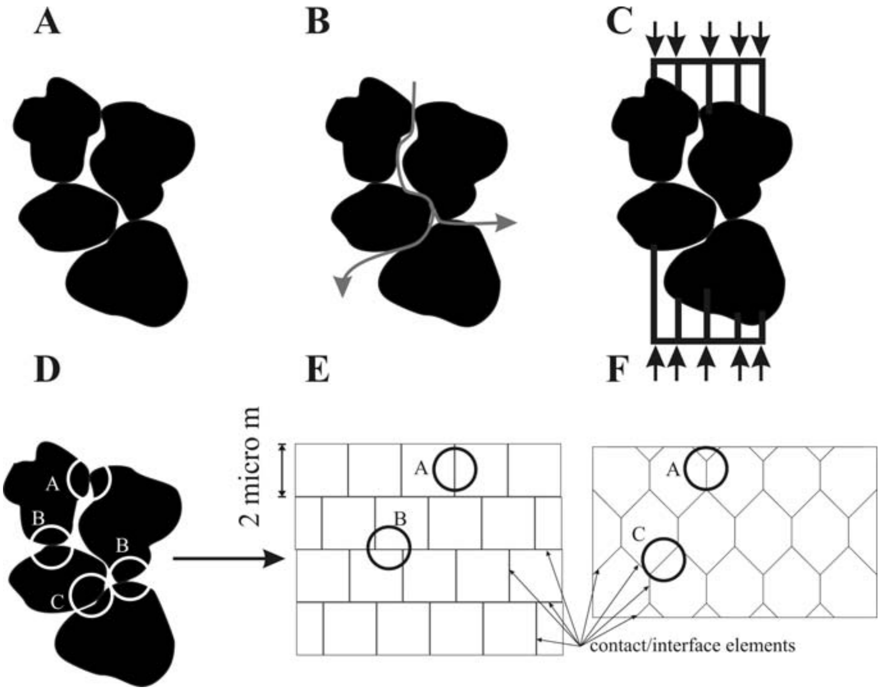

Figure: C7-8

Considering the clay assemblage shown in A: If liquid flows along and in-between these particles in the way shown in B, the fluid will pass along bottlenecks with different orientation (D) with respect to the major principle stress (C). These different orientations can be analysed with the block model (E) and the hexagonal model (F).

C 7.3.2 Boundary and loading conditions

The lower boundary is fixed vertically and is horizontally free (**Figure: C7-9**). Normal stresses are applied on the top (surface) boundary. The pore pressure is set to the desired value at the top of the model and free at the bottom of the model. The boundaries on the right and the left are x-fixed and y-free and impermeable. Flow of contaminants is not modelled, the concentration is changed directly at the integration points of the interface elements.

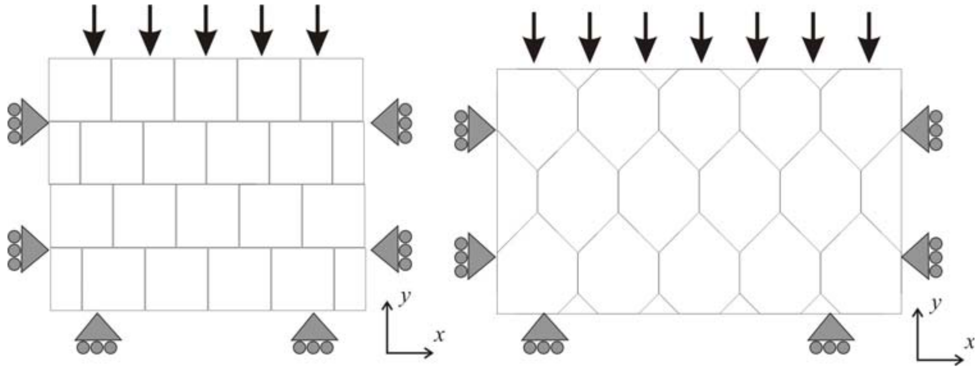

Figure: C7-9

Boundary and loading conditions.

C 7.3.3 Initial stress and pressure state

The initial $\sigma_y = \sigma_x = 100$ kPa ($K_0 = 1$) (see **Figure: C7-9**). The initial load at the upper boundary is also 100 kPa.

The whole model is supposed to be saturated with a fluid of a specific density equal to 1. The fluid compressibility has been taken to 3GPa^{-1} for the whole model.

C 7.3.4 Geomechanical and hydraulic characteristics of the clay particles

The mechanical behaviour of the clay particles is modelled with an elastic model (see **Table: C7-5**). It was assumed that the clay particles themselves are nearly incompressible (compared to the interfaces) and do not contain voids (apparent density = density solids).

Table: C7-5

Mechanical constants: properties of the mechanical law of the 8-node quadrangle elements.

	Young's modulus (GPa)	Poisson's ratio (–)	Apparent density (kg/m³)
Clay particles	100(45)	0.4	2750

The clay particles themselves were considered impermeable to flow. Therefore no hydraulic properties were specified for the 8-node quadrangle elements.

Within the clay particles (interlayer level), mineral alteration processes occur. If potassium is leached out of an open Illite, the Illite will be able to swell and the clay particles "explode". The number of TOT-layers per particle decreases and the number of particle-to-particle interfaces increases. This process can be translated as a strain perpendicular to the TOT-layers. The reverse can happen as well. If the concentration of cations in the permeate exceeds a certain concentration the space between the clay particles will collapse and become an interlayer. Other processes like Kaolinisation have to be taken into account as well. Depending on the type of Kaolinisation: Either transformation or neoformation, the strain will be isotropic or anisotropic.

Such strains are introduced into the continuum elements representing the clay particles by using a modified thermal law:

$$\varepsilon = \alpha \cdot \Delta CEMC \qquad \textbf{(C7 - 25)}$$

In which:

ε = *The strain of a clay particle, which is produced as a consequence of the increase or decrease of its basal spacing due to mineral alteration* *(-)*

CEMC= *The concentration of the substance in question that enters the interlayer space* *(mol/m^3)*

α = *Coefficient relating the strain to the concentration* *(-)*

---

[45] *Dynamic Young's modulus tested on dry (no interparticle fluid present; no interlayer fluid?) Illite, Chlorite and Kaolinite: Compressional velocity 8km/s, dry density 2700kg/m³ (Katahara 1996).*

In the case that cations enter a Smectite the change in basal spacing *i.e.* the strain can be related to the concentration as a series of discontinuous functions as shown in **Figure: C7-10**. The graphs are valid at atmospheric pressure. If the clay samples are loaded the interlayers are less accessible.

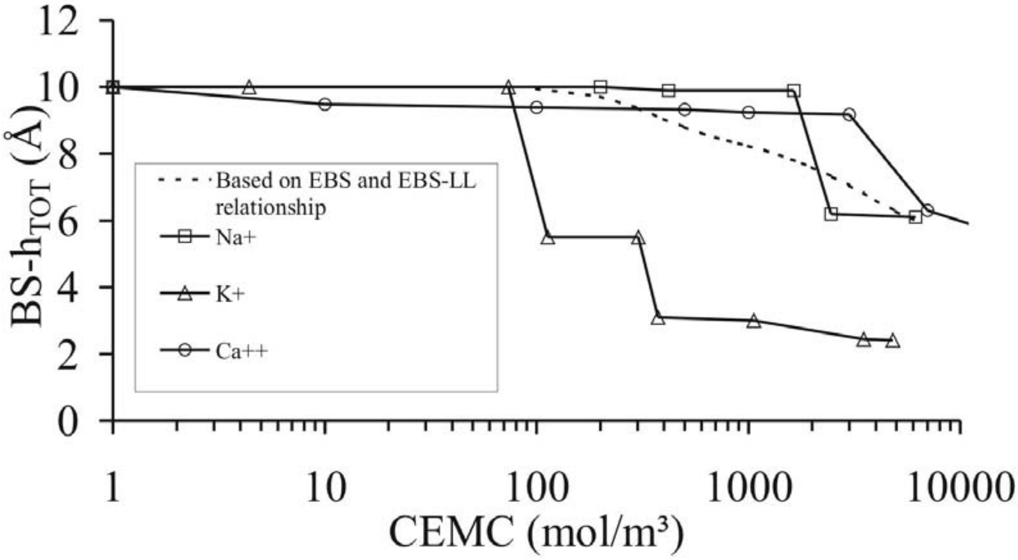

Figure: C7-10

*Depending on the concentration and the type of cations, the distance between the TOT-layers (Smectite) varies as a function of the concentration and cation type. Note that in presence of K^+ cations the distance between the TOT-layers or entire particles approaches 0 ("Illitisation"). Data-set: Lagaly (1993). The dashed line shows a derivation of the BS-h_{TOT} relationship based on the EBS theory, the relationship between the ESB and the LL and LL-salt concentration measurements (**C 5.3.4**). Notice the close resemblance to the XRD-measurements by Lagaly (1993). Note that these values were determined at atmospheric pressure. At higher pressures the values are smaller (no data is available in literature to determine how much smaller).*

Of course other than the above-mentioned function relating the strain to concentration are possible. Except for salts, the exact evolution of the basal spacing has not been analysed systematically in literature. To differentiate between all (potential) interlayer interactions leading to a strain of the clay particle, the mineral alteration processes have been grouped into different modes:

Mode 0:
Mode 0 represents the situation in which the interlayers are not accessible for the permeating fluid and no interlayer fluid can leave the interlayers. This situation represents the:

- Permeation with fluids that cannot enter the interlayer space, but which change the double layer thickness.
- Initial phase of permeation in which the fluids starts to flow around the clay particles first.

Mode I:
Osmotic effects are driven by a concentration gradient. The situation where in a clay sample osmotic effects occur is not very clear (see **Part: A**). The clay sample as a whole can be considered to behave as an imperfect semi-permeable membrane, or some pore spaces with respect to others, or as in the case presented here the interlayer space with respect to the fluid surrounding the pores. Uptake or expel of water by the interlayer space will result in a strain as a function of the concentration. The strain was in this mode, therefore related to the concentration of the fluid. A reduction factor takes into account phenomena like imperfectness of the semi-permeable membranes *etc.* The major difficulty is the determination of the concentration of elements in the interparticle space. These concentrations cannot be measured directly (PC Dohrman). Although the definition of concentration is obscure in a situation where the fluid is bound water a notion can be obtained by deducing the amount of ions present in this interlayer space (Dohrman method: Amount of ions = CAC_{tot} - CAC_{edges}) and dividing this by the volume of the interlayer space ($V \cdot Q \cdot (BS-h_{TOT})$).

Mode III, IV and V:
These modes represent the percolation of solutions containing Ca^{2+}, K^+ or Na^+ cations. If only the charge is considered and if a double layer is formed, the distance between the clay particles depends on the stress and repulsion law described in paragraph **C 7.2.1.1** (see the concentration range where diffuse double layers are present in **Figure: C7-2**). If the concentration of cations increases, the thickness of the double layer decreases. The clay particles approach each other if driven by external stresses up to a point where the double layer disappears completely (see **Table: C7-6** and **Figure: C7-2**). In reverse, interlayers can become double layers as mentioned by Lagaly (1993) for TOT clay minerals: “Up to 0-4 water layers, the TOT to TOT arrangement remain existent even though the mobility of the interlayer cations starts to be relatively high. Once the basal spacing exceeds 20 Å the order of the TOT-layers is lost and diffuse double layers are formed.”

Table: C7-6

The double layer disappears (coagulation) at a concentration level depending on the valence of the cations (Lagaly 1993).

Metal ions with valence equal to 1, 2 or 3:	Concentration of cations (Mol/m^3)	Concentration of cations (if edges are + charged and faces are charged -) (Mol/m^3)	Concentration of cations (Mol/m^3) if Na-Smectite are exposed to solutions containing Ca^{2+} cations
M^+	25-150 (1)	5	
M^{2+}	0.5-3 (1)		< 1 (2)
M^{3+}	0.01-0.1 (1)		

(1) Lagaly (1993: 115); (2) Lagaly (1993: 116)

In this paragraph it has been shown how different mineral alteration processes (on the interlayer level) can be incorporated into a simulation. In paragraph **A 3.2.2** and paragraph **C 6.4** it has been shown that in the case that natural clays are permeated by leachates under landfill conditions the interlayers are hardly accessible for substances found in these leachates. Therefore, the simulations discussed in the next paragraphs were performed in mode 0 *i.e.* the clay blocks are nearly not deformable and not subject to chemical-physical processes (no reactions on the interlayer level), all chemical-physical activity is located in the interparticle space (particle level).

C 7.3.5 Simulation of the permeation

During the first step the vertical stress is increased from 100kPa to the desired value (example from 100kPa to 200kPa, path 1-2 **Figure: C7-11**). After the first step the flow of permeate is simulated (paths 2 - 3 **Figure: C7-11**). A pressure gradient is applied between the top and bottom of the mesh. The change in concentration of cations in the interparticle fluid or the change in the dielectric constant occur in the laboratory simultaneously with the penetration of the permeate into the sample. During the simulation this is modelled by changing at each integration point of the contact elements simultaneously either:

- Concentration of cations, or
- The dielectric constant,

as a function of integration time that passes.

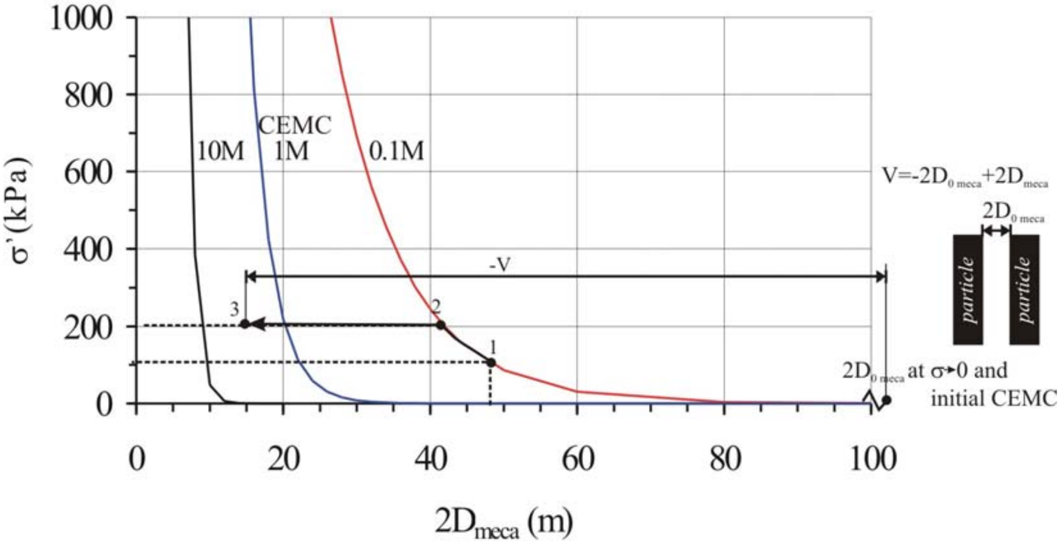

Figure: C7-11

Normal stress (σ') deformation ($2 \cdot D_{meca}$) characteristics of two clay particles as a function of the concentration of cations in the interparticle fluid (CEMC). In this figure an example of the relationship described in ***Figure: C7-3*** *is shown. Depending on the concentration of monovalent cations in the permeate, the pressure - distance relationship is different. The initial aperture $2 \cdot D_{0\ meca}$ was determined at a pressure of $1 \cdot 10^{-4}$ kPa and a CEMC of 0.1M.*

In the simulations presented in the following paragraph, no fluid flow is modelled. The concentration of cations or changes of the relative dielectric constant of the leachate, which are actually modified by advection, are imposed at each integration point of the interface elements. The concentration is uniform over all elements, but varies with time.

C 7.3.6 Results of the simulation

In this paragraph the results of the simulated permeation with a monovalent cation solution starting at a concentration of 100mol/m³ and a progressively increasing concentration is discussed.

Deformation:
The overall behaviour of the sample during the simulation (hexagonal and block model) shows a homogeneous settlement of the sample. Note that at the same time the settlement occurs in the vertical direction, the horizontal dimensions of the sample cannot change (oedometric boundary conditions). This shows that the presumed shrinkage of the sample often thought to be responsible (*e.g.* Fernandez and Quigley 1985) for an enormous increase of the hydraulic conductivity is not related to changes in the double layer thickness. What happens instead can be understood if the development of stresses is analysed.

The evolution of stresses and changes in the interparticle fluid composition determine the evolution of the aperture of the interface elements. The aperture of the interface elements changes as a function of the concentration. It is evident that two different reactions must be discerned. This difference is based on the orientation of the contact elements as a function of the direction to the major principle stress (the exterior compressive stress in y direction **Figure: C7-9**).

The interface elements parallel or sub-parallel to the exterior compressive stress remain at their initial aperture whereas the aperture of the interface elements perpendicular or sub-perpendicular to the exterior compressive stress decreases as a function of the concentration of the cations in the permeate. While the aperture of the interface elements parallel or sub-parallel to the exterior compressive stress remains constant, the normal stress decreases with increasing concentration of ions in the permeate. In the interface elements perpendicular or sub-perpendicular to the exterior compressive stress, opposite effect can be observed and the normal stress in the interface elements remains identical to that applied to the top of the sample (see **Figure: C7-12**).

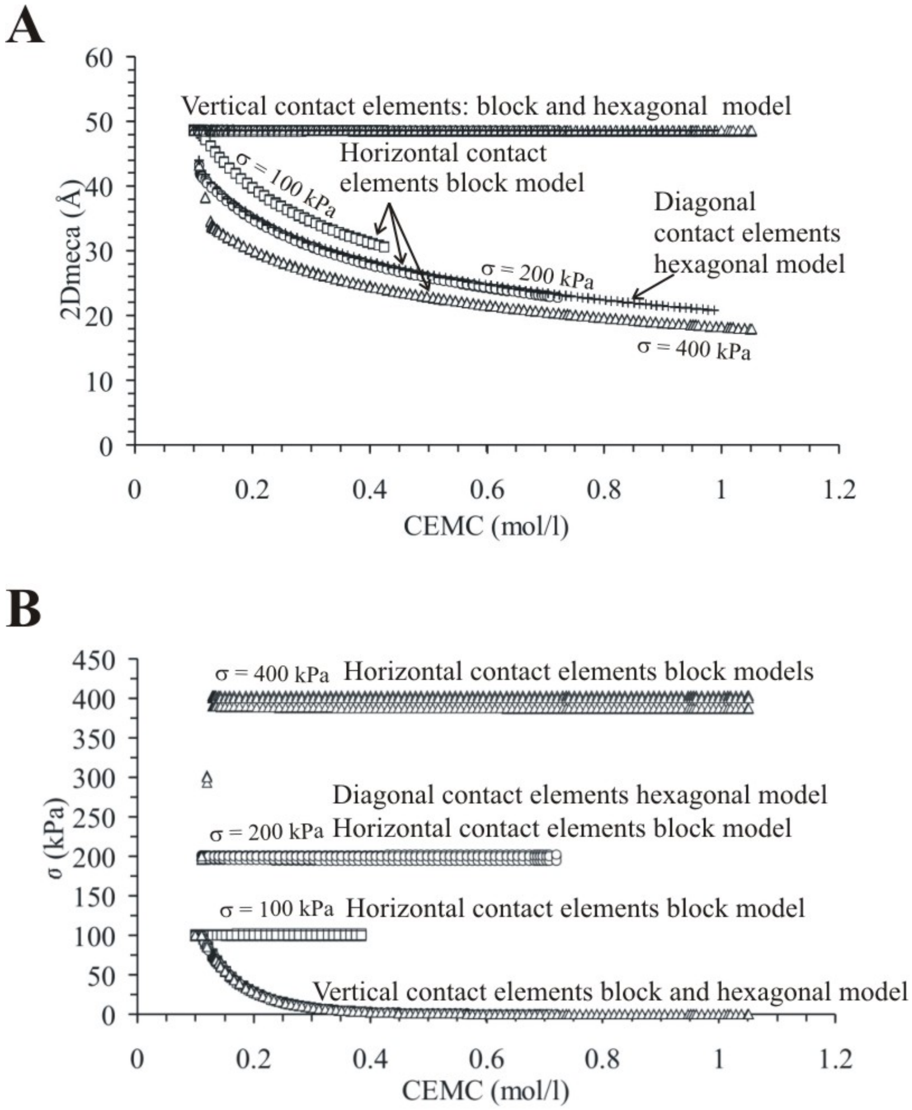

Figure: C7-12

Numerical results of (A) the aperture of different contact/interface elements and (B) the stress in the contact/interface elements, as a function of the CEMC. Note that the simulation stops to converge (negative stress in contact elements) before collapse of the double layer occurs.

The simulations show that as long as the interfaces between the clay particles are oriented horizontally or sub-horizontally with respect to the exterior compressive stress (see **Figure: C7-13**) the flow of fluids that decreases the double layer thickness will be hindered by a diminution of the interparticle distance *i.e.* the flow path width. These processes occur in each sub-layer with horizontal or sub-horizontal particles within a clay barrier. The thickness of the layer with horizontal or sub-horizontal particles is not necessarily identical to the thickness of the entire clay barrier.

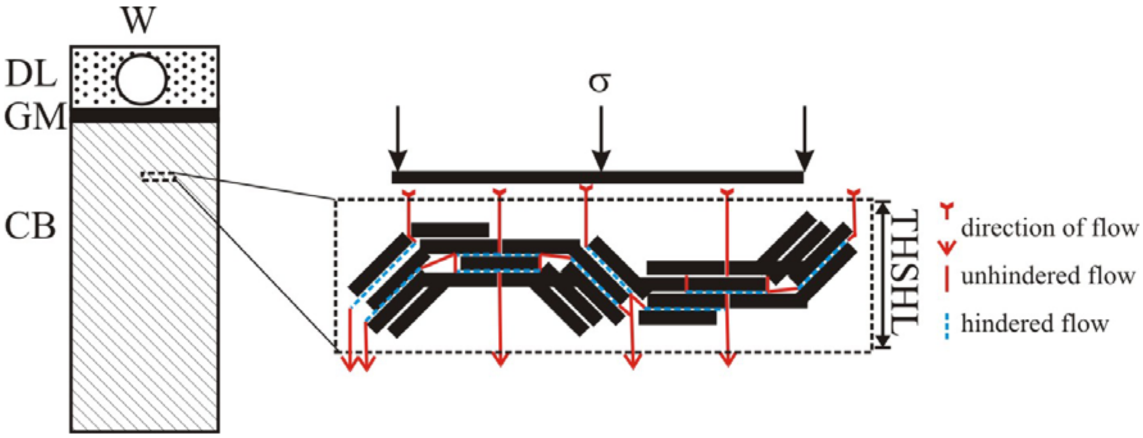

Figure: C7-13

On the left: A section through the liner of a waste containment site. On the right: A magnification of a part of the clay barrier. The thicker the layer with horizontal or sub-horizontal clay particles (the thicker THSHL) the larger the influence of the flow of fluids that decreases the double layer thickness will be. CB = Clay barrier; GM = Geomembrane; DL = Drainage layer; W = Waste; THSHL = Thickness of layer with horizontal or sub-horizontal clay particles.

C 7.4 Interpretation of the numerical simulations

C 7.4.1 Introduction

The numerical simulation showed that some interparticle contacts are influenced by the permeation of chemicals. Others remain constant. To interpret the closure or opening of some of the interparticle voids in terms of changes in hydraulic conductivity on an oedometer or clay barrier scale the results of the simulation have to be upscaled. An approach is described in this paragraph.

In the previous paragraph it was concluded that as long as the clay particles are oriented horizontally or sub-horizontally with respect to the vertical exterior compressive stress the flow of fluids decreasing the double layer thickness will be hindered. In this paragraph it will be discussed what this hindrance means in terms of changes in hydraulic conductivity on the clay sample or barrier scale.

C 7.4.2 Extrapolation of hydraulic conductivity to the sample and barrier size[46]

Interface elements and changes in hydraulic conductivity

The closure of the interparticle voids can be expressed in terms of changes in hydraulic conductivity. If the interparticle void is represented as a rectangular tube, the expression for flow can be related to the aperture of the tube. If it is assumed that the flow is a

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[46] *The extrapolation scales, changes on the nanometer level, up to the dimensions where the geomaterial cannot longer be modelled as a homogenous assembly of discrete particles. From thereon other tools, geostatistical, can be used to perform further upscaling to the desired level.*

quasi-one-dimensional, internal, laminar, viscous, incompressible, steady and fully developed flow with friction (Swanson 1970) the expression for flow is given by:

$$Q_1 = \frac{g \cdot e_1^{\,3}}{12 \cdot v_{kin} \cdot L_1} \cdot \Delta H_1 \cdot W_1 \qquad \textbf{(C7 - 26i)}$$

In which:

Q = *Total flow traversing a clay sample or clay barrier* *(m^3/s)*
g = *Gravitational acceleration* *(m/s^2)*
v_{kin} = *Kinematic viscosity* *(m^2/s)*
L_1 = *Length flow tube 1 or height clay particle* *(m)*
L_2 = *Length flow tube 2 or width clay particle* *(m)*
e_1 = *Hydraulic aperture flow tube 1* *(m)*
e_2 = *Hydraulic aperture flow tube 2* *(m)*
ΔH = *Hydraulic head* *(m)*
W = *Breadth flow tubes* *(m)*

For two rectangular tubes in series with different apertures (e_1 and e_2) flow is given by:

$$\frac{1}{Q} = \frac{1}{\dfrac{g \cdot e_1^{\,3}}{12 \cdot v_{kin} \cdot L_1} \cdot \Delta H \cdot W} + \frac{1}{\dfrac{g \cdot e_2^{\,3}}{12 \cdot v_{kin} \cdot L_2} \cdot \Delta H \cdot W} \qquad \textbf{(C7 - 26ii)}$$

The flow can be related to the width, height and distance between clay particles as is shown in **Figure: C7-14**.

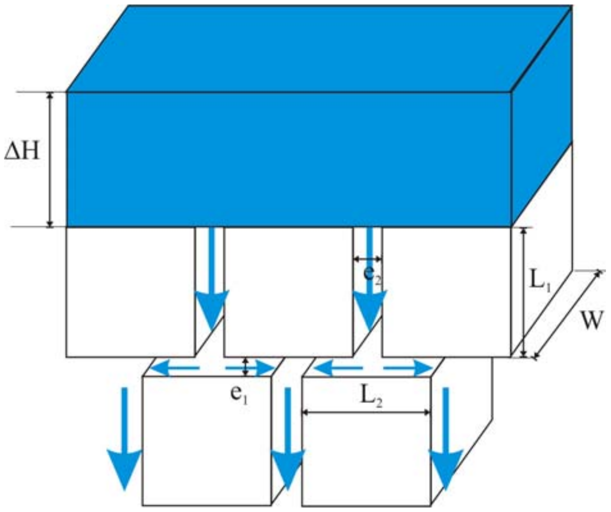

Figure: C7-14

An assembly of particles can be described as assemblage of rectangular tubes with different dimensions (L_1, L_2) and apertures (e_1, e_2). ΔH is much larger (factor $1 \bullet 10^7$) than L_1.

The assembly of clay particles shown in **Figure: C7-14** can be simplified as an assemblage of rectangular tubes shown in **Figure: C7-15-A**. The assembly shown in **Figure: C7-15-A** can be simplified to the assembly shown in **Figure: C7-15-B** and a formula expressing the flow as a function of the tube thickness and height can be derived (see expression (**C7 - 26iii**)).

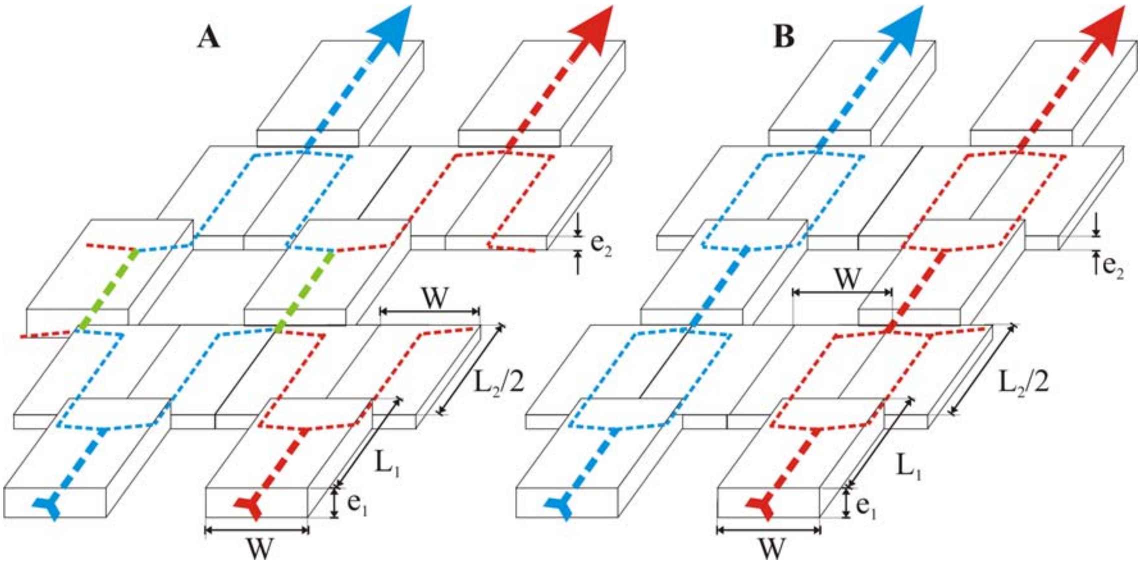

Figure: C7-15

A: An assembly of particles can be described as assemblage of rectangular tubes. Such an assembly can be represented as an assembly of thin and thick rectangular tubes. B: The assembly shown in A can be simplified.

$$\frac{1}{Q}=\frac{1}{\frac{g\cdot e_1^{3}}{12\cdot v_{kin}\cdot L_1}\cdot\Delta H\cdot W}\cdot 3+\frac{1}{\frac{g\cdot e_2^{3}}{12\cdot v_{kin}\cdot\frac{L_2}{2}}\cdot\Delta H\cdot W+\frac{g\cdot e_2^{3}}{12\cdot v_{kin}\cdot\frac{L_2}{2}}\cdot\Delta H\cdot W}\cdot 2 \qquad \textbf{(C7 - 26iii)}$$

This expression can be written for an entire clay sample as:

$$Q=\left(\frac{1}{\frac{g\cdot e_1^{3}}{12\cdot v_{kin}\cdot L_1}\cdot\Delta H\cdot W}\cdot m+\frac{1}{\frac{g\cdot e_2^{3}}{12\cdot v_{kin}\cdot\frac{L_2}{2}}\cdot\Delta H\cdot W+\frac{g\cdot e_2^{3}}{12\cdot v_{kin}\cdot\frac{L_2}{2}}\cdot\Delta H\cdot W}\cdot n\right)^{-1} \qquad \textbf{(C7 - 27)}$$

In which:

$$m=number\ of\ particles\ in\ width\ of\ sample=\frac{width\ sample}{width\ particle}=\frac{width\ sample}{L_2} \qquad \textbf{(C7 - 28)}$$

$$n=number\ of\ particles\ in\ height\ of\ sample=\frac{height\ sample}{height\ particle}=\frac{height\ sample}{L_1} \qquad \textbf{(C7 - 29)}$$

To relate the changes in flow Q (expressed as a ratio between the initial Q_{ini} and final value Q_{fin}) due to the narrowing of flow channels by permeation with leachate the expression of flow through an assembly of tubes with different widths (e_1 and e_2) can be written as:

$$\frac{Q_{fin}}{Q_{ini}} = \frac{\left(\dfrac{1}{\dfrac{g \cdot e_{1ini}{}^{3}}{12 \cdot v_{kin} \cdot L_1} \cdot \Delta H \cdot W} \cdot m + \dfrac{1}{\dfrac{g \cdot e_{2ini}{}^{3}}{12 \cdot v_{kin} \cdot \dfrac{L_2}{2}} \cdot \Delta H \cdot W + \dfrac{g \cdot e_{2ini}{}^{3}}{12 \cdot v_{kin} \cdot \dfrac{L_2}{2}} \cdot \Delta H \cdot W} \cdot n \right)}{\left(\dfrac{1}{\dfrac{g \cdot e_{1fin}{}^{3}}{12 \cdot v_{kin} \cdot L_1} \cdot \Delta H \cdot W} \cdot m + \dfrac{1}{\dfrac{g \cdot e_{2fin}{}^{3}}{12 \cdot v_{kin} \cdot \dfrac{L_2}{2}} \cdot \Delta H \cdot W + \dfrac{g \cdot e_{2fin}{}^{3}}{12 \cdot v_{kin} \cdot \dfrac{L_2}{2}} \cdot \Delta H \cdot W} \cdot n \right)} = \frac{\dfrac{m \cdot L_1}{e_{1ini}{}^{3}} + \dfrac{n \cdot L_2}{4 \cdot e_{2ini}{}^{3}}}{\dfrac{m \cdot L_1}{e_{1fin}{}^{3}} + \dfrac{n \cdot L_2}{4 \cdot e_{2fin}{}^{3}}}$$

(C7 - 30)

If r is defined as:

$$r = \frac{width\ sample}{height\ sample} \qquad \textbf{(C7 - 31)}$$

If s is defined as:

$$s = \frac{L_2}{L_1} \qquad \textbf{(C7 - 32)}$$

Subsequently, expression (**C7 - 30**) can be simplified with expressions (**C7 - 31**) and (**C7 - 32**) to:

$$\frac{Q_{fin}}{Q_{ini}} = \frac{\dfrac{m \cdot L_1}{e_{1ini}{}^{3}} + \dfrac{n \cdot L_2}{4 \cdot e_{2ini}{}^{3}}}{\dfrac{m \cdot L_1}{e_{1fin}{}^{3}} + \dfrac{n \cdot L_2}{4 \cdot e_{2fin}{}^{3}}} = \frac{\dfrac{\frac{m}{n}}{e_{1ini}{}^{3}} + \dfrac{\frac{L_2}{L_1}}{4 \cdot e_{2ini}{}^{3}}}{\dfrac{\frac{m}{n}}{e_{1fin}{}^{3}} + \dfrac{\frac{L_2}{L_1}}{4 \cdot e_{2fin}{}^{3}}} = \frac{\dfrac{\frac{r}{s}}{e_{1ini}{}^{3}} + \dfrac{s}{4 \cdot e_{2ini}{}^{3}}}{\dfrac{\frac{r}{s}}{e_{1fin}{}^{3}} + \dfrac{s}{4 \cdot e_{2fin}{}^{3}}} = \frac{\dfrac{r}{s \cdot e_{1ini}{}^{3}} + \dfrac{s}{4 \cdot e_{2ini}{}^{3}}}{\dfrac{r}{s \cdot e_{1fin}{}^{3}} + \dfrac{s}{4 \cdot e_{2fin}{}^{3}}} \qquad \textbf{(C7 - 33)}$$

From Darcy's law one knows that:

$$Q = K_{hc} \cdot A \cdot i \qquad \textbf{(C7 - 34)}$$

To relate the changes in flow Q (expressed as a ratio between the initial Q_{ini} and final value Q_{fin}) due to a change in hydraulic conductivity due to the permeation with leachate, expression (C7 - 34) can be written as:

$$\frac{Q_{fin}}{Q_{ini}} = \frac{K_{hc\ fin} \cdot A \cdot i}{K_{hc\ ini} \cdot A \cdot i} = \frac{K_{hc\ fin}}{K_{hc\ ini}} \qquad \textbf{(C7 - 35)}$$

Opposing expression (**C7 - 33**) to (**C7 - 35**) renders an expression in which the relative change in hydraulic conductivity of a clay sample or a clay barrier before and after permeation with a leachate can be expressed in terms of relative closure of flow paths, relative size of the clay particles and relative size of the sample or barrier:

$$\frac{K_{hc\ fin}}{K_{hc\ ini}} == \frac{\dfrac{r}{s \cdot e_{1ini}{}^{3}} + \dfrac{s}{4 \cdot e_{2ini}{}^{3}}}{\dfrac{r}{s \cdot e_{1fin}{}^{3}} + \dfrac{s}{4 \cdot e_{2fin}{}^{3}}} \qquad \textbf{(C7 - 36)}$$

Regarding expression (**C7 - 36**) one can conclude that the decrease of the hydraulic conductivity with respect to the initial value, depends on the width to length ratio of the sample or barrier, the clay particle and the ratio of the initial opening of the flow paths and their final value. These relationships have been plotted in **Figure: C7-16** for different particle forms in oedometer and triaxial samples and on the scale of a landfill barrier.

C 7.4.3 Extrapolation of percolation-time: laboratory sample to clay barrier

The results of the numerical simulation presented in this chapter and the laboratory measurements presented in the previous chapter **C 6** were based on laboratory tests on clay samples tested and leachate during several months (corresponds to the leaching of several pore volumes, paragraph **B 3.6.2**). Up to this time $t_{\min\ val}$ (minimum validity) and possibly beyond, the results of the numerical simulation are valid. In this paragraph it is discussed to how much time this minimum validity corresponds *in situ*.

The total volume of the clay sample tested in the oedometer is:

$$V_{total} = V \cdot Q \cdot W = V_{solids} + V_{voids} \qquad \textbf{(C7 - 37)}$$

In which:

V_{total}	=	*The total volume of the clay sample*	*(m^3)*
V	=	*The breadth of the clay sample*	*(m)*
Q	=	*The width of the clay sample*	*(m)*
W	=	*The height of the clay sample*	*(m)*
V_{solids}	=	*The total volume of solids in the sample*	*(m^3)*
V_{voids}	=	*The total volume of voids in the sample*	*(m^3)*

The volume of voids can be expressed in terms of the total volume of the clay sample as:

$$V_{voids} = \frac{V_{tot}}{1 + \dfrac{1}{e}} \qquad \textbf{(C7 - 38)}$$

In which:

e	=	*The void ratio*	*(-)*

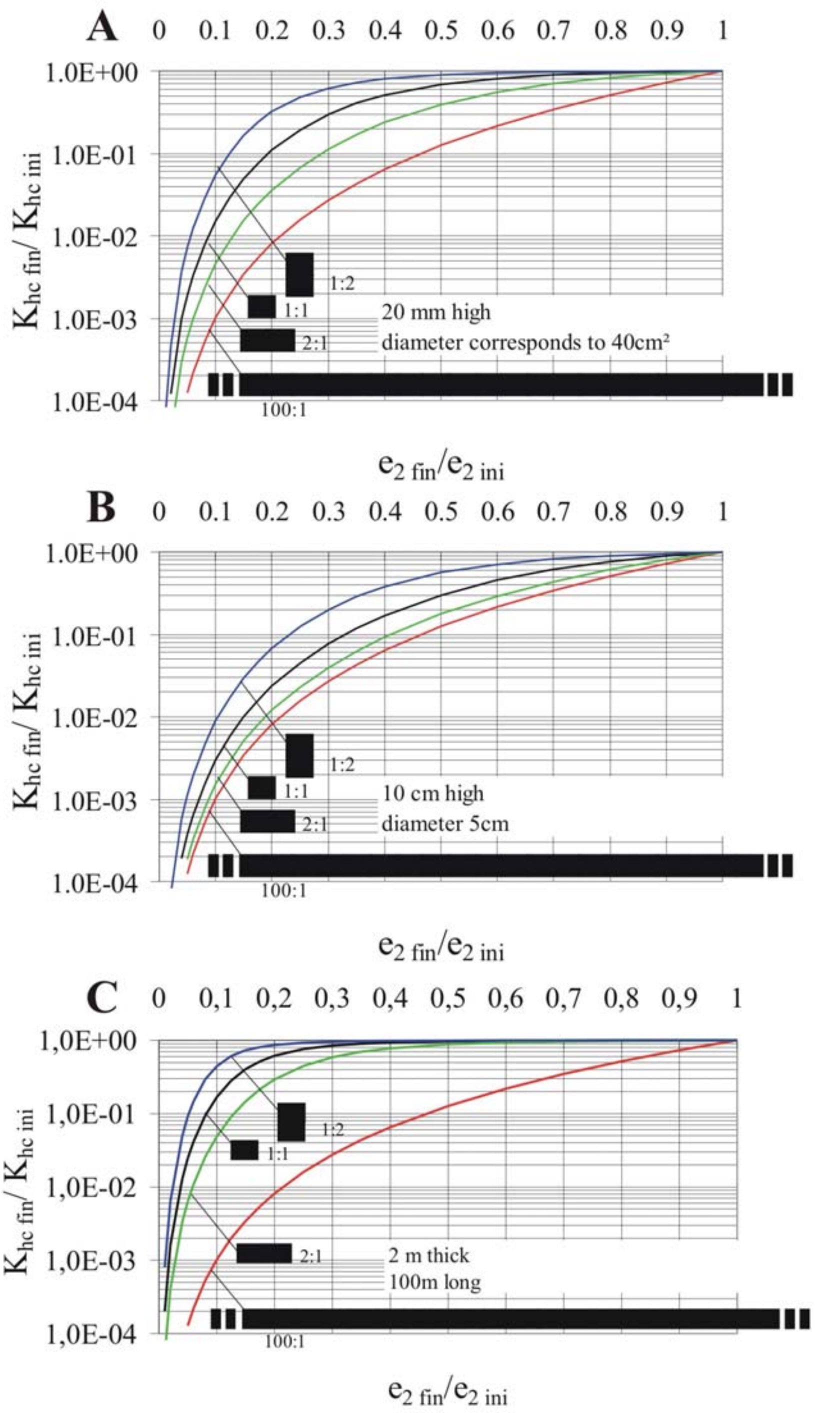

Figure: C7-16

This figure shows the relationship between particle form (s = width:height from 1:2 to 1:100), closure in horizontal flow paths ($e_{2\ ini}/e_{2\ fin}$), at constant e_1, dimension of the sample (r, oedometer sample: A; triaxial sample: B; landfill barrier: C) and the relative change in hydraulic conductivity ($K_{hc\ fin}/K_{hc\ ini}$).

All reactions that were measured during the oedometer tests with leachate percolation, took place after percolation of a volume of leachate equal to or greater than the available void volume. This volume is called:

$$V_{lim} = f \cdot V_{voids} \qquad \textbf{(C7 - 39)}$$

In which:

V_{lim} = *If a volume of leachate equal to* V_{lim} *is percolated through the clay, all measured reactions e.g. decrease/increase of hydraulic conductivity or chemical settlement have taken place (up to* $t_{min\ val}$*)* (m^3)

f = *A factor* ≤ 5 *(-)*

The flow can be expressed as the volume of leachate permeated through the sample in a time $t_{\text{min val}}$ with the expressions (**C7 - 37**), (**C7 - 38**) and (**C7 - 39**) as:

$$Q = \frac{V_{\text{lim}}}{t_{\min val}} = \frac{f \cdot V_{voids}}{t_{\min val}} = \frac{f \cdot V \cdot Q \cdot W}{\left(1 + \frac{1}{e}\right) \cdot t_{\min val}} \qquad \textbf{(C7 - 40)}$$

Darcy's law expressed in dimensions of the sample is:

$$Q = K_{hc} \cdot A \cdot i = K_{hc} \cdot Q \cdot V \cdot \frac{H}{W} \qquad \textbf{(C7 - 41)}$$

In which:

Q = *Flow* (m^3/s)

K_{hc} = *Hydraulic conductivity* *(m/s)*

A = *Cross sectional area of the sample =* $V \cdot Q$ (m^2)

i = *Hydraulic gradient* *(-)*

H = *Height of the leachate table* *(m)*

Combining the expressions of the flow (**C7 - 40**) and (**C7 - 41**) results in:

$$K_{hc} \cdot Q \cdot V \cdot \frac{H}{W} = \frac{f \cdot V \cdot Q \cdot W}{\left(1 + \frac{1}{e}\right) \cdot t_{\min val}} \qquad \textbf{(C7 - 42)}$$

Expression (**C7 - 42**) provides an expression for the time t needed for reactions to occur in the laboratory:

$$t_{\min val\ lab} = \frac{f \cdot {W_{lab}}^2}{\left(1 + \frac{1}{e_{lab}}\right) \cdot K_{hc\ lab} \cdot H_{lab}} \qquad \textbf{(C7 - 43)}$$

and in the field:

$$t_{\min val\ field} = \frac{f \cdot {W_{field}}^2}{\left(1 + \frac{1}{e_{field}}\right) \cdot K_{hc\ field} \cdot H_{field}} \qquad \textbf{(C7 - 44)}$$

Now the time needed in the field can be expressed as a function of the time needed in the laboratory:

$$t_{\min\,val\,field} = \frac{\left(1+\frac{1}{e_{lab}}\right)\cdot K_{hc\,lab}\cdot H_{lab}\cdot W_{field}{}^{2}}{\left(1+\frac{1}{e_{field}}\right)\cdot K_{hc\,field}\cdot H_{field}\cdot W_{lab}{}^{2}}\cdot t_{\min\,val\,lab} \qquad \textbf{(C7 - 45)}$$

With expression (**C7 - 45**) it is possible to determine the minimum extent of the validity of the results presented in this chapter in time *in situ* ($t_{\min\,val\,field}$).

Because care was taken that the laboratory tests correspond to the field/landfill conditions the hydraulic conductivity ($K_{hc\,lab}$ and $K_{hc\,field}$) and the void ratio (e_{lab} and e_{field}) are assumed to be identical. Differences exist in the height of the laboratory sample and the barrier and the height of the leachate table in the laboratory and the landfill. Plausible values for these variables have been given in **Table: C7-7** (*e.g.* overview in Schmitz 2001a).

Table: C7-7

Units needed to find the minimum validity of changes in hydraulic conductivity in time in situ on the basis of the minimum validity in time in the laboratory.

	laboratory	field
W (m)	$20\bullet10^{-3}$	2
H (m)	1	10

With the information in **Table: C7-7** the minimum validity of the extent of time under field/landfill conditions can be expressed in terms of the time in the laboratory (see expression (**C7 - 45**)) as:

$$\frac{t_{\min\,val\,field}}{t_{\min\,val\,lab}} = \frac{1\cdot(2)^{2}}{10\cdot\left(20\cdot10^{-3}\right)^{2}} = 1000$$

Since $t_{\min\,val\,lab}$ had a value in the order of months, the $t_{\min\,val\,field}$ has a value in the order of tens to hundreds of years.
To these ten to hundred of years, one must add the time:
- The clay is separated by the geomembrane *i.e.* the maximum technical life of the geomembrane, during a 30 to 50 years.
- Waste needs to produce leachate.
- Needed for meteoric water to enter the landfill *i.e.* the maximum technical life of the landfill cover.

As to summarise, these values show that the observed phenomena measured in the laboratory and modelled with *LAGAMINE*, which were related to the particle level, outstretch the biological life of the waste and thus the required engineering life of the landfill. Processes like the decrease of the hydraulic conductivity when Tournai clay is leached by brines - modelled with *LAGAMINE* - and the limited interlayer accessibility, will thus be maintained during the engineering life of the barrier. However if the waste confinement exceeds this time span like in the case of confinement of other *e.g.* industrial waste, the processes on the interlayer and TOT/TO level must be taken into account.

C 7.5 Conclusion

In this chapter it was shown how clay - leachate interactions on the particle level *e.g.* during permeation of a clay barrier with leachates can be related to changes in distance between clay particles using the numerical finite element method and the *LAGAMINE* code developed at the University of Liège.

First a constitutive model for interface elements was proposed which was based on the diffuse double layer theory. Subsequently it was shown how this constitutive model was introduced into the numerical code *LAGAMINE*.

Next the simulation of a 2d cross section of two different assemblies of clay particles under oedometer conditions was shown.

The results showed that the interparticle contacts, orientated perpendicular or sub-perpendicular to the principled stress, closed, when the clay was permeated with a fluid with a higher cation concentration or lower dielectric constant than the original interparticle fluid.

It was shown how the closure of interparticle voids could be interpreted in terms of decrease of the hydraulic conductivity at an oedometer scale or at a landfill barrier scale.

C 8 Application examples: Clay-barrier - leachate interaction

With the information contained in this thesis (*e.g.* chapters **C 5**, **C 6** and **C 7**) one is able to determine the interactions between clay barriers and a multitude of fluids this barrier[47] should contain and predict possible decreases / increases of the hydraulic conductivity qualitatively and quantitatively not only for a laboratory sample but at a landfill scale as well.

In the following paragraphs several waste confinement scenarios will be discussed, analysing leachate - clay reactions on the TOT/TO, interlayer and particle level.

C 8.1 Tournai clay - leachate-C, change of hydraulic conductivity in a landfill barrier

C 8.1.1 Introduction

In this first example Tournai clay will confine domestic waste producing leachate-C under stress conditions that resemble those of a modern municipal landfill.

C 8.1.2 Interactions on the TOT/TO level

Interactions on the TOT/TO level were discussed in chapter **B 4**. If a comparison between these interactions and a natural analogue is made, the clay minerals species contained in the Tournai clay will transform completely, with a Kaolinite as possible end-product. This process requires a long time, a long history of subsequent physical and chemical steps in nature to be accomplished. Under normal waste decomposition conditions this transformation will occur after the waste will have been “fossilised” *i.e.* when the waste will not be biological active anymore.

C 8.1.3 Interactions on the interlayer level

On the interlayer level many onsets of mineral alteration have been observed (**Figure: B3-10**). Once these mineral alteration processes will have been completed, major hydraulic and mechanical changes will have affected the clay barrier. However in paragraph **A 3.2.2** and paragraph **C 6.4** it has been shown that the stress conditions to which a landfill barrier is subjected allow only for a very low interlayer accessibility. At least on the short-term leaching (amount of fluid leached through the clay equals a few pore volumes). Under landfill conditions this short-term leaching corresponds to tens to hundred of years as was shown in paragraph **C 7.4.3**.

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[47] *With the information contained in chapters* **C 7** *and* **C 8** *one is able to determine the interactions between clay barriers and a multitude of fluids and additionally one can deduce valuable information concerning the type of remediation of contaminated sites on clayey soils (see Schmitz et al. 2004c).*

C 8.1.4 Interactions on the particle level

The reactions on the particle level are discussed on the basis of the theory in chapter **C 7**:

1) If natural Tournai clay is used, the initial CEMC = 41.3mol/m³ (see **Table: B3-19**).

2) If the initial load at installation is 100kPa, the initial interparticle distance $2D_{meca} = e_2 = 62.4$ Å (**Figure: C8 - 1**).

3) If after some time (30-50 years) the geomembrane is deteriorated, the landfill leachate starts to penetrate the clay barrier.

4) In the case considered here this is leachate-C: The CEMC in the interparticle space will mount to 113mol/m³ (see **Table: B3-19**).

5) During the infill of waste, the vertical effective stress at the base of the landfill will rise to max. 300kPa (see *e.g.* overview in Schmitz 2001a).

6) As a consequence $2D_{meca} = e_2$ will decrease to 36.8 Å (**Figure: C8 - 1**).

7) The ratio $e_{2\ fin}/e_{2\ ini} = 0.6$. As shown in **Figure: C7-16** for an oedometer test, this ratio corresponds to a decrease of the $K_{hc\ fin} = 0.22$ to $0.81 \cdot K_{hc\ ini}$ (clay particle width to height as 1:1 to 100:1).

8) The value measured in the laboratory was at maximum $K_{hc\ fin} = 0.32 \cdot K_{hc\ ini}$ which corresponds to a width to height ratio of 1:4.5.

9) For Tournai clay used as landfill barrier (2m thick, 100m long, width to height ratio 1:4.5) the hydraulic conductivity decreases to 75% of the original value in a leachate-C producing landfill (see **Figure: C7-16**).

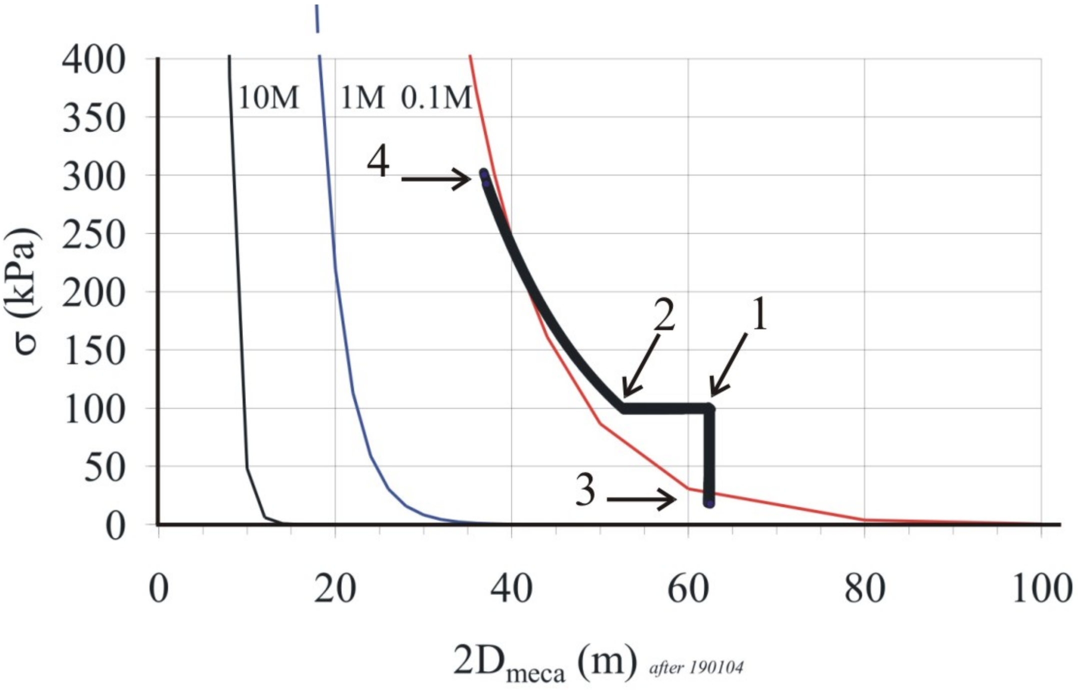

Figure: C8-1

Installation of Tournai clay liner at a vertical stress of 100 kPa (point: 1) Landfill leachate permeates the barrier. The vertical stress is still 100 kPa. The horizontal flow channels narrow (point: 1 to 2). The vertical flow channels remain open (points: 1 to 3). While the concentration increases the vertical effective stress increases to 300 kPa due to the infill of new waste.

C 8.1.5 Conclusion

If Tournai clay will confine domestic waste producing leachate-C under stress conditions resembling those of a modern municipal landfill one does not need to be afraid of a malfunctioning of the clay barrier due to physico-chemical interactions with the leachate. Contrary the leachate will even decrease the hydraulic conductivity. This beneficial process will pertain, up to the end of the biological active life of the waste in tens to hundreds of years after malfunction of the geomembrane. The changes that occur after this stage are highlighted in Part: **Synthesis**.

C 8.2 Barrier for whiskey distillery

C 8.2.1 Introduction

In this second example a hypothetical barrier will be discussed. Imagine that a client, a whiskey distillery, wants to store solid waste soaked in bad quality ethanol in a pond. Imagine that this client has already stored sufficient Tournai clay to be used as liner. How can one quickly assess the possible advantages and disadvantages of this type of storage, possible interactions on the long and the short-term?

C 8.2.2 Interactions on the TOT/TO level

Reactions on the TOT/TO level can be analysed with the method presented in chapter **B 4**. If there is no time for such experiments one can have a look at the clay mineral literature. A brief look at the literature or a call/e-mail to a colleague in this branch shows that on the short-term it is difficult to disintegrate the TOT/TO-layers. Another possibility to test the influence of ethanol with clays on the TOT/TO level on the short-term is to perform a batch tests in which the clay is mixed with ethanol. The slurry obtained by mixing these components can be used to determine the liquid limit or the XRD. In the latter case a destruction of the TOT/TO level would result in a decrease of the clay content or a complete absence of the clay fraction; this corresponds - as one knows from the equivalent basal spacing (chapter **C 5**) - to a decrease of the liquid limit. The author asked for a liquid limit determination of the Tournai - ethanol sample and the results showed a slight increase of the LL and thus the EBS, at least not a decrease. Thus, no destruction of the TOT/TO level will occur.

C 8.2.3 Interaction on the interlayer level

To determine the reactions on the interlayer level one can proceed as discussed above but not to check a complete disintegration of the clays thus a disappearance of the clay fraction from the diffractogram or the complete loss of liquid limit but more in detail to changes in liquid limit and equivalent basal spacing. As discussed above a batch test with Tournai clay and ethanol caused a slight increase of the liquid limit and the EBS. But under oedometer-conditions representing the conditions of a barrier under a landfill it was shown (paragraph **A.3.2** and paragraph **C 6.4**) that the interlayers are not accessible (on the short-term, tens to hundreds of years). If the clay is cured with ethanol the hydraulic conductivity after installation will be even lower than in the case the clay is cured with demineralised water. During permeation with additional ethanol no changes will occur in the latter case.

C 8.2.4 Interactions on the particle level

On a particle level, ethanol behaves like other alcohols. If this behaviour is modelled as was shown in the previous paragraphs (based on the double layer model) the permeation will cause a decrease of the hydraulic conductivity. This was validated by the author using Tournai clay.

C 8.2.5 Conclusion

If the Tournai clay is cured with water and subjected to a significant (few hundred kPa) effective stress there is no evidence that during the next tens to hundreds years the clay minerals will disintegrate. If the effective stress is maintained the interlayers are not accessible. The permeation will cause a decrease of the hydraulic conductivity which is beneficial[48].

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[48] *A warning must be given: some authors measure a large increase of the hydraulic conductivity probably due to (PC Hueckel) loss of contact of clay sample and sidewall of the oedometer during the test, a low effective stress or drying of the sample. On a short-term leaching (several pore volumes, corresponding to several tens of years in a clay barrier) these effects were not observed by the author.*

If the Tournai clay is cured with ethanol the equivalent basal spacing increases (interlayer level) therefore the liquid limit as well. If this clay is used, the initial hydraulic conductivity will be lower as the hydraulic conductivity of the Tournai clay with demineralised water. Upon further permeation with ethanol no changes occur.

C 8.3 Conclusions

Physico-chemical reactions will occur between clays and fluids if:

TOT/TO - level:

$$\frac{TCF_{ini}}{TCF_{fin}} \neq 1 \qquad \textbf{(C8 - 1)}$$

Interlayer level:

$$\frac{EBS_{ini}}{EBS_{fin}} \neq 1 \qquad \textbf{(C8 - 2)}$$

Particle level:

$$\frac{\varepsilon'_{ini} \cdot CEMC_{fin}}{\varepsilon'_{fin} \cdot CEMC_{ini}} \neq 1 \qquad \textbf{(C8 - 3)}$$

The impact of physico-chemical processes on the geomechanical properties of clay increases in the order of the expressions (**C8 - 3**) - (**C8 - 2**) - (**C8 - 1**).

Depending on the value determined for the ratios 5 different cases can be discerned:

I) Ratios of expressions (C8 - 1) and (C8 - 2) much smaller than 1
Physical properties:
The initial material will become more clayey: Larger liquid limit, larger plasticity index, lower friction angle, lower hydraulic conductivity if mixed with the fluid before the test.
Recognisable:
Increase of the total clay mineral fraction in XRD plots or increase of the crystallinity of peaks characteristic of clays. Shift of clay peaks to higher basal spacing values. Increase of the liquid limit, increase of stickiness.

II) Ratios of expressions (C8 - 1) and (C8 - 2) slightly smaller than 1, expression (C8 - 3) much smaller than 1
The differences in Atterberg limits and clay mineralogy are hardly measurable. Differences exist in the measured hydraulic conductivity for clay barriers. It will increase slightly[49].

III) Ratios equal to 1

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[49] *if under oedometric boundary conditions with an exterior effective stress larger than a hundred kPa or more.*

No physico - chemical changes occur. Except for chemical - physical processes like dissolution or precipitation of cementing agents.

IV) Ratios of expressions (C8 - 1) and (C8 - 2) slightly larger than 1, expression (C8 - 3) much larger than 1

The differences in Atterberg limits and clay mineralogy are hardly measurable. Differences exist in the measured hydraulic conductivity for clay barriers. It will decrease slightly[50].

V) Ratios of expressions (C8 - 1) and (C8 - 2) much larger than 1

Physical properties:
The initial clay material will start to loose its clayey behaviour: Lower liquid limit or no determination of liquid limit possible, lower plasticity index, higher friction angle, higher hydraulic conductivity, if mixed with the fluid before the test.
Recognisable:
Decrease of the total clay mineral fraction in XRD plots or absence of peaks characteristic of clays or shift of basal spacings to lower values. Loss of cohesion. Starts to behave silt-like.

Advice:
If a client is concerned about a possible physico - chemical interaction or a new research programme stretching over years is started, it is advised to invest time to check the unity or the non-unity of the three ratios given by expressions (**C8 - 3**) - (**C8 - 2**) - (**C8 - 1**). If these ratios are determined a first assessment of the degree of impact of a clay - fluid/leachate interaction can be determined. With the information contained in **Part: A**, **B** and **C** this first assessment can be fine-tuned to give an accurate qualitative and quantitative nano-engineering geological judgement of clay - leachates interactions.

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[50] *see previous footnote*

C 9 Conclusions

Large changes in geomechanical properties:

- The Smectite treated with salt changed its geomechanical properties with respect to the untreated one to such an extent that the comparison of untreated and treated Smectite is identical to that of two different clays.
- The geomechanical properties of clays are seriously affected by the presence of brines. Cations enter the interlayer space and change the mineralogy on the interlayer level. Therefore the changes in the liquid limit are large.

Consequence of sample homogenisation:

- Kruibeke and Soignies clay suffer more from the homogenisation process (drying at 30°C and grinding) than the Tournai clay.
- An overwhelming part of the standard deviation of the liquid limit test is not due to objective and subjective faults of the tests but to the natural heterogeneity (including the homogenisation) of the tested natural clays.
- The homogenisation process seriously affects clays.

Equivalent basal spacing:

- A link between the result obtained by X-ray diffraction analyses and geomechanical properties can be made using the equivalent basal spacing concept (EBS).
- The equivalent basal spacing takes into account the amount of clay in the sample and the type of clay (Smectite but also Kaolinite and other clay minerals).

Effect of landfill leachate on clay:

- Clays with the highest equivalent basal spacing are most affected by landfill leachates and changes in fluid content (only natural clays).
- With the opening of the data by converting the data into Niggli numbers correlations within the clay mineral data of Tertiary clays-landfill-leachate-mixtures were discerned. Thereby the clay mineral alteration pathways presented in **Figure: B3-10** were validated and an additional one (path 3B) was proposed.
- The influence of the landfill leachate is low compared to the influence of the clay type, *i.e.* leachates were not able to modify the nature of the soils. The clay type is given by its mineralogy, thus its equivalent basal spacing thus its liquid limit. As long as the interlayers are not affected, the equivalent basal spacing does not change and the liquid limit changes only on the particle level, thus the changes are relatively small.
- Batch tests like Atterberg tests in which leachate is mixed with clay to speed up reactions are not representative of the reaction in landfill barriers younger than 100 years because during these batch tests reactions are measured that play on another level of the clay structure (dominantly the interlayer level and less the particle level).
- Landfill leachates and salt solutions cause a considerable increase in heterogeneity and coefficient of variation of the liquid limit of clays: the most in reference Smectite, the least in Soignies and Kruibeke clay.

Permeation of natural clay under oedometer conditions:

- During permeation (oedometer conditions, 100kPa vertical stress, homogenised Tournai clay, hydraulic gradient of max. 50, permeate is KCl solution) the permeate does not enter the interlayer space. The $BS_{AS} = BS_{BSBH}$. Note that the same conclusion was drawn for permeation of Tournai clay with EG.
- Note that no shrinkage occurs (often thought to be responsible for large increases in hydraulic conductivity) but that the pressure drops to 0.
- The void ratio will hardly change during permeation.
- Barriers in landfills containing municipal solid waste landfills younger than:
  - 30 to 50 years will not be leached due to protection by a geomembrane;
  - Older than 50 years: Leachate-clay contact will occur, the hydraulic conductivity will be affected. If the hydraulic conductivity will increase or decrease and to which extent was discussed in chapter **C 7**. The void ratio remains the same, as well as the cation exchange capacity, the shear strength and the specific surface.
  - Older than 100 to 1000 years: The interlayers will be affected. Major changes in hydraulic conductivity will occur. If the hydraulic conductivity will increase or decrease and to which extent was discussed in chapter **C 5**. Once the TOT level is affected, the shear strength, the cation exchange capacity and the specific surface will change drastically (how these properties will change can be assessed with the equivalent basal spacing).
- On particle level the influence of the landfill leachates are dominated by their cation content. NH_4^+ cations will be produced and consumed by the organisms in the landfill and the production depends on the bioactivity and the state of life of the waste. Other cations will not be involved in the biochemical decomposition of the waste and their production is not directly related to the "age" of the landfill. Their origin is inorganic.

Permeation in general:

- If one wants to take advantage of a decrease of the hydraulic conductivity of clays, particles should be oriented perpendicular to the stress and the flow. This can be achieved by oedometric loading to several 100 kPa. In practise this will require some modifications of the common clay liner construction method.
- It has been shown that the form of the clay particle within reasonable variations - *e.g.* height to width ratios up to a factor 100 - is negligible. The relative particle form does not change the void ratio.
- Changes in interparticle fluid composition do not influence the void ratio (or other geomechanical parameters related to the void ratio) as long as the chemicals do not enter the interlayer space. The modifications upon permeation are restricted to the modification of geomechanical properties that are influenced by local changes within the clay structure on a particle level. An example is the hydraulic conductivity, which is influenced by choking of the flow paths. Such localised effects, which do not change other macroscopic parameters, are not easily detectible (see Schmitz *et al* 2002a).
- During permeation interlayers are not accessible. They are accessible during mechanical remoulding. This implies that during permeation the void ratio and related geomechanical parameters do not change measurably.

- Small changes in the dimensions of the pathways (*e.g.* local choking) without large changes in void ratio can have a significant influence on the hydraulic conductivity.
- For realistic values of the particle-particle distance, the space in-between the TOT-layers (*i.e.* the interlayers) dominates the value of the void ratio rather than the void between the particles (*i.e.* the interparticle void).
- If a clay is permeated with a substance that changes the double layer thickness the effect, *e.g.* the decrease of the hydraulic conductivity, is larger in the laboratory than under landfill conditions due to different height to width ratios of the clay sample and the clay barrier. In both cases a decrease of the hydraulic conductivity will occur but this decrease will hardly be noticed under field conditions. This can be quantified. The dimensions of the sample play a role, the effects are exaggerated in the triaxial cell, more than in the oedometer cell; only if platy minerals are used (*e.g.* Smectite) which are oriented perpendicular to the stress, the relative dimensions are less important.

Belgian Tertiary clay deposits:

- Tournai clay possesses the largest natural heterogeneity.
- The equivalent basal spacing showed that natural clays like the Belgian Tertiary clays are in geomechanical terms complex active mixtures of initially pure clays.
- The coefficient of variation and the coefficient of variation describing the natural heterogeneity of the reference Smectite samples cured with demineralised water at the liquid limit is extraordinary low. This reflects that this material (in contrast to the other clays collected by the author) is a well-homogenised industrial product.

Relation between the liquid limit and the plasticity index:

- Especially for clays with a large liquid limit the liquid limit and plasticity index seem to be linearly related even after leachate contact.

Prediction of the liquid limit

- Liquid limit predictions on the basis of the double layer model like the Fam-Dusseault model used for the analyses above do not give correct quantitative predictions of the values of the liquid limit because this model exaggerates the effects on particle level and omits to include the effects on interlayer level.
- Since the changes in liquid limit are best predicted if based on the squeezed-out clay-fluid (*i.e.* the fluid most representative of the interlayer space) it underlines the fact that the liquid limit values are related to the interlayer behaviour.
- The liquid limit depends on reactions on the interlayer and the particle level. Because effects on a lower level - here the interlayer level - are more powerful than changes on a higher level - here represented by the particle level - reactions on the interlayer level may mask reactions on the particle level. Therefore the liquid limit depends on the mineralogy and on the clay-fluid chemistry. Large changes (more than tens of %) occur if substances enter the interlayer space (*i.e.* a mineral alteration). Small changes occur if the fluid chemistry changes the particle to particle arrangement by changes in double layer thickness (less than tens of %). Because clays with low liquid limit have a low equivalent basal spacing, the interlayer is less available: Changes in interlayer level do not occur.

Changes can occur on the higher particle level, but because this level is less fundamental the changes will be smaller.

Mixtures of clay:

- The behaviour of mixtures of clays can be predicted in terms of clay mineralogy (equivalent basal spacing) and Atterberg limits. Different rules apply, depending if the mixtures are reactive (new clay minerals are formed like interlayered clay minerals) or inert.

Physico-chemical reactions will occur between clays and fluids if:

- TOT/TO - level:

$$\frac{TCF_{ini}}{TCF_{fin}} \neq 1 \qquad \textbf{(C8 - 1)}$$

- Interlayer level:

$$\frac{EBS_{ini}}{EBS_{fin}} \neq 1 \qquad \textbf{(C8 - 2)}$$

- Particle level:

$$\frac{\varepsilon'_{ini} \cdot CEMC_{fin}}{\varepsilon'_{fin} \cdot CEMC_{ini}} \neq 1 \qquad \textbf{(C8 - 3)}$$

The impact of physico-chemical processes on the geomechanical properties of clay increases in the order of the expressions (**C8 - 3**) - (**C8 - 2**) - (**C8 - 1**).

Pure Smectites versus natural clays:

- In literature commercial Bentonites (containing predominantly Smectite) are often used in geomechanical tests. In practice an engineer will mostly work with natural clays. Can the results obtained on Smectites be used to predict the behaviour of natural clays?
  - No, because many of distinctly different features of Smectites are related to the fact that Smectite particles consist of one to a few TOT-layers (small N_{layers}, large N_{int}) in contrast to most other clays (large N_{layers}, small N_{int}). Thus Smectite clay samples contain much more interparticle voids which can be transformed to interlayers (increase N_{layers}, decrease N_{int}). Therefore the particle level laws apply to Smectites (fast) up to interlayer formation (large shifts in geomechanical properties and reduction of reaction rate). Especially this transition causes shifts in geomechanical properties for which Smectites are famous. In other clays this transition does not occur (*e.g.* because it had occurred earlier during the geological history of the deposit). Therefore wrong conclusion can be drawn if one wants to analyse the applicability of natural clays as barrier using laws developed for Smectites.

  - No, because commercial Bentonites do not contain the rich melange of ions and acids present in natural clays.

Can batch test be used as first insight into clay - leachate interactions in clay barriers?

- The liquid limit depends on reactions on the interlayer and the particle level. Because effects on a lower level - here the interlayer level - are more powerful to change geomechanical properties than changes on a higher level - here represented by the particle level - reactions on the interlayer level may mask reactions on the particle level. During batch tests the interlayer is more accessible than during percolation tests during which a mechanical stress is applied. Therefore if batch tests, like the liquid limit, are used to represent a first insight into clay - leachate interaction their results must not be interpreted as long-term behaviour *sensu stricto*, thus not as a continuous evolution from the results measured on a short-term (months in laboratory) on a particle level. But the results must be interpreted more (vaguely) as long-term effects when the interlayers will have become more accessible due to a lower effective stress (after rise pore pressure, after failure of the geosynthetic) or after a long history of leaching that ravels the clay particles and renders them more accessible.

Conclusions

During its function as a barrier, clay will be exposed to different mechanical and chemical stresses. Nevertheless it must be guaranteed that the clay will fulfil its barrier function during the necessary waste confinement period. The main question that needed to be answered was:

How can the suitability of a clay to act as barrier to the flow of a specified fluid be determined?

To answer this question first an answer to the following questions had to be found:
- *Which physical or chemical reactions occur once this barrier is permeated by different fluids such as e.g. leachates?*
- *How will these reactions affect the geomechanical properties, like the hydraulic conductivity, of the clays?*
- *Will these reactions cause such large changes that the clay barrier cannot stand to the required task, the confinement of hazardous materials?*

To answer theses question geomechanical tools needed to be used that were in fact poorly understood. Therefore these methods needed to be analysed as well.
- *The results of clay mineral analyses are vaguely interpreted referring only to a qualitative presence or absence of Smectite. Perhaps other minerals equally play an important role.*
- *Batch tests like the Atterberg tests are often thought to represent the long-term behaviour (Arrhenius principle) of clay - fluid interaction. Perhaps even on long-term these interactions will not occur in barriers percolated by fluids.*
- *Results obtained on commercial Bentonites (nice, pure and easy to interpret in the laboratory) are thought to be representative of natural clays (actually used on-site). Perhaps some processes do not occur at all or occur differently in other clays.*

First the conclusions of the questions given above will be given. The method that should be followed to determine if a specific clay is suitable to restrain the flow of a specified fluid will be given in Part: **Synthesis**.

Which physical or chemical reactions occur once this barrier is permeated by different fluids such as e.g. leachates?

- On each level other physical mechanisms steering the geomechanical properties are important.

- On the particle level especially the theory of the diffuse double layer is illustrative to predict changes in properties if the clay is percolated by fluids with different cation concentrations or with other relative dielectric constants than the original fluid phase of the clay. Although the double layer theory is well established, there is no consensus how changes in double layer thickness can be linked to geomechanical properties.

- One must rely on clay mineral analyses by X-ray diffraction to study changes on interlayer level. Many clay mineral alterations are possible but only a few will occur under geomechanical conditions.

- Changes on TO, TOT level need a long history of subsequent physical and chemical steps. But for a few, these have not been reproduced in the laboratory. Therefore one must rely on geological analogues to analyse these changes.

- Dominant clay mineral alteration processes caused by landfill leachate contact are secondary Illitisation and Smectitisation. The clay mineral alterations of the Tertiary clays caused by the different leachates is the same, irrespective of the age of landfill leachate that is used.

- The chemical composition of the fluid phase contained in the Tertiary clays remains important even after homogenisation of the clay. If the fluid phase of the clays is acid the clay-leachate combinations are acid even if the landfill leachates themselves are basic. This clay-fluid in its original or modified form is responsible for the clay mineral alteration processes of Kaolinisation and removal of organic material from the interlayer space of Smectite.

How will these reactions affect the geomechanical properties, like the hydraulic conductivity, of the clays?

- Fluids can change clays at the:

- Particle level.
- Interlayer level.
- TOT- or TO-layer level.

- Physico-chemical reactions will occur between clays and fluids if:

TOT/TO - level:

$$\frac{TCF_{ini}}{TCF_{fin}} \neq 1 \qquad \textbf{(C8 - 1)}$$

Interlayer level:

$$\frac{EBS_{ini}}{EBS_{fin}} \neq 1 \qquad \textbf{(C8 - 2)}$$

Particle level:

$$\frac{\varepsilon'_{ini} \cdot CEMC_{fin}}{\varepsilon'_{fin} \cdot CEMC_{ini}} \neq 1 \qquad \textbf{(C8 - 3)}$$

The impact of physico-chemical processes on the geomechanical properties of clay increases in the order of the expressions (**C8 - 3**) - (**C8 - 2**) - (**C8 - 1**).

- The most impressive changes in geomechanical properties on the interlayer level are caused by the alteration of Illite into a Smectite or vice versa.

- Changes in hydraulic conductivity are caused by modifications on each level: TOT, interlayer and particle. Changes on the particle level are the fastest and therefore the first to occur during testing.

- With the double layer concept the clay mineralogy and clay mineralogical alteration processes, knowledge of the chemical composition of the leachates and of the initial fluid contained in the clays the observed changes in Atterberg limits upon leachate contact can be explained.

- Once the clay mineral alteration processes during permeation of domestic landfill leachate through the Tertiary clay barrier are recognised comparison to natural analogues can be made to predict the behaviour of the clay barrier on the long-term. Based on this knowledge suitable clay deposits can be chosen to limit the changes in geomechanical and clay mineral alteration properties during the technical life of the clay barrier.

- Large changes in geomechanical properties: The Smectite treated with salt changed its geomechanical properties with respect to the untreated one to such an extent that the comparison of untreated and treated Smectite is identical to that of two different clays.

- Large changes in geomechanical properties: The geomechanical properties of clays are seriously affected by the presence of brines. Cations enter the interlayer space and change the mineralogy on the interlayer level. Therefore the changes in the liquid limit are large.

- Effect of landfill leachate on clay: Landfill leachates and salt solutions cause a considerable increase in heterogeneity and coefficient of variation of the liquid limit of clays: the most in reference Smectite, the least in Soignies and Kruibeke clay.

- Permeation in general: It has been shown that the form of the clay particle within reasonable variations - *e.g.* height to width ratios up to a factor 100 - is negligible. The relative particle form does not change the void ratio.

- Permeation in general: Changes in pore fluid composition do not influence the void ratio (or other geomechanical parameters related to the void ratio) as long as the chemicals do not enter the interlayer space. The modifications upon permeation are restricted to the modification of geomechanical properties that are influenced by local changes within the clay structure on a particle level. An example is the hydraulic conductivity, which is influenced by choking of the flow paths. Such localised effects, which do not change other macroscopic parameters, are not easily detectible.

- Permeation in general: Small changes in the dimensions of the pathways (*e.g.* local choking) without large changes in void ratio can have a significant influence on the hydraulic conductivity.

- Permeation in general: For realistic values of the particle-particle distance, the space in-between the TOT-layers (*i.e.* the interlayers) dominates the value of the void ratio rather than the void between the particles (*i.e.* the interparticle void).

- Prediction of the liquid limit: Liquid limit predictions on the basis of the double layer model like the Fam-Dusseault model used for the analyses above do not give correct quantitative predictions of the values of the liquid limit because this model exaggerates the effects on particle level and omits to include the effects on interlayer level.

- Prediction of the liquid limit: Since the changes in liquid limit are best predicted if based on the squeezed-out clay-fluid (*i.e.* the fluid most representative of the interlayer space) it underlines the fact that the liquid limit values are related to the interlayer behaviour.

- Prediction of the liquid limit: The liquid limit depends on reactions on the interlayer and the particle level. Because effects on a lower level - here the interlayer level - are more powerful than changes on a higher level - here represented by the particle level - reactions on the interlayer level may mask reactions on the particle level. Therefore the liquid limit depends on the mineralogy and on the clay-fluid chemistry. Large changes (more than tens of %) occur if substances enter the interlayer space (i.e. a mineral alteration). Small changes occur if the fluid chemistry changes the particle to particle arrangement by changes in double layer thickness (less than tens of %). Because clays with low liquid limit have a low equivalent basal spacing, the interlayer is less available: Changes in interlayer level do not occur. Changes can occur on the higher particle level, but because this level is less fundamental the changes will be smaller.

Will these reactions cause such large changes that the clay barrier cannot stand to the required task, the confinement of hazardous materials?

- Upon clay - fluid contact physical and chemical reactions take place on the TOT/TO-, interlayer and particle level of clays. Thereby geomechanical properties like the hydraulic conductivity can change. Changes on the particle level are the fastest and are therefore the first to occur during testing. Depending on the boundary conditions the same fluid - clay combination can show different behaviour. These boundary conditions should correspond to those in a barrier to determine if the barrier will still function properly after e.g. leachate contact.

- The hydraulic conductivity of the Tertiary Tournai, Kruibeke and Soignies clays, does not change or decreases slightly, when percolated by landfill leachates (representative of domestic landfill leachates in humid regions) with respect to the hydraulic conductivity measured with water. Other geomechanical properties, elastic (*e.g.* Young's modulus) and plastic (*e.g.* friction angle) are barely affected by landfill leachate percolation.

- The clay mineral alteration processes and changes in geomechanical properties are small. Tournai clay remains Tournai clay, Soignies clay remains Soignies clay and Kruibeke clay remains Kruibeke clay. The alteration processes introduce scatter but not substantial change.

- Effect of landfill leachate on clay: The influence of the landfill leachate is low compared to the influence of the clay type, *i.e.* leachates were not able to modify the nature of the soils. The clay type is given by its mineralogy, thus its equivalent basal spacing thus its liquid limit. As long as the interlayers are not affected, the equivalent basal spacing does not change and the liquid limit changes only on the particle level, thus the changes are relatively small.

- Permeation of natural clay under oedometer conditions: During permeation (oedometer conditions, 100kPa vertical stress, homogenised Tournai clay, hydraulic gradient of max. 50, permeate is KCl solution) the permeate does not enter the interlayer space. The $BS_{AS} = BS_{BSBH}$. Note that the same conclusion was drawn for permeation of Tournai clay with EG.

- Permeation of natural clay under oedometer conditions: Depending on the orientation of the clay-clay interfaces with respect to the exterior compressive stress and the composition of the percolating fluid, the stress perpendicular to the compressive stress can decrease to zero but no tensile stresses are generated. Therefore no shrinkage occurs (often thought to be responsible for large increases in hydraulic conductivity).

- Permeation of natural clay under oedometer conditions: The void ratio will hardly change during permeation.

- Permeation of natural clay under oedometer conditions: Barriers in landfills containing municipal solid waste landfills younger than:
  - 30 to 50 years will not be leached due to protection by a geomembrane;
  - Older than 50 years: Leachate-clay contact will occur, the hydraulic conductivity will be affected. If the hydraulic conductivity will increase or decrease and to which extent was discussed in chapter **C 7**. The void ratio remains the same, as well as the cation exchange capacity, the shear strength and the specific surface.
  - Older than 100 to 1000 years: The interlayers will be affected. Major changes in hydraulic conductivity will occur. If the hydraulic conductivity will increase or decrease and to which extent was discussed in chapter **C 5**. Once the TOT level is affected, the shear strength, the cation exchange capacity and the specific surface will change drastically (how these properties will change can be assessed with the equivalent basal spacing).

- Permeation in general: During permeation interlayers are not accessible. They are accessible during mechanical remoulding. This implies that during permeation the void ratio and related geomechanical parameters do not change measurably.

- Permeation in general: If one wants to take advantage of a decrease of the hydraulic conductivity of clays, particles should be oriented perpendicular to the stress and the flow. This can be achieved by oedometric loading to several 100kPa. In practise this will require some modifications of the common clay liner construction method.

- Permeation in general: If a clay is permeated with a substance that changes the double layer thickness the effect, e.g. the decrease of the hydraulic conductivity, is larger in the laboratory than under landfill conditions due to different height to width ratios of the clay sample and the clay barrier. In both cases a decrease of the hydraulic conductivity will occur but this decrease will hardly be noticed under field conditions. This can be quantified. The dimensions of the sample play a role, the effects are exaggerated in the triaxial cell, more than in the oedometer cell; only if platy minerals are used (e.g. Smectite) which are oriented perpendicular to the stress, the relative dimensions are less important.

The results of clay mineral analyses are vaguely interpreted referring only to a qualitative presence or absence of Smectite. Perhaps other minerals equally play an important role.

- It has been shown that other clay minerals play a role. This role can be analysed with the equivalent basal spacing: The equivalent basal spacing takes into account the amount of clay in the sample and the type of clay (Smectite but also Kaolinite and other clay minerals).

- A link between the result obtained by X-ray diffraction analyses and geomechanical properties can be made using the equivalent basal spacing concept (EBS).

- Effect of landfill leachate on clay: Clays with the highest equivalent basal spacing are most affected by landfill leachates and changes in fluid content (only natural clays).

Batch tests like the Atterberg tests are often thought to represent the long-term behaviour (Arrhenius principle) of clay - fluid interaction. Perhaps even on long-term these interactions will not occur in barriers percolated by fluids.

- Atterberg tests depend on the clay mineralogy but also on the chemistry of the fluid contained in the clay. It is a very potent tool to analyse the activity of clay - leachate interactions.
- Effect of landfill leachate on clay: Batch tests like Atterberg tests in which leachate is mixed with clay to speed up reactions are not representative of the reaction in landfill barriers younger than 100 years because during these batch tests reactions are measured that play on another level of the clay structure (dominantly the interlayer level and less the particle level).
- Can batch test be used as first insight into clay - leachate interactions in clay barriers? The liquid limit depends on reactions on the interlayer and the particle level. Because effects on a lower level - here the interlayer level - are more powerful to change geomechanical properties than changes on a higher level - here represented by the particle level - reactions on the interlayer level may mask reactions on the particle level. During batch tests the interlayer is more accessible than during percolation tests during which a mechanical stress is applied. Therefore if batch tests, like the liquid limit, are used to represent a first insight into clay - leachate interaction their results must not be interpreted as long-term behaviour *sensu stricto*, thus not as a continuous evolution from the

results measured on a short-term (months in laboratory) on a particle level. But the results must be interpreted more (vaguely) as long-term effects when the interlayers will have become more accessible due to a lower effective stress (after rise pore pressure, after failure of the geosynthetic) or after a long history of leaching that ravels the clay particles and renders them more accessible.

Results obtained on commercial Bentonites (nice, pure and easy to interpret in the laboratory) are thought to be representative of natural clays (actually used on-site). Perhaps some processes do not occur at all or occur differently in other clays.

- Pure Smectites versus natural clays: In literature commercial Bentonites (containing predominantly Smectite) are often used in geomechanical tests. In practice an engineer will mostly work with natural clays. Can the results obtained on Smectites be used to predict the behaviour of natural clays?

  No, because many of distinctly different features of Smectites are related to the fact that Smectite particles consist of one to a few TOT-layers in contrast to most other clays. Thus Smectite clay samples contain much more interparticle voids which can be transformed to interlayers. Therefore the particle level laws apply to Smectites (fast) up to interlayer formation (large shifts in geomechanical properties and reduction of reaction rate). Especially this transition causes shifts in geomechanical properties for which Smectites are famous. In other clays this transition does not occur (*e.g.* because it had occurred earlier during the geological history of the deposit). Therefore wrong conclusion can be drawn if one wants to analyse the applicability of natural clays as barrier using laws developed for Smectites.

  No, because commercial Bentonites containing Smectites do not contain the rich melange of ions and acids present in natural clays.

In addition new geological and geomechanical information of the clay deposits and suggestions related to the construction of a barrier will be given

- The difference in clay mineralogy and geomechanical properties between the two Ypresian clays (Soignies and Tournai clay) is sometimes even larger than the difference between an Ypresian clay and the Rupelian clay (Kruibeke). The data of one lithological unit as a whole is only of limited use. Thus a detailed analysis (clay mineralogical and geomechanical) of each outcrop is needed.

- F^- and SiO_2 in Belgian Tertiary clays are of volcanic origin and deposited with the neoformed Montmorillonite and are freed from the matrix during the homogenisation process.

- To avoid processes related to an acid attack (*e.g.* on short-term the Kaolinisation of Chlorite and removal of organic material from the interlayer space of Montmorillonite) the clay has to be installed directly after excavation. If the clay is not pretreated, the clay has to be installed and covered directly after excavation to avoid oxidation of *e.g.* pyrite. Note that the pH of domestic landfill leachates in humid regions is nearly neutral.

- Next to a compulsory investigation into the nature of the leachates and the mineralogy of the clays, one must also pay attention to the nature of the fluid phase contained in the clay for each batch of excavated clay separately.

- Mixtures of clay: The behaviour of mixtures of clays can be predicted in terms of clay mineralogy (equivalent basal spacing) and Atterberg limits. Different rules apply, depending if the mixtures are reactive (new clay minerals are formed like interlayered clay minerals) or inert.

- Consequence of sample homogenisation: The homogenisation process seriously affects clays.

- Consequence of sample homogenisation: Kruibeke and Soignies clay suffer more from the homogenisation process (drying at 30°C and grinding) than the Tournai clay.

- Consequence of sample homogenisation: An overwhelming part of the standard deviation of the liquid limit test is not due to objective and subjective faults of the tests but to the natural heterogeneity (including the homogenisation) of the tested natural clays.

- Permeation of natural clay under oedometer conditions: On particle level the influence of the landfill leachates are dominated by their cation content. NH_4^+ cations will be produced and consumed by the organisms in the landfill and the production depends on the bioactivity and the state of life of the waste. Other cations will not be involved in the biochemical decomposition of the waste and their production is not directly related to the “age” of the landfill. Their origin is inorganic. Their mobility towards the clay barrier is however related to the biochemical conditions.

- Belgian Tertiary clay deposits: Tournai clay possesses the largest natural heterogeneity.

- Belgian Tertiary clay deposits: The equivalent basal spacing showed that natural clays like the Belgian Tertiary clays are in geomechanical terms complex active mixtures of initially pure clays.

- Belgian Tertiary clay deposits: The coefficient of variation and heterogeneity of the reference Smectite samples cured with demineralised water at the liquid limit is extraordinary low. This reflects that this material (in contrast to the other clays collected by the author) is a well-homogenised industrial product.

- Relation between the liquid limit and the plasticity index: Especially for clays with a large liquid limit the liquid limit and plasticity index seem to be linearly related even after leachate contact.

Synthesis

How can the suitability of a clay to act as barrier to the flow of a specified fluid be determined?

Because there was no standard approach to answer this question a suitable approach has been developed (see **Figure: S-1**).

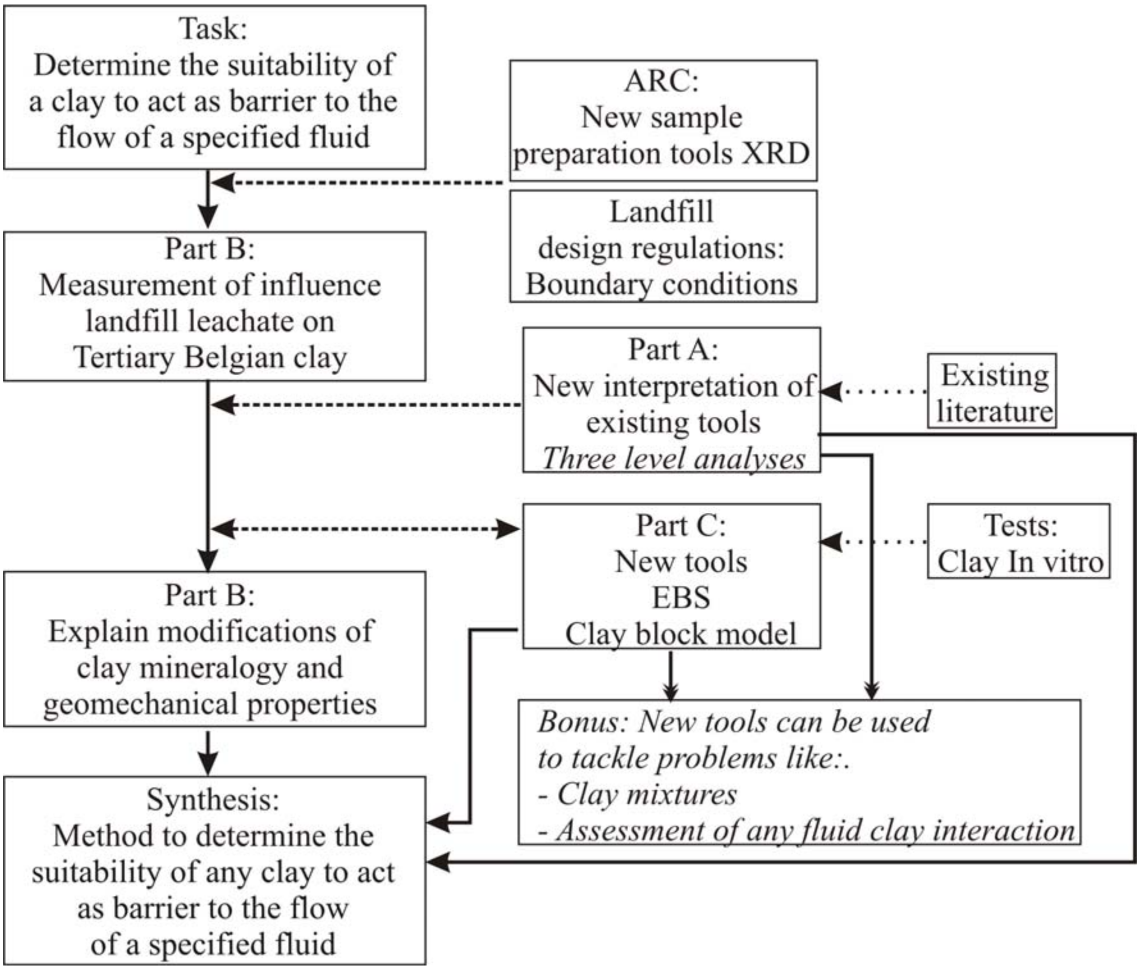

Figure: S-1

Synthesis of this thesis.

Based on literature a new approach was developed separating physical, chemical and mineralogical processes between clays and leachates in reactions on the (see **Table: S-1**):

- Particle level, see **Figure: S-3**,
- Interlayer level, see **Figure: S-4**,
- TOT/TO level, see **Figure: S-5**,

of a clay.

Table: S-1

The three different levels on which a nano-engineering geological analysis should be based

	Level		
	TOT/TO	Interlayers	Particles
Time needed for alteration in nature	Longest	↔	Shortest
Degree of modification of geomechanical properties	Largest	↔	Smallest
Information needed Greek letters refer to Figures: S2-S5. The analyses methods are illustrated in Figure: S-2.	ζ: Analyses of thin sections combined with X-ray diffraction analyses of samples subjected to leaching tests might lead to the identification of an appropriate natural analogue	α: Chemical analyses of the fluid contained in the clay sample obtained by squeezing the sample gives information about the interlayer and interparticle fluid ε: X-ray diffraction analyses allows the determination of the equivalent basal spacing (EBS)	α: Chemical analyses of the fluid contained in the clay sample obtained by mixing the clay powder with large amounts of demineralised water (contact fluid) gives information about the interparticle fluid β: Chemical analyses of the fluid contained in the clay sample obtained by squeezing the sample gives information about the interlayer and interparticle fluid γ: Oedometer test with percolation of brines gives information about the particle size δ: The analyses of thin sections informs about the particle to particle arrangement
Example of mineralogical or physical or chemical processes	e.g. Podzolisation	Illitisation, Smectitisation Chloritisation	Electrostatic interactions Dissolution/precipitation (e.g. Calcite)
Summary given in:	Figure: S-5	Figure: S-4	Figure: S-3

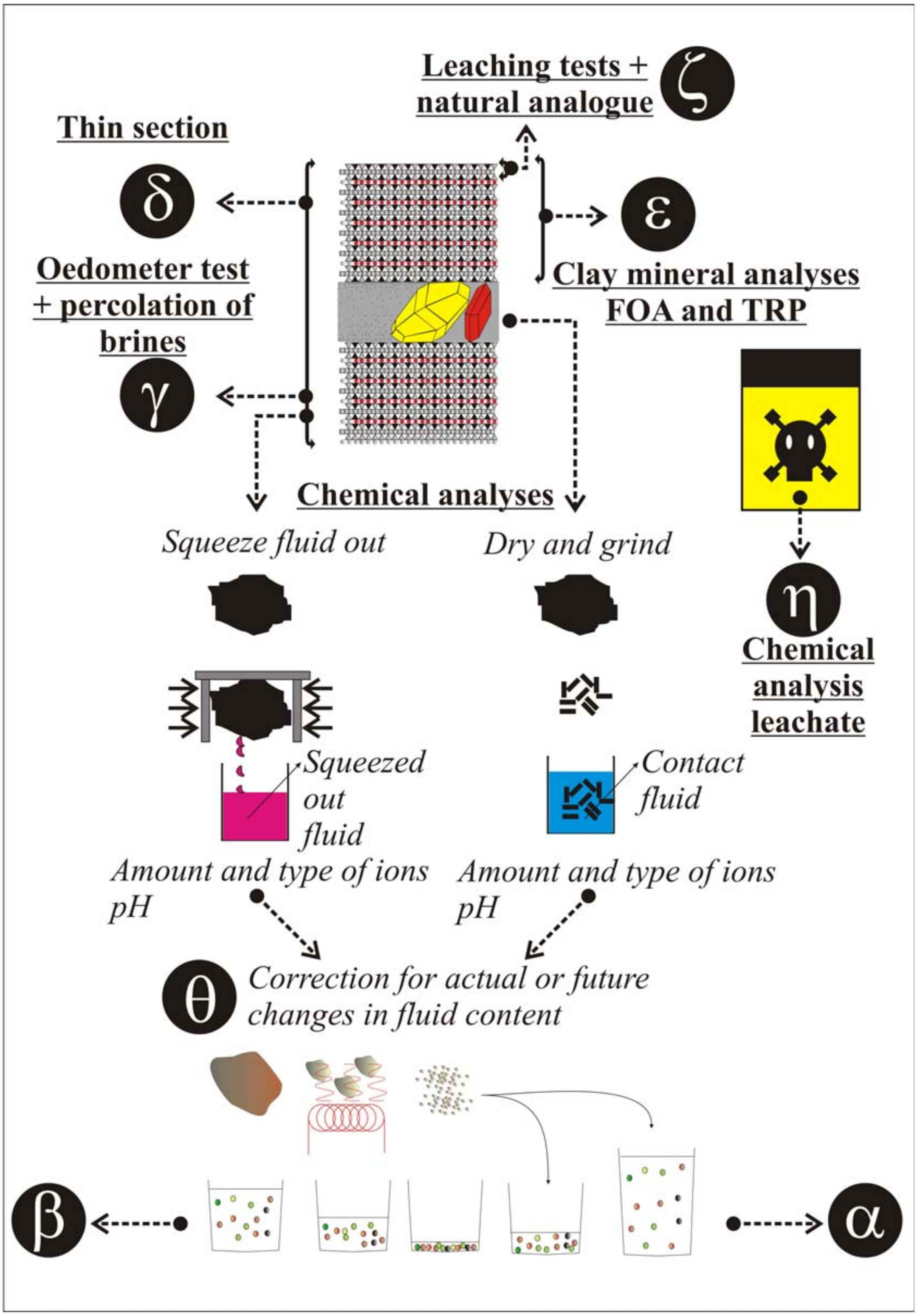
Leaching tests +
natural analogue
ζ
Thin section
δ
ε
Oedometer test
+ percolation of
brines
Clay mineral analyses
FOA and TRP
γ
Chemical analyses
Squeeze fluid out
Dry and grind
η
Chemical
analysis
leachate
Squeezed
out
fluid
Contact
fluid
Amount and type of ions
pH
Amount and type of ions
pH
θ
Correction for actual or future
changes in fluid content
β
α

Figure: S-2

In this figure the information needed to assess the impact of clay-leachate interaction is shown. ***α:*** *Chemical analyses of the fluid contained in the clay sample obtained by mixing the clay powder with large amounts of demineralised water (contact fluid) gives information about the interparticle fluid.* ***β:*** *Chemical analyses of the fluid contained in the clay sample obtained by squeezing the sample gives information about the interlayer and interparticle fluid.* ***γ:*** *Oedometer test with percolation of brines gives information about the clay particle size.* ***δ:*** *The analyses of thin sections informs about the particle to particle arrangement.* ***ε:*** *X-ray diffraction analyses allows the determination of the EBS.* ***ζ:*** *Analyses of thin sections combined with X-ray diffraction analyses of samples subjected to leaching tests might lead to the identification of an appropriate natural analogue.* ***η:*** *Analyses of the chemical composition of the leachates which will contact the clay.* ***θ*** *a correction needs to be made for the concentration changes due to changes in fluid content of the clay during analysis and future engineering use in the field.*

More information (figures on 1:1 scale) can be found in:
α,β: *§ B 3.1.3, B 3.4.3, B 3.6.2.4*
γ: *§ C 6.3*
δ: *§ C 6.2*
ε: *§ B 3.1.2, C 5.2.4*
ζ: *§ B 4.2*
η: *§ B 3.4.3*
θ: *§ C 3*

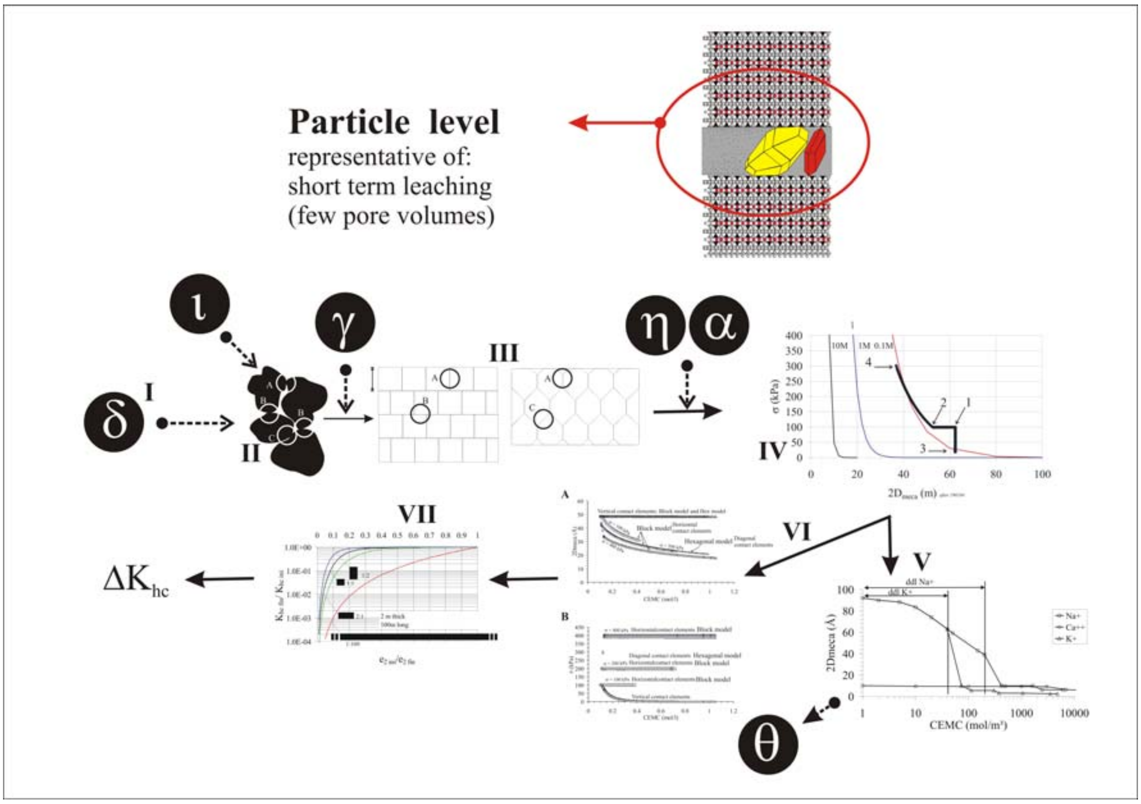

Figure: S-3

Clay-fluid interaction on the particle level.

*(**I**) The analysis of thin sections **(δ)** informs about the particle to particle arrangement (**II**). Together with information from oedometer test with percolation of brines (**γ**) the clay particle size can be determined. With this information the clay sample can be reproduced as discontinuous homogenised arrangement of particles (**III**). Analysis of the chemical composition of the leachates (**η**) that will percolate through the clay and the analysis of the initial composition of the interparticle fluid (**α**) is needed to determine how the interparticle distance changes during percolation (**IV**). Depending on the concentration of cations (**V**) an interparticle contact can be transformed into an interlayer (**θ**). If the concentration remains low, double layers remain existent (**V**). Next the changes in the interparticle distance can be determined for complex clay particle arrangements (**VI**). The information about the change in interparticle distance can be related to a change in hydraulic conductivity in the barrier, with the appropriate extrapolation law (**VII**).*

More information (figures on 1:1 scale) can be found in:
*I: § C 6.2 ; II, III:Figure: C7-8 ; IV: Figure: C7-1 ; V: Figure: C7-2 ; VI: Figure: C7-12 ; VII: Figure: C7-16 ; θ: An interlayer is formed, proceed to Figure: S-4 ; α: § B 3.1.3, B 3.4.3, B 3.6.2.4 ; γ: § C 6.3 ; δ: § C 6.2 ; η: § B 3.4.3 ; ι: A new particle-particle contact is formed from an interlayer (see **Figure: S-4**).*

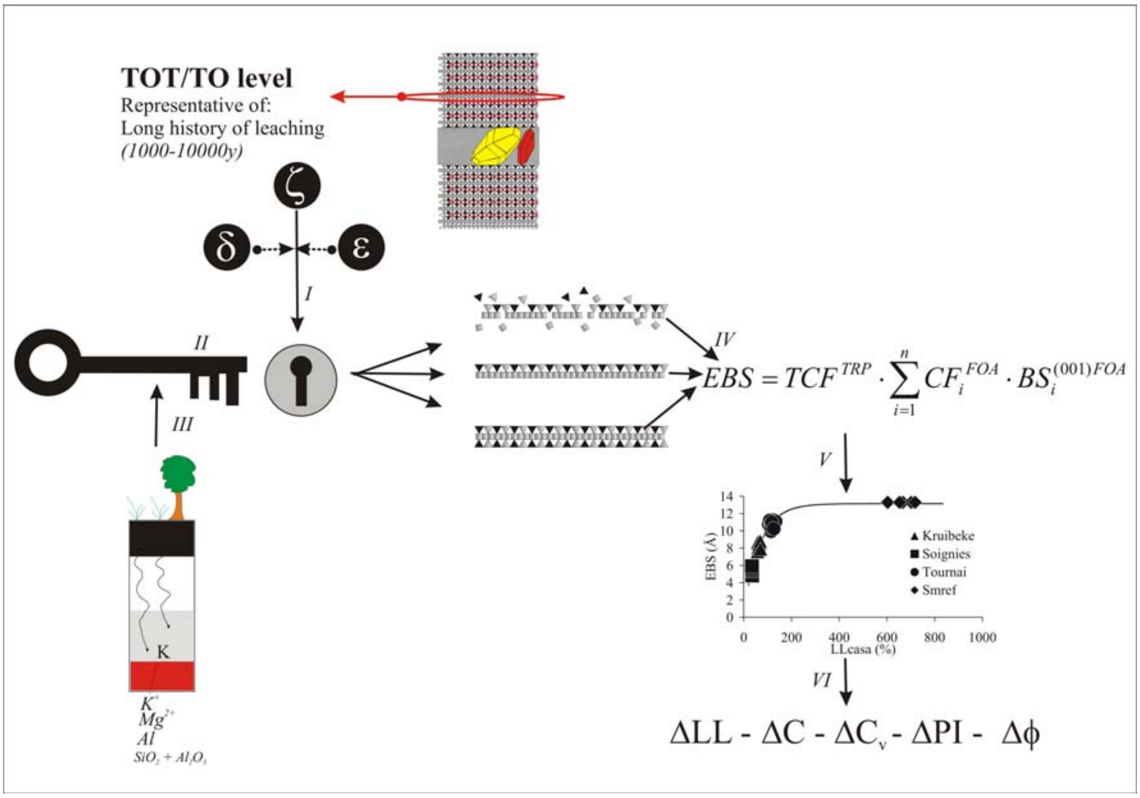

Figure: S-5

Clay-fluid interaction on the TOT/TO level.

*The leaching pathway of samples leached in the laboratory during long periods can be analysed in thin sections (**δ**). Together with a XRD analysis (**ε**) of different locations in this section (**ζ**), this can lead to the recognition of an identical process in nature (**I, III**). With this information the key (**II**) has been found which opens the door to information about the duration of the processes and the involved changes on interlayer level if the recognised process is followed to completion (often 1000-10000 years). These changes can be expressed as changes in equivalent basal spacing (**IV**). In the case that the TOT- or TO-layers are completely disintegrated the EBS→0. Since the EBS can be correlated (**V**) to other geomechanical properties, the frictional shear strength, the hydraulic conductivity etc. the impact on the changes on the TO/TOT level can be interpreted in engineering terms.*

More information (figures on 1:1 scale) can be found in:
III: Figure: B 4-1 ; V: Figure: C5-3, Figure: C5-4 ; δ: § C 6.2 ; ε: § B 3.1.2, C 5.2.4 ; ζ: B 4.2

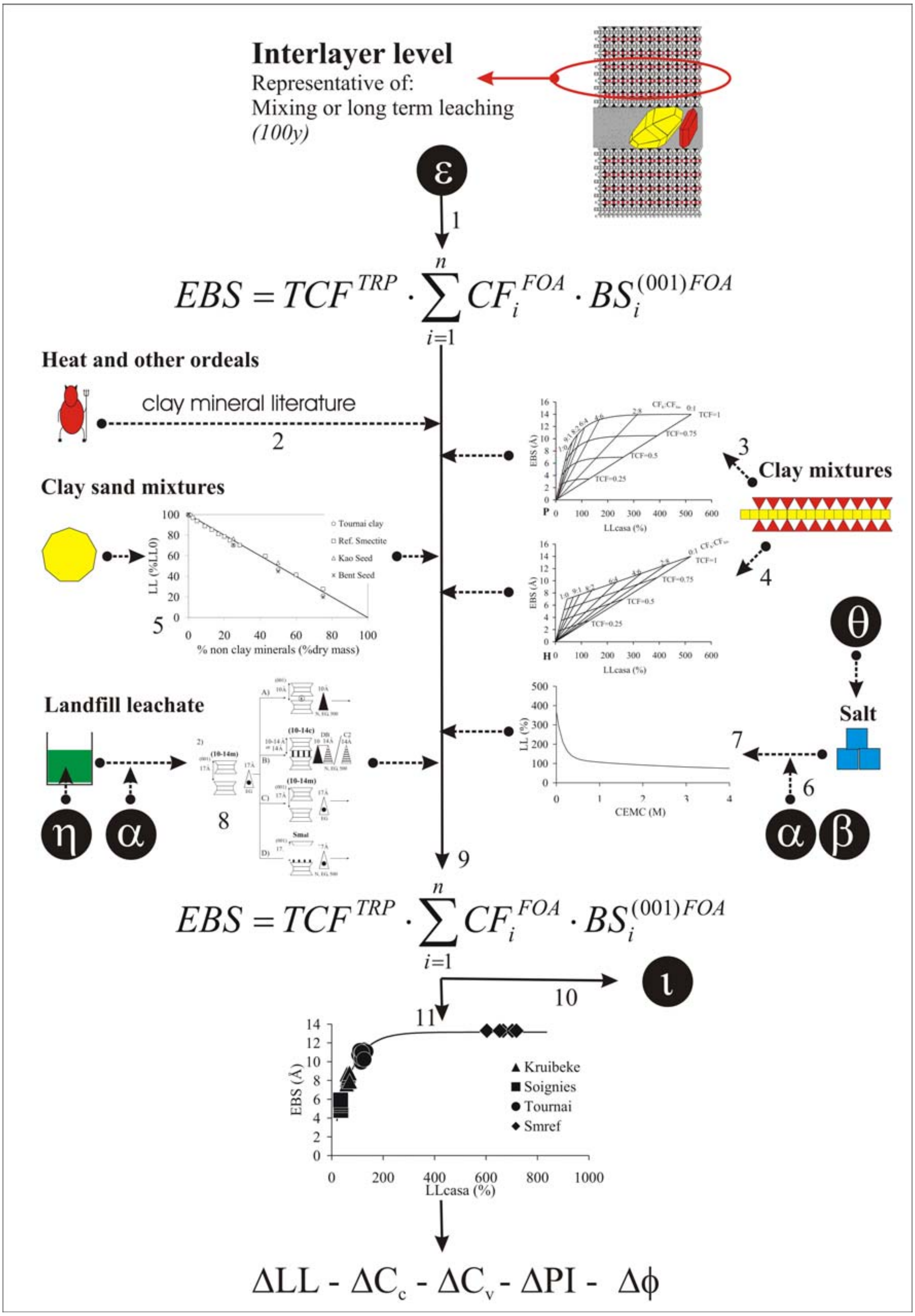
Interlayer level
Representative of:
Mixing or long term leaching
(100y)
ε
1
EBS = TCF^TRP · Σ_{i=1}^{n} CF_i^FOA · BS_i^(001)FOA
Heat and other ordeals
clay mineral literature
2
Clay sand mixtures
LL (%LL0)
% non clay minerals (%dry mass)
Tournai clay
Ref. Smectite
Kao Seed
Bent Seed
5
Clay mixtures
3
4
EBS (Å)
LLcasa (%)
TCF=1
TCF=0.75
TCF=0.5
TCF=0.25
P
H
θ
Salt
7
6
α β
LL (%)
CEMC (M)
Landfill leachate
η α
8
9
EBS = TCF^TRP · Σ_{i=1}^{n} CF_i^FOA · BS_i^(001)FOA
10
ι
11
EBS (Å)
LLcasa (%)
Kruibeke
Soignies
Tournai
Smref
ΔLL - ΔC_c - ΔC_v - ΔPI - Δϕ

Figure: S-4

Clay-fluid interaction on the interlayer level.
*With the X-ray diffraction analyses (**1**,**ε**) of the clay sample the individual clay species contained in the clay sample and the equivalent basal spacing (**1**) of the clay sample can be determined.*
*- If the clay is heated during its life as a barrier, it is unknown how the clay as an entity reacts but (**2**) the behaviour of the individual clay species can readily be found in literature (e.g. this thesis). With this information the new equivalent basal spacing can be determined (**9**). With other ordeals, addition of ethanol etc. one can proceed in the same manner.*
*- If the clay is mixed with other clays and these mixtures are inert, a nomogramme can be constructed to determine the liquid limit of any clay-clay-sand mixture (**3**). If active clays are mixed the mixtures will follow the clay mineral alteration curve (**11**). Nomogrammes can be constructed for this case as well (**4**).*
*- If clays are mixed with sands or other non-clayey substances the equivalent basal spacing can be calculated to find the liquid limit of the mixture (**5**).*
*- If salts are added to the clay interparticle spaces can be transformed into interlayers (**θ**). With information on the composition of the original fluids (**6**) that are contained in the clay (**α,β**) the change in liquid limit of any clay can be determined with an empirical formulation (**7**). If this information is transformed into equivalent basal spacing values (**9**) the amount of precipitated salt grains can be determined.*
*- Mineral alteration pathways have been determined (**8**) for the interaction between genuine landfill leachates and the tested Tertiary clays. The completion of such a mineral alteration can be expressed in terms of (**9**) equivalent basal spacing of the original (**1**) clay.*
*With these procedures any ordeal can be transformed into a change of the equivalent basal spacing. With appropriate links (**12**) to other geomechanical properties the impact of any clay mineral alteration can be analysed in geomechanical terms.*

More information (figures on 1:1 scale) can be found in:
1 :§ ***C 5.2.4***
2: § ***C 5.3.1****,* ***C 5.3.3***
3,4: § ***C 5.3.2****,* ***Figure: C5-14***
5: ***Figure: C5-7***
6: see α,β
7: ***Figure: C5-17***
8: ***Figure: B3-10***
9: § ***C5.2.4***
10: see ι
11: ***Figure: C5-3****,* ***Figure: C5-4***
α,β: § ***B 3.1.3****,* ***B 3.4.3****,* ***B 3.6.2.4***
ε: § ***B 3.1.2****,* ***C 5.2.4***
η:§ ***B 3.4.3***
θ: An interparticle contact transforms into an interlayer (see ***Figure: S-3****).*
ι: An interlayer transformed into an interparticle contact, proceed to ***Figure: S-3***

New tools that were developed on the **interlayer level** were:

- The equivalent basal spacing (EBS).
- Relation between the equivalent basal spacing and the liquid limit.

With these tools a link can be made between the clay mineralogy and geomechanical properties.

With these tools, not only the leachate clay interactions can be analysed but other processes can be described quantitatively as well.

The liquid limit of:

- Complex inert or active sand-clay mixtures can be predicted
- Multi-mineral clays upon heating can be predicted
- *etc.*

With existing correlations between the liquid limit and other geomechanical properties (which were shown to be valid for the Tournai, Kruibeke and Soignies clay as well as for the reference Smectite and Kaolinite) the changes in liquid limit can be related to changes in the consolidation coefficient, the hydraulic conductivity and the frictional shear strength *etc.*

New tools that were developed on the **particle level** were:

- Integration of the chemistry of the natural fluids contained in the clay in further analyses.
- The discretisation of clay samples into discontinuous but homogeneous discrete clay particle with the use of information from thin sections and oedometer tests.
- The implementation of a constitutive law into a numerical code to simulate the interparticle distance to interparticle fluid chemistry and mechanical stress.

New tools that were developed on the **TO/TOT level** were:

- The link between the clay leached in the laboratory to natural analogues using thin sections and XRD diffraction analyses.

With these tools it was possible to respond to the question: How can the suitability of Tertiary natural clays to act as barrier to the flow municipal landfill leachates be determined?

Based on **Figures: S2**, **S3**, **S4** and **S5**:

Tertiary clays, municipal landfill leachates - Waste containment period I (From the time the clay barrier is contacted by municipal waste leachate to the end of the biological life of landfill waste, period from 30-50 years after construction to +/- first 100 years after construction)

What happens on the particle level:

- Oxidation of pyrite, decrease pH.
- Changes in interparticle distance.
- As long as the clay particles are oriented perpendicular to the principle stress the percolation with leachates will not increase the hydraulic conductivity. Even a slight decrease is possible.

- The workability of the clays to construct the liner decreases in the order: Tournai, Kruibeke, Soignies clay. Whereas the workability of Tournai clay is outside the limit given by the ManWal (2000).
- The hydraulic conductivity decreases in the order: Tournai, Kruibeke, Soignies clay. Whereas the hydraulic conductivity of the Soignies clay is close to the limit given by the ManWal (2000).

What happens on the interlayer level:

- Onset of various mineral alteration processes: however, due to the restricted accessibility of the interlayers, under boundary conditions corresponding to those of a landfill clay barrier, these processes will not continue to the end.
- The susceptibility for mineral alteration decreases in the order: Tournai, Kruibeke, Soignies clay.

What happens on the TOT/TO level:

- Nothing happens.

Tertiary clays, municipal landfill leachates - Waste containment period II (From 100 years onwards)

What happens on the particle level:

- Increase particle size due to Podzolisation, decrease hydraulic conductivity, in the case Tournai clay is used.
- Decrease particle size due to Podzolisation, increase hydraulic conductivity, in the case Soignies clay is used.
- Least change if Kruibeke clay is used.

What happens on the interlayer level:

- Transformation of other mineral species into a Kaolinite.

What happens on the TOT/TO level:

- Destruction of the TOT clay minerals due to Podzolisation.

Tertiary clays, municipal landfill leachates - conclusion:

In **Table: S-2** is a summary of the suitability of the Soignies Kruibeke and Tournai as clay barrier to confine domestic landfill waste is given. As shown previously the clay deposits are heterogeneous therefore the results of this table are not omnivalent (see ManWal 2000 for details about the heterogeneity).

Table: S-2

Overview of different parameters related to the suitability of the three tested natural clays to be used as barrier clay to confine domestic waste..

	Soignies clay	Kruibeke clay	Tournai clay
Excavability (natural clay) (1)	+	?	++
Workability (homogenised clay) (2)	+	+	-
Acid attack of geomembrane by the clay (homogenised clay; natural clay between brackets) (3)	+ (-)	- (-)	+ (-)
Hydraulic conductivity (2)	+/-	++	++
Changes hydraulic conductivity during the next tens to hundreds of years (4) with respect to test with water	+	+/-	+
Changes hydraulic conductivity after tens to hundreds of years (4)	+	+/-	-

++ = *(2) Well within limits (ManWal 2000) - (1) good*
\+ = *(2) Within limits - (1) reasonable - (4) favourable change - (3)* No acid attack
+/- = *(2) Just within limits - (4) hardly any change*
\- = *(2) Outside limits - (3) acid attack possible - (4) non favourable change*

It is obvious that waste containment is relative. Although the clay barrier will retain the waste with its initial properties (the hydraulic conductivity will not change) it will still allow the leachate to pass, although very slowly. On the long-term its properties will change drastically. Fortunately, the municipal waste will have been fossilised by then. On the short-term the percolation of landfill leachate (as long as the clay particles are oriented perpendicular to the principle stress) will not increase the hydraulic conductivity. Even a slight decrease is possible.

With the methods developed in this thesis it is very thrilling to analyse existing literature with the new interpretation in mind or to think about the feasibility of possible engineering applications of clay without having them even tested.

I hope that the reader of this thesis will learn from this and enjoy it as much as I did.

Outlook

In this chapter a brief outlook, part pedagogical part dependent on advances in other domains of science, is given of what the future will hold based on the application of the knowledge presented in this thesis:

- No civil-engineer will say anymore: We're only interested in Smectite.

- No clay mineralogist will say anymore: Clay mineralogy is not quantifiable.

- Contrary to what Skempton stated in 1953, the X-ray diffraction analysis (XRD) will be part of any soil investigation programme. With the sample preparation method developed by the Liege Clay Mineral Laboratory for the ARC programme it has been shown in this thesis that the sample preparation is fast and gives results which are of great value to engineering practice.

- Tests in engineering soil laboratories for research programmes will focus more on natural soils and not on Smectite only because Smectites represent a physical simplification because $N_{\text{layers}} \rightarrow 0$ as this thesis showed. In this same light liquid limit results will not be interpreted anymore only on the particle level (in terms of double layer thickness) but predominantly on the interlayer level.

- Advances in visualisation of undisturbed clay samples will continue. The environmental electron scanning microscopy (ESEM) technique will be available for the study of clays. Together with a XRD analysis, the clay mineralogy and the particle build-up of clay samples can be determined. With appropriate image treatment software the ESEM images will be automatically discretised. With computer aided design (CAD) this treated image will be meshed automatically. All tools are then available to simulate any mechanical and chemical stress path with a finite element code like e.g. *LAGAMINE*. In this way the behaviour of clays in any engineering application will be studied. Like in tunnelling not the whole engineered structure will be modelled but only some parts, critical in the design.

- A research programme should be started to test the correct placement method of clay barriers *in situ* that should lead to the preferred clay particle orientation.

- Before a new test programme on soils is started/presented to analyse any physical or chemical impact on an engineered clay structure the responsible engineer should directly think about the following question:

How will these ratios change? $\frac{TCF_{ini}}{TCF_{fin}}$; $\frac{EBS_{ini}}{EBS_{fin}}$; $\frac{\varepsilon'_{ini} \cdot CEMC_{fin}}{\varepsilon'_{fin} \cdot CEMC_{ini}}$

References

ALLMANN R (2003) Röntgenpulverdiffraktometrie. Second edition. Springer

ANCEAU A (1987) Les Minéraux argileux du paléogène du sondage de Mol. Mémoire pour l'obtention du grade de Licencié en Sciences Géologiques et Minéralogiques. Université de Liège

ANSON RWW, HAWKINS AB (1998) The effect of calcium ions in pore water on the residual shear strength of Kaolinite and sodium Montmorillonite, Géotechnique 48, No. 6, pp. 787-800

ARCH J, STEVENSON E, MALTMAN A (1996) Factors affecting the containment properties of natural clays, in: 'Engineering geology of waste disposal', editor: S.P.Bentley, Geological Society Engineering Geology Special Publications, No. 11, 1996, pp. 259-265

ATTERBERG A. (1911) Die Plastizität der Tone, Internationale Mitteilungen für Bodenkunde, Vol. 1, pp.10-43

BARDET JD (1997) Experimental Soil Mechanics, Prentice Hall 1997

BATTEY MH (1994) Mineralogy for students. Second edition. Longman Scientific & Technical

BELL FG (1998) Environmental Geology, principles and practise. Blackwell Science, 1998

BLOOMER ST, COUPE PS (1994) Some effects of nitrates on the properties of clay. 7th International IAEG Congress, Balkema, Rotterdam, pp. 751-757

BOLLE A (2000) Approche probabiliste en reconnaissance et en simulation. Lecture notes, Faculté des Sciences appliquées, Université de Liège

BOLT GH (1956) Physico - Chemical analysis of the compressibility of pure clays. Géotechnique. Vol. 6. N° 2. pp 86-93

BORUS S, RÉV E (1968) Die Verlässlichkeit der Ermittlung des Plastizitätsindexes. Proc. of 3rd Budapest Conf. on Soil Mechanics and Foundation Engineering. Akadémiai Kiadó
Budapest, pp. 23-29

BRIEN O' NR, SLATT MR (1990) Argillaceous Rock Atlas. Springer-Verlag

BRINKMAN R (1979) Clay transformations: aspects of equilibrium and kinetics. In: Developments in Soil Science 5B: Soil chemistry B. Physico-chemical models, ed: G.H. Bolt, Elsevier Scientific Publishing Company, pp. 433-457

CAPPER PL, CASSIE WF (1963) The Mechanics of Engineering Soils. Fourth edition, E.&F. N. Spon, London

CARMUTI KS, GUIRE Mc RT (1999) Preparation of polished thin sections from poorly consolidated regolith and sediment materials. Sedimentary Geology. Vol. 128, pp. 171-178

CASAGRANDE A (1932) Research on the Atterberg limits of soils. Public Roads. Vol. 13, N° 8, pp. 121-136

CASAGRANDE A (1947) Classification and identification of soils. American Society of Civil Engineers, pp. 783-810

CASAGRANDE A (1958) Notes on the design of the liquid limit device. Géotechnique, VOl. 8, N° 2, pp. 84-91

CEKEREVAC C (2003) Thermal effects on the mechanical behaviour of saturated clays: an experimental and constitutive study. Dr Thesis. EPF Lausanne

CESCOTTO S, CHARLIER R (1993) Frictional contact finite elements based on mixed variational principles, International journal for numerical methods in engineering, Vol. 36, pp. 1681-1701

CHARLIER R, CESCOTTO S (1988) Modélisation du phénomène de contact unilatéral avec frottement dans un contexte de grandes déformations. Journal of theoretical and applied mechanics (special issue, supplement N°1 to vol. 7), pp. 177-192

CLARK RG, DAVIES G (1996) The construction of clay liners for landfills. In: Engineering geology of waste disposal. editor: S.P. Bentley, Geological Society Engineering Geology Special publication N° 11, pp. 171-176

DANIEL DE (1987) Waste disposal and underground storage. In: Ground engineer's reference book. Edited by: F.G. Bell, Butterworth and Co., pp. 43/1-43/10

DELVAUX B (2003) Analyse géotechnique d´argiles Belges en fonction de la nature du fluide interstitiel. TFE Fac.Sc.Appl. Université de Liège

DOUWES-DEKKER DM (1991) Soil Mechanics. M.Sc.-course in Engineering Geology, ITC-Delft

ENTENMANN W (1998) Hydrogeologische Untersuchungsmethoden von Altlasten. Springer

FAM M, DUSSEAULT MB (1999) Determination of the reactivity of clay-fluid systems using liquid limit data. Canadian Geomechanical Journal, Volume 36, pp. 161-165

FAM M, SANTAMARINA JC (1996) Coupled diffusion-fabric-flow phenomena: an effective stress analysis. Canadian Geotechnical Journal, Vol. 33, pp. 515-522

FERNANDEZ F, QUIGLEY RM (1985) Hydraulic conductivity of natural clays permeated with simple liquid hydrocarbons. Canadian Geotechnical Journal, Vol. 22, pp. 205-214

FOURMARIER P (1954) Prodrome d'une Description Géologique de la Belgique. Société Géologique de Belgique. H. Vaillant-Carmanne, Liège

GUIDUCCI C, PELLEGRINO A, RADU JP, COLLIN F, CHARLIER R (2002) Hydro-mechanical behavior of fractures: 2D, F.E.M. modelling. In: Proceedings of the second Biot conference on poromechanics, Grenoble, eds. L. Auriault, C. Geindreau, P. Royer, C. Boutin, J. Lewandowska, Balkema, Rotterdam, 955p

GUIMARAES L, GENS A, SANCHEZ M, OLIVELLA S (2001) A chemo-mechanical model for unsaturated expansive clays. Proceedings conference Maratea: Clay Behaviour: Chemo-Mechanical Coupling, editors: C. di Maio, T. Hueckel and B. Loret, Maratea Italy, pp. 1-27

HASENPATT R (1988) Bodenmechanische Veränderungen reiner Tone durch Adsorption chemischer Verbindungen (Batch- und Diffusionsversuche. Mitteilungen des Instituts für Grundbau und Bodenmechanik ETH-Zürich, Vol. 134

HEAD KH (1992) Manual of soil laboratory testing, volume 1: Soil classification and compaction tests. second edition, John Wiley & Sons

HOEK E, KAISER PK, BAWDEN WF (2000) Support of underground excavations in hard rock. Balkema, Rotterdam

HOLZLÖHNER U, MEGGYES T (1998) Physikalische, chemische und biochemische Einwirkungen auf mineralische Abdichtungsschichten. In: Optimierung von Deponiedichtungssystemen. eds.: H. August, U. Holzlöhner and T. Meggyes, Springer, pp. 43 - 52

ISRAELACHVILI J (1998) Intermolecular surface forces. Academic press, London

JACKSON ML (1964) Chemical compositions of Soils. In: Chemistry of the Soil, ed. F.E. Bear, Reinhold Publishing Corporation, New York

JASMUND K, LAGALY G (1993) Tonminerale und Tone. Steinkopff Verlag Darmstadt

KATAHARA KW (1996) Clay mineral elastic properties. SEG Expanded Abstracts, Paper RP1.4, pp. 1691-1694

KEIJZER TJS (2000) Chemical osmosis in natural clayey materials. PhD thesis Universiteit Utrecht

KEIJZER TJS, KLEINGELD PJ, LOCH JPG (1999) Chemical osmosis in compacted clayey material and the prediction of water transport. Engineering Geology, Vol. 53, pp. 151-159

KENNEY TC (1967) The influence of Mineral Composition on the Residual Strength of Natural Soils. Proceedings of the Geotechnical Conference Oslo 1967. Norwegian Geotechnical Institute.

KEVERLING-BUISMAN AS (1940) Grondmechanica, A.A.Balkema, Rotterdam, reprint of the original work, 1966

KOHLER E (1988) Beständigkeit mineralischer Dichtstoffe gegenüber organischen Prüfflüssigkeiten. Abfallwirtschaft in Forschung und Praxis, vol. 30, pp. 117-124 Ernst Schmidt Verlag, Berlin

KOLYMBAS D (1998) Geotechnik. Springer

KOMODROMOS A, GÖTTNER JJ (1988) Beeinflussung von Tonen durch Chemikalien, Teil II Gefüge- und Festigkeitsuntersuchungen. Müll und Abfall, Vol. 12, pp. 552-562

KOOISTRA A (1996) Atterberg Limits, comparing test methods for the determination of the liquid limit. Geological Survey of the Netherlands, project number: OP 6073

KÖSTER HM, SCHWERTMANN U (1993) Beschreibung einzelner Tonminerale. In: Tonminerale und Tone eds: K. Jasmund and G. Lagaly, pp. 33-88, Steinkopff Verlag Darmstadt

LAGALY G (1993) Reaktionen der Tonminerale. In: Tonminerale und Tone, eds: K. Jasmund and G. Lagaly, Steinkopff Verlag Darmstadt, pp. 89-167

LAGALY G, KÖSTER HM (1993) Tone und Tonminerale. In: Tonminerale und Tone. eds: K. Jasmund and G. Lagaly, Steinkopff Verlag Darmstadt, pp. 1-32

LALOUI L, CEKEREVAC C, VULLIET L (2002) Thermo-plasticity of clays: a simple constitutive approach. Conference organised by the EPF Laussanne: Environmental Geomechancis. Monte Verita, pp. 45 - 57

LITTLETON I, FARMILOS M (1977) Some observations on liquid limit values. Ground Engineering. Vol. 10. N° 4. pp. 39-40

MAIO di C (1996) Exposure of Bentonite to salt solution: osmotic and mechanical effects. Géotechnique, Vol. 46, pp. 695-707

MAIO di C, FENELLI GB (1994) Residual strength of Kaolin and Bentonite: the influence of their constituent pore fluid, Géotechnique, Vol. 44, No. 4, pp. 217-226

MATULA M, DEARMAN WR, GOLODKOVSKAJA GA, PAHL A, RADBRUCH-HALL DH, SANEJOUAND R (1979) Classification of rocks and soils for engineering geological mapping. Part 1- Rock and soil materials. Report of the Commission of Engineering Geological Mapping of the International Association of Engineering Geology, Bulletin of the international Association of Engineering Geology, Vol. 19, pp. 364-371

MESRI G, OLSON RE (1971) Mechanisms controlling the permeability of clays. Clays and Clay minerals, Vol. 19, pp. 151 - 158 (Note: C_v values no direct hydraulic conductivity measurement)

MITCHELL JK (1993) Fundamentals of Soil Behavior. Second edition, John Wiley & Sons Inc.

MOORE R (1991) The chemical and mineralogical controls upon the residual strength of pure and natural clays. Géotechnique, Vol. 41, N°1, pp. 35-47

MOORE R (1992) Discussion: the chemical and mineralogical controls upon the residual strength of pure and natural clays. Géotechnique, Vol. 42, N°1, pp. 151-153

MORGENSTERN NR, TCHALENKO JS (1967) The optical determination of preferred orientation in clay and its application to the study of microstructure in consolidated kaolin. I & II. In: Proceedings of the Royal Society of London, series A. Mathematical and Physical Sciences, Vol. 300, pp. 218-234 & 235-250, Published by the Royal Society

MORROW C, RADNEY B, BYERLEE J (1992) Frictional Strength and the Effective Pressure Law of Montmorillonite and Illitic Clays. In: Fault mechanics and transport properties of rocks, a Festschrift in honour of W.F. Brace, eds: B. Evans, T.F. Wong, pp. 69-88, Acad. Press. San Diego

MOUM J, ROSENQVIST IT (1961) Mechanical Properties of Montmorillonite and Illitic clays related to electrolytes of the pore water. In: Proceedings 5th International Conference Soil Mechanics and Foundation Engineering, Paris, Vol. 1, pp. 263-267

MUIR-WOOD D (1990) Soil behaviour and critical state soil mechanics. Cambridge university press

MÜLLER-VONMOOS M, KOHLER EE (1993) Geotechnik und Entsorgung. In: Tonmineralogie und Tone. eds: K. Jasmund, G. Lagaly, Steinkopff, Darmstadt. pp. 312-357

OLPHEN van H (1963) An Introduction to Clay Colloid Chemistry. John Wiley & Sons, 1963

OURTH AS, VERBRUGGE JC (1999a) Influence of Leachates on Geomechanical properties of Clay used as Confining Barriers. XIth Panamerican Conference on Soil

Mechanics and Geomechanical Engineering, ISSMGE, Foz do Iguassu, Brazil. Balkema, Rotterdam, Vol. I, pp. 497 - 500

OWEIS IS, KHERA RP (1998) Geotechnology of waste management. Second edition. PWS Publishing Company. 472 p.

PAASSEN van L (2002) The influence of pore fluid salinity on the consolidation behaviour and undrained shear strength development of clayey soils. Memoirs of the Centre of Engineering Geology in the Netherlands, No. 216, TU-Delft

POLO-CHIAPOLINI CI, MONJOIE A, RIGO JM (1992) Vade-mecum pour la réalisation des systèmes d'étanchéité-drainage artificiels pour les sites d'enfouissement technique en Wallonie. Université de Liège

POWRIE W (1997) Soil Mechanics: Concepts and Applications. E & FN Spon

PRINZ H (1997) Abriß der Ingenieurgeologie. Ferdinand Enke Verlag Stuttgart

QUIRK JP, SCHOFIELD RK (1955) The effect of electrolyte concentration on soil permeability. Journal of Soil Science, Vol. 6, N°. 2, pp. 163 - 178

RÉTHÁTI L (1988) Probabilistic solutions in geotechnics. Akadémiai Kiadó. Budapest. Developments in Geotechnical Engineering, N° 46, Elsevier, Amsterdam

ROMERO E (1999) Characterisation and thermo-hydro-mechanical behaviour of unsaturated Boom clay: an experimental study. Dr. thesis. UP-Barcelona

SANTAMARINA JC, FAM M (1995) Changes in dielectric permittivity and shear wave velocity during concentration diffusion. Canadian Geotechnical Journal, Vol. 32, pp. 647-659

SCHMIDT K, WALTER R (1990) Erdgeschichte. Walter de Gruyter, Berlin

SCHMITZ RM, SCHROEDER C, CHARLIER R (2004a) Chemo-mechanical interactions in clay: a correlation between clay mineralogy and Atterberg limits. Applied Clay Sciences. Vol. 26, Issue 1-4, pp. 351-358

SCHMITZ RM, SCHROEDER C, CHARLIER R (2004b) Using the complete Engineering Geological Nano Spectrum to assess the Performance of Clay Barriers. Lecture Notes in Earth Sciences N° 104, pp.236-243

SCHMITZ RM, SCHROEDER C, CHARLIER R (2004c) L'effet des polluants sur le comportement géomécanique des argiles: une approche généralisée. Journées Nationales de Géotechnique et de Géologie de l'Ingénieur, Lille, pp. 163-173.

SCHMITZ RM, PAASSEN VAN LA (2003) The decay of the liquid limit of clays with increasing salt concentration. Ingeokring Newsletter, published by the Dutch association of Engineering geology. Vol 9., N°1, 2003, pp.10-14

SCHMITZ RM, SCHROEDER C, CHARLIER R (2003a) Influence of microstructure on geotechnical properties of clays. Springer Proceedings in Physics, Vol. 93, pp. 89-100

SCHMITZ RM, SCHROEDER, C, BOLLE A, THOREZ J, CHARLIER R (2003b) Änderung der geotechnischen und mineralogischen Eigenschaften natürlicher Tone durch Einwirkung von Deponiesickerwasser. Müll und Abfall, Vol. 35, N° 12, pp. 635-639

SCHMITZ RM, SCHROEDER C, CHARLIER R (2003c) Influence of microstructure on geotechnical properties of clays. ISSMGE International Conference. From experimental evidence towards numerical modeling of unsaturated soils. September 2003 Weimar. p. 30 (Abstract)

SCHMITZ RM, SCHROEDER C, THOREZ J, CHARLIER R (2003d) Evolution of mechanical properties of natural clays: predictions on the basis of their clay mineralogy. Joint MiDi-DIGA Meeting on Physics and Mechanics of granular media. Marseille 2003. (abstract published on internet)

SCHMITZ RM, BOUKPETI N, COLLIN F, RADU JP, SCHROEDER C, THOREZ J, HUECKEL T, CHARLIER R (2003e) Modelling the effect of contaminants, salts and organic matter, on the geotechnical properties of natural clays. 15th ALERT Workshop 2003, Session 2: Multi - physics coupling (Abstract)

SCHMITZ RM, OURTH AS, DOSQUET D, ILLING P, SCHROEDER C, VERBRUGGE JC, BOLLE A, CHARLIER R , THOREZ J (2002a) The suitability of some Belgian Tertiary clays as construction material for landfill seals: Interaction with domestic landfill leachates, Aardkundige Mededelingen Vol. 12, pp. 261-264

SCHMITZ RM, SCHROEDER C, CHARLIER R (2002b) A correlation between clay mineralogy and Atterberg limits. Proceedings International Workshop of Young Doctors in Geomechanics. Editors V. De Gennaro and Pierre Delage. December 4th-6th 2002. Ecole Nationale des Ponts et Chaussées. pp. 27-30 (Proceedings)

SCHMITZ, RM, HILIGSMANN S, SCHROEDER C, VERBRUGGE JC, CHARLIER R (2002c) Chemo-mechanical interactions in clay: are the Atterberg limits useful?. Clays in Natural and Engineered Barriers of Radioactive Waste Confinement. International Meeting Reims December 9-12 2002. pp 187 (Proceedings)

SCHMITZ RM, DOSQUET D, ILLING P, RODRIGUEZ C, OURTH AS, VERBRUGGE JC, HILLIGSMAN S, SCHROEDER C, BOLLE A, THOREZ J, CHARLIER R (2001) Clay - leachate interaction: a first insight, 6th KIWIR International Workshop on Key Issues in Waste Isolation Research, Ecole Nationale des Ponts et Chaussées, 28 - 30 November 2001, pp.245-269, Paris France. (Proceedings)

SCHMITZ RM (2001a) Assessment of the influence of leachates on the mechanical behaviour of clay by analysing changes in geotechnical and mineralogical properties, Faculté des Sciences Appliquées, Institut de Mécanique et de Génie civil, Université de Liège, 2001. (MSc-Thesis University of Liège)

SCHMITZ RM (2000) Experimental Shear Deformation of Thinly Bedded Clay and Sand Layers. Memoirs of the Centre of Engineering Geology in the Netherlands, N°199, ISSN 1386-5072, TU-Delft, 2000. (MSc-Eng Thesis TU-Delft)

SEED BH, WOODWARD RJ, LUNDGREN R (1964) Clay mineralogical aspects of the Atterberg limits. Journal of the Soil Mechanics and Foundations Division, Proceedings of the American Society of Civil Engineers, pp. 107-131

SELBY MJ (1993) Hillslope Materials and Processes. Oxford University Press, second edition

SINGER MJ, MUNNS DN (1996) Soils. Third Edition, Prentice Hall

SKEMPTON AW (1948) A study of the geomechanical properties of some post-glacial clays, Géotechnique, Vol. 1, No. 1, pp. 7 - 22

SKEMPTON AW (1953) The colloidal “activity” of clays. In: Proceedings, 3rd International Conference of Soil Mechanics and Foundation Engineering, Vol.1, pp. 57-61

SKEMPTON AW (1970) The consolidation of clays by gravitational compaction. Q.J. Geol. Soc. London, Vol. 125, pp. 373-411

SRIDHARAN A, NAGARAJ HB (2000) Compressibility behaviour of remoulded, fine-grained soils and correlation with index properties. Canadian Geomechanical Journal, Vol. 37, N° 3, pp. 712-722

STAPEL EE, VERHOEF PNW (1989) The use of the methylene blue adsorption test in assessing the quality of basaltic tuff rock aggregate. Engineering Geology, Vol. 26, N° 3, pp. 233-246

SWAN ARH, SANDILANDS M (1995) Introduction to geological data analysis. Blackwell Science, London, 446 pages

SWANSON WM (1970) Fluid mechanics. Holt, Rinehart and Winston. New York

TCHALENKO JS (1968) The evolution of kink-bands and the development of compression textures in sheared clays. Tectonophysics, Vol. 6, N° 2, pp. 159-174, Elsevier Publishing Company, Amsterdam

TERZAGHI K (1925) Erdbaumechanik auf Bodenphysikalisher Grundlage, Leipzig: Franz Deiticke, 399 pages

TERZAGHI K (1926) Simplified soil test for subgrade and their physical significance. Public Roads, October 1926. Vol. 7, N° 8, pp. 153-162+170

TERZAGHI K, PECK RB (1967) Soil Mechanics in Engineering Practice. Second edition. John Wiley &Sons Inc. New York

TERZAGHI K, PECK RB, MESRI G (1996) Soil Mechanics in Engineering Practice. Third edition, John Wiley &Sons, Inc.

THOREZ J (1976) Practical identification of clay minerals, a handbook for teachers and students in clay mineralogy, Editions G. Lelotte, Belgium

THOREZ J (1983) Qualitative clay mineral analyses biased by sample treatments. 5th Meeting of the European clay groups, Prague, Karls University, p 383-389

THOREZ J (2000) Cation-saturated swelling physils: An XRD revisitation. In: First Latin-American Clay Conference, Ed: C.S.F. Gomes, Proc. 1, Invited Lecture, pp. 71-85, Madeira

THOREZ J, DOSQUET D, ILLING P, SCHROEDER C (2001) Behaviour of two Tertiary clayey materials leached with a complex domestic waste fluid under high pressure: triaxial permeability, and qualitative and semi-quantitative clay mineral changes. In: KIWIR International Workshop on Key Issues in Waste Isolation Research, Ecole Nationale des Ponts et Chaussèes, Paris, pp. 223 - 243

THOREZ J, KANDA V (1987) Final Report on the evaluation of the extraction method and the qualitative identification of the clay composition of the selected sample. A.I.P.E.A. Project on the Standardization of Preparation Techniques (SPT Committee). In: Procedure di Analisi di Materiali Argillosi, ENEA Comitato Nazionale per la Ricerca e per lo sviuppo dell'energia nucleare e delle energie anternative, Atti del Workshop tenutosi al Centre Ricerche Energia Ambiente di S.Teresa, pp. 181-213

VERBRUGGE JC (2000) La Géomécanique des déchets ménagers. Notes handed out for the: Chaire Francqui Belge 1999-2000, Presses Universitaires de Bruxelles, 79 pages

VOGELSANG D (1988) Grundwasser. Springer Verlag, 1988

VRIES de J, TOLLENAERE de F (1983) Etymologisch Woordenboek. Prisma Handwoordenboek. Uitgeverij het Spectrum Utrecht/Antwerpen

WAGNER JF (2000) Clay barriers and their long-term stability. In: Proceedings of the first Latin American Clay Conference, Funchal, Vol. 1, pp. 250-257

WALTER R (1995) Geologie von Mitteleuropa. 6. Auflage, E. Schweizerbart'sche Verlagsbuchhandlung, Stuttgart

WENDEHORST R (1996) Bautechnische Zahlentafeln. 27. Auflage, Teubner, Stuttgart

WETZEL A (1990) Interrelationship between porosity and other geomechanical properties of slowly deposited, fine-grained marine surface sediments. Marine Geology, Vol. 92, N° 1 - 2, pp. 105-113, Elsevier Amsterdam

WIENBERG R (1990) Zum Einfluß organischer Schadstoffe auf Deponietone - Teil 1: Unspezifische Interaktionen. Abfallwirtschaftsjournal, Vol. 2, N°. 4, pp. 222-230

YONG RN, WARKETIN BP (1975) Soil properties and behaviour. Elsevier, Amsterdam, 449 pages

Contributions in ARC reports:

SCHMITZ RM (2004b) Geotechnical properties of clay mineral transformations in engineered barriers. In : Convention n° 99/04-243, Action de recherche concertée: Confinement de centres d'enfouissement technique à l'aide de barrières argileuses. Annexe 1, pp. 1 - 28 (Report)

SCHMITZ RM (2004c) Geomac - barrières argileuses, rapport d'activités. In : Convention n° 99/04-243, Action de recherche concertée: Confinement de centres d'enfouissement technique à l'aide de barrières argileuses. Rapport d'activités 2003, pp. 20 - 23 (Report)

SCHMITZ RM (2003a) Rapport d'activités Département GéomaC - Géomécanique et L.I.G.. In : Convention n° 99/04-243, Action de recherche concertée: Confinement de centres d'enfouissement technique à l'aide de barrières argileuses. Rapport d'activités 2002, pp. 15-19 (Report)

SCHMITZ RM (2003b) Geotechnical properties of clay mineral transformations in engineered barriers. In : Convention n° 99/04-243, Action de recherche concertée: Confinement de centres d'enfouissement technique à l'aide de barrières argileuses. Rapport d'activités 2002. Annexe 2, more than 200 pages (Report)

SCHMITZ RM (2002a) Influence des lixiviats sur les limites d'Atterberg et sur la minéralogie des argiles. In: Aspects thermo-hydro-mécaniques du comportement de géomateriaux: essais de laboratoire à saturation et température variable des argiles, des limons et des craies; élaboration de lois constitutives; convention FRFC 2.4542.98 F - Rapport Final, edtiors: R. CHARLIER, F. COLLIN, A-S OURTH, J-P. RADU, R. SCHMITZ, C. SCHROEDER, J-F. THIMUS, J-C VERBRUGGE, 2002. Chapter 3.2. p.p. 6-29 (Report)

SCHMITZ RM (2002b) Assessment of the influence of leachates on the mechanical behaviour of clay by analysing changes in geotechnical and mineralogical properties. In : Convention n° 99/04-243, Action de recherche concertée: Confinement de centres d'enfouissement technique à l'aide de barrières argileuses. Rapport d'activités 2001. Annexe 1, more than 200 pages (Report)

SCHMITZ RM, BOUKPETI, N (2002) Rapport d'activités M.S.M. - L.I.G. In : Convention n° 99/04-243, Action de recherche concertée: Confinement de centres d'enfouissement technique à l'aide de barrières argileuses. Rapport d'activités 2001. pp. 17-26 (Report)

SCHMITZ RM (2001b) Discussion of the results of the Atterberg tests performed during the summer and autumn 2000 at the LIG. In: Convention n° 99/04-243, Action de recherche concertée: Confinement de centres d'enfouissement technique à l'aide de barrières argileuses. Rapport d'activités 2000. Annexe 1. pp. 1-65 (Report)

SCHMITZ RM (2001c) Literature review of physico-chemical interactions in clay, the basis for a thorough chemical analyses of the leachates. In: Convention n° 99/04-243. Action de recherche concertée: Confinement de centres d'enfouissement technique à l'aide de barrières argileuses. Rapport d'activités 2000. Annexe 3. pp. 1-23 (Report)

SCHMITZ RM, COLLIN F (2001) Standardisation of the construction of clay-leachate samples for triaxial and Atterberg tests. In : Convention n° 99/04-243, Action de recherche concertée: Confinement de centres d'enfouissement technique à l'aide de barrières argileuses. Rapport d'activités 2000. Annexe 4 (Report)

SCHMITZ RM (2001d) The acquisition of Soignies and Tournai clay in November and December 2000, Convention n° 99/04-243, Action de recherche concertée: Action de recherche concertée: 'Confinement de centres d'enfouissement technique à l'aide de barrières argileuses', rapport d'activités 2000. Annexe 5. pp. 1-10 (Report)

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Recommendations:

(SP-XRD 2004) Forced oriented aggregate and Total random powder clay sample preparation for XRD analysis. R.M. Schmitz, D. Dosquet and J. Thorez. Internal report Université de Liège.

European Union Directive 1999/31/CE du conseil du 26 avril 1999 concernant la mise en décharge des déchets. 199L0031-Fr-16.07.1999.000.001.-1; JO L 282 du 16.7.1999

Directorate-General: Environment, Nuclear Safety and Civil Protection: EU focus on waste management. Luxembourg: Office for Official Publications of the European Communities, 1999

(GDA 1997): GDA-Empfehlungen Geotechnik der Deponien und Altlasten, 3. Auflage, edited by the working group 6 of the DGGT, the German Geomechanical Society, Ernst&Sohn, 1997

(ManWal 2000): Manuel relatif aux matières naturelles pour barrières argileuses ouvragées pour centres d'enfouissement technique et réhabilitation de dépôtoirs en Région Wallonne, version 1, 30 juin 2000. MARCOEN J.M., TESSIER, D., THOREZ, J., MONJOIE, A., SCHROEDER, Ch.

(TaSi): Technische Anleitung zur Verwertung, Behandlung und sontigen Entsorgung von Siedlungsabfällen, Banz. S. 4967 und Beilage, Dritte Allgemeine Verwaltungsvorschrift zum Abfallgesetz, 14 Mai 1993.

Other literature sources:

(Merck 2000): Merck catalogue Réactifs Produits chimiques, 1999-2000

(Huette 1996) Die Grundlagen der Ingenieurwissenschaften. 30. Auflage. ed. H. Czichos. Springer, Berlin.

Physical parameters:

Information of physical and chemical constants:

(Binas 1986) Informatieboek natuurwetenschappen, tweede editie, Wolters-Noordhoff

(PT 1994) Prisma Techniek. Uitgeverij het Spectrum. Utrecht/Antwerpen

Geological timescale:

Pan Terra Inc.: A correlated history of earth, second edition, 1998

Definitions of chemical substances:

www.dictionary.com

Definitions of geological terms:

DGM (1994) McGraw-Hill Dictionary of Geology & Mineralogy. ed. S.P. Parker, McGraw-Hill, New York

Definition of chemical vocabulary:

Dictionary of Chemistry, Intercontinental Book Publications, 1981; Dutch translation: Woordenboek Scheikunde, Oberon, 1983

Definition of conversion factors Imperial - S.I. system:

(FWB 1981): Fachwörterbuch Bergbau, editors: H. Georgen, R.D. Stoll, B. Welzenberg, Verlag Glückauf GmbH, Essen

Cultural information:

(WP 1977): Winkler Prins Encyclopedie in drie delen. Elsevier Argus, Amsterdam - Brussel