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# Chemo-mechanical interactions in clay: a correlation between clay mineralogy and Atterberg limits

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#### Abstract

Among some few others tests, the evaluation of the Atterberg limits is a very basic soil mechanical test allowing a first insight into the chemical reactivity of clays. Basically, the liquid limit and the plasticity index are highly and mainly influenced by the ability of clay minerals to interact with liquids. In this contribution, a correlation between the Atterberg limits and clay mineralogy is proposed. This correlation increases the understanding between clay mineralogists and engineers in soil mechanics; additionally a wealth of information in clay mineralogy literature is now available to predict the mechanical behaviour of clays via index tests. © 2003 Elsevier B.V. All rights reserved.

Keywords: Clay; Atterberg limits; Boom clay

### 1. Introduction

The long-term mechanical and hydraulic behaviour of natural or engineered clay barriers may be modified due to interactions with various chemical or biochemical materials. However, it is very complex to analyse such interactions in the laboratory and quite impossible in situ. Due to the very low permeability of clay used as seepage barrier, mechanical tests like oedometer tests or triaxial compression tests as well as permeability tests may take a very long time, up to some months or some years. Therefore, it would be very useful to have some more time-efficient procedures to obtain a first evaluation of potential interactions with various pollutants. If a correlation between the Atterberg tests (Atterberg, 1911) and the clay mineralogy would be available to engineers working in soil mechanics, an estimate of the changes in mechanical properties could be given when the changes in clay mineralogy are known.

## 2. Materials studied

During the Tertiary, there is a regional depression of the North Sea basin. The Ardennes were weathered down and were highly karstified. There was a succession of transgressions and regressions, during which kaolinite, smectite and sand-silt were deposited on the shelf. The first regression occurred during the Eocene, during which the Ypresian clays (Soignies and Tournai

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clay) are deposited in the Belgian basin. On the bordering mainland in the south, lateritic erosion and extensive kaolinitisation planes develop. During the Oligocene, the second transgression occurs, and the Kruibeke clays (Rupelian; has the same formation as the Boom clay) are deposited. Towards the end of this epoch, the sea retreated to its present location. During the following Miocene epoch, only short invasions of the sea on the Belgian coast occurred, and the Ardennes started to rise. Quaternary sediments afterwards covered the clay (Schmitz et al., 2001). The syn- and postsedimentary activity and the present geomorphological situation lead to the fact that the deposits have only a limited extend in the Walloon region and possess a varied mineralogy (the Tournai and Soignies clay; MANWAL, 2001), whereas those in Flanders (the Kruibeke clay) are more homogeneous and more extensive. Tournai, Soignies and Kruibeke clay are natural Tertiary clays acquired in guarries in Belgium. Two industrial clays: Colclay (reference smectite) and Speswhite (reference kaolinite) are industrial clays used as reference material.

### 3. Testing methods

The samples are analysed following the Liege Clay Lab' X-Ray Diffraction (XRD) analysis method. This involves the record of analytical data contained in diffractograms; these are related to three kinds of preparation, two of them concerning oriented aggregates of either the less-than  $2\mu m$  or of the bulk material, whereas the third mode of preparation concerns the mineralogical composition from a random powder mount of the bulk material. An extensive description is given in the manual for the selection of clay minerals for barrier purposes in the Walloon region (see MANWAL, 2001). In order to preserve

Table 1				
Characteristics	of	the	materials	studied

the in situ natural state of the material to be investigated, no chemical pretreatment is applied, contrary to many published methods which aim to remove organic matter or sesquioxides (Fe, Al or Mn oxides and hydroxides) prior to the preparation of the material for its XRD analysis. Only in case of carbonate occurrence, this mineral provokes flocculation of the clay particles and hampers their suspension, the material is pretreated with dilute HCl (0,1N).

The Atterberg test results of the natural clays were obtained using the Casagrande cup according to NF P94-051; the Atterberg test results of the Colclay were determined using the cone penetrometer method according to BS1377:Part 2: 1990. 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 limits for extreme soil types (Muir-Wood, 1990). Above a liquid limit of 100% (overview by Head, 1992), the cone method tends to give slightly lower values. Because the cone method is preferred to the Casagrande method (Muir-Wood, 1990), we used the data for the clay with a high-liquid limit determined with the cone method and the Casagrande liquid limit for the clays with smaller liquid limit values. If no cone data was available and the sample had a liquid limit higher than 100%, the liquid limit was corrected in order to obtain a corrected liquid limit (LL<sub>equi-cone</sub>) using an empirical formulation:

$$LL_{equi-cone} = 2.56 \cdot LL_{casa}^{0.78} \text{ for } LL > 100\%$$
(1)

this formulation is based on a reanalysis of the results collected by Head (1992) and the addition of the results of the reference bentonite tested by van Paassen (2002) using the Cone penetrometer and tested in Liege using the Casagrande cup.

	LL <sub>equi-cone</sub>	CF <sub>Illite</sub>	$CF_{(10-14c)}^{FOA}$	$CF_{(10-14m)}^{FOA}$	$CF_{SmAl}^{FOA}$ (%)	CF <sub>Kaolinite</sub>	CF <sup>FOA</sup> (%)	TCF <sup>TRP</sup> (%)
Reference kaolinite	62	~ /	( )	0	~ /	100	( )	100
Kruibeke average	63	28	18	17	5	13	19	65
Tournai average	104	16	7,5	68	9,0			61
Soignies average	35	33	15	16	6,4	20	10	52
Reference smectite	388			100				100

# 4. Results

A summary of the results is presented in Table 1. The three natural clays, Tournai, Soignies and Kruibeke clay, were exposed to different leachates, and different temperatures; only the averaged values are given in Table 1.

# 5. Discussion using mineralogy to predict geotechnical properties

5.1. Atterberg versus clay content and smectite content

When, in geotechnical literature, reference is made to clay mineralogy and, the aspect of sample preparation for X-ray diffraction analysis (XRD) is discussed, the fact that usually only the fraction smaller than 2  $\mu$ m is analysed is defended with the proclamation that smectites (or illite–smectite mixed layer) are:

- the most dominant clay mineral, and they are
- nearly completely present in the smaller than 2  $\mu$ m fraction.

These are two hypotheses we're going to test.

**Hypothesis 1:** (LL is a function of the smectite content). We tested the hypothesis that the liquid limit depends only on the smectite (or illite–smectite mixed layer) content. This relationship is plotted in Fig. 1.



**Correlation mineralogy-Atterberg limits** 

Fig. 1. The smectite content alone does not account for all clay reactivity expressed in terms of the  $LL_{equi-cone}$ .



**Correlation mineralogy-Atterberg limits** 

Fig. 2. The amount of clay minerals plotted versus the LL<sub>equi-cone</sub>.

It is obvious (Fig. 1) that this assumption is a very large generalisation for two reasons:

- The Soignies (Tertiary natural clay) and Kruibeke (Tertiary natural clay from the same formation as the famous Boom clay) samples show a large difference in LL, although their relative smectite content is comparable.
- When the reference kaolinite is considered, we can see that this clay, consisting almost completely of kaolinite, has a fairly large liquid limit which is not taken into account when the focus is on smectite only.

Thus, not only smectite is a reactive clay mineral, the other clay minerals need to be considered as well.

**Hypothesis 2:** (LL is a function of the amount of clay minerals present in the sample). If only the amount of clay minerals is considered irrespective of possible differences between these minerals, we obtain a situation that exists when the activity of the clays is determined according to Skempton (1953). This is shown (considering only the liquid limit and not the plasticity index) in Fig. 2.

In this case, the same liquid limit is expected for the reference kaolinite and the reference smectite which, obviously, is not true.

These examples show that it is not sufficient to consider only the smectite content or the total amount of clay minerals present in the sample. A formulation needs to include, at least, information on the:

- clay mineralogy qualitatively,
- clay mineralogy quantitatively.

It was apparent that both the amount of smectite *and* the amount of clay minerals are needed to be considered *but* not only the amount of clay counted, and, besides smectite, other clay minerals (like kao-linite) should be considered as well.

On this basis a clay parameter was developed which takes into account:

- the amount of clay in the sample,
- the type of clay: smectite but also kaolinite and other clay minerals.

In Fig. 3, this clay parameter (given in Å) is correlated to, e.g., the liquid limit.

Before it is explained how these two properties were combined in one relationship, we are going to have a look at one example that shows how we can use clay mineral data to obtain an estimate of mechanical properties.

What can we do with this clay parameter?

We can use clay mineral literature and obtain an estimate of the clay index properties as will be shown in the following examples.

**Example I:** (Heating). Imagine that nuclear waste is isolated using a bentonite plug, and that the temperature rises locally up to 500 °C. What will the undrained shear strength be? What will the compression index be? It is difficult to tell but a clay mineralogist knows what happens. A standard test during XRD analysis is the heating of the clay sample to 500 °C during 4 h. This causes collapse of the



Fig. 3. A unique clay parameter related to the LL<sub>equi-cone</sub>-



Fig. 4. A standard test in clay mineralogy: heating to 500 °C.

interlayer space. The relationship to the liquid limit is shown in Fig. 4.

If the reference bentonite, with an initial basal spacing of 14 Å is heated to 500 °C, this will cause a collapse to 10 Å. The liquid limit will decrease from its original value near 400% to a value slightly lower than 200%. To check if the predicted Atterberg results obtained were reliable, several hundred grams of the reference smectite were heated to 500 °C during 4 h; the Atterberg limit was determined: LL=191%, close to the predicted value!

### 5.2. Equivalent basal spacing distance (EBS)

In the previous section, an example was given that showed how the clay parameter and its correlation to the liquid limit can be used to obtain an estimate of the liquid limit if the changes in clay mineralogy are known. But how does this clay parameter look like?

To relate the interlayer space of a polymineral clay to the liquid limit, we introduce (Schmitz et al., 2002) the concept of equivalent basal spacing (EBS):

$$EBS = TCF^{TRP} \cdot \sum_{i=1}^{n} CF_{i}^{FOA} \cdot BS_{i}^{(001)FOA}$$
(2)

The relative amount of a clay mineral is multiplied with the basal spacing (Å) of this mineral known from literature (e.g., Mitchel, 1993). This step is repeated for all measured clay fractions, and then these values are summed. This sum is then corrected for the total amount of clay minerals in the sample. In this way, the EBS 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 nonclay constituents, like sand, and the reactivity of interstratified clay minerals which, as Yong and Warketin (1975) state, have properties intermediate between those of the two components.

**Example:** If the sample consists only of smectite, then the TCF<sup>TRP</sup>=1, the CF<sup>FOA</sup><sub>smectite</sub>=1 and the  $BS_{smectite}^{(001)FOA} = 15$  Å. Therefore, the EBS will be 15 Å as well. If the sample consists only of sand, then the EBS = 0 Å.

In Fig. 3, the EBS is plotted versus the liquid limit. If a linear correlation is assumed, then:

$$EBS = (0.0246 \cdot LL + 5.487) \tag{3}$$

with a coefficient of correlation equal to 0.92.

The utility of this parameter is shown by two other examples in the following sections.

**Example II:** (Salt concentrations). For «pure» clays, the decrease of the liquid limit with increasing salt concentration is well documented. In Fig. 5 (test results by van Paassen, 2002; di Maio, 1996), 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<sub>2</sub>. Note that, for the latter, a correction for the higher valence has been made.

The curve fits well to, e.g., a second-order exponential decay function (Schmitz and van Paassen, 2002) (Fig. 6).



Fig. 5. The evolution of the liquid limit  $LL_{equi-cone}$  when two bentonites are exposed to different salt concentrations.



LL vs [salts] Ponza Bentonite and Colclay

Fig. 6. The decay of the liquid limit  $LL_{equi-cone}$  of bentonite as a function of the concentration of monovalent cations.

Using these relationships, a function for the  $LL = f(LLs, CF, C_{mc})$  can be found, e.g.:

$$LL = (26.8 \cdot LN(LLs) - 69.1) + (0.772 \cdot LLs - 22.7) \cdot e^{R}$$
$$R = \frac{-C_{mc}}{95.9 \cdot e^{-0.066 \cdot CF}}$$
(4)

This empirical relationship can be used to obtain a prediction of the liquid limit if salts in a known concentration are added. Once the evolution of the liquid limit is known, a prediction of mechanical parameters, like the compression index, can be given as well. In Fig. 7, the prediction of the compression index (solid line) was compared to the compression index measured directly by van Paassen (2002) (dots) using the well-known relationship between the liquid limit and the compression index by Terzaghi and Peck (1967), discussed recently by Sridharan and Nagaraj (2000) and Cherubini et al. (2001):

$$C_{\rm c} = 0.009 \ (\rm LL - 10) \tag{5}$$

Using the concept of the equivalent basal spacing introduced previously in this contribution, we can have a look at the evolution of the interlayer distance with increasing salt (e.g., KCl) concentration (see Fig. 8).

After one cycle of exposure of the reference bentonite to a saturated KCl solution, not a complete collapse of the basal spacing to 10 Å but only a partial collapse to 12 Å was measured. If we take a look at



Fig. 7. The decay of the liquid limit of bentonite as a function of the concentration of monovalent cations.

Fig. 8, we can see however that even the theoretical limit of 10 Å is passed. What happened to the clay? If we expose our reference bentonite to a saturated salt solution, this would cause a reduction of the liquid limit (see Fig. 9) from a little less than 400% to a value between 200–300%. The actual measured values are however between 60% and 70%.

In fact, the operators that performed the Atterberg tests noted that the clay, after exposure to salt solutions, had become like a silty or sandy clay. This nonclay fraction that had been formed consisted of precipitated salt crystals as XRD analysis showed. Can we quantify this decrease and give an estimation of the amount of salt crystals formed using the clay parameter?





Fig. 8. The evolution of the basal spacing with increasing salt concentration.

If the additional "collapse" of the interlayer space would be related to the relative decrease of clay minerals by the formation of salt crystals, how much crystals would have been formed?

Measured LL corresponds to 7.2 Å

 $12\text{\AA}^*X = 7.2\text{\AA}$  (measured)

X=0.6, thus 0.4 mass fraction nonclay minerals dominantly salts would have been formed. XRD results performed later showed that the clay content was about 61.5% clay, 3.6% nonclay minerals and additionally 33.4% Sylvite (which is KCl salt), the



Fig. 9. Clay mineralogy related to the LL<sub>equi-cone</sub> to explain the effect of salt solutions on the liquid limit.

Table 2				
The liquid	limit	of the	pure	clays

	Kaolinite	Bentonite
LL (%)	45	521.5
LL equi cone (%)	45	337.1
Equivalent basal spacing (Å)	6.6	13.8

same order predicted by the equivalent basal spacing Atterberg correlation.

**Example III:** (Mixtures of clay). In this example, we want to show that the principle of equivalent basal spacing and the correlation with the Atterberg limits can be used to predict the liquid limit of clay mixtures before they have actually been made. Seed et al. (1964) tested several mixtures of kaolinite, illite and bentonites mixed with sands in different proportions. In the case shown here, we will concentrate on the mixtures of kaolinite and smectite without sand. Because the mineralogy of the clays that were used is not known, we first have to determine [using expression (3)] the equivalent basal spacing using the liquid limit data provide by Seed et al. (1964) for the pure samples (see Table 2).

Because the Casagrande Cup was used to determine the liquid limit, these values are corrected [using expression (1)] as explained above.

In Table 3, the composition of each sample is given in the first two columns. In the third column, the equivalent basal spacing is given, using expression (2). In the fourth column, a prediction of the liquid limit is given using the correlation between the equivalent basal spacing and the liquid limit plotted in Fig. 3.

This value can be compared with the actual liquid limit measured by Seed et al. (1964). The actual measured value is given in Table 4. In the first two

Table 3					
The predicted	liquid	limit	of the	clay	mixtures

Kaolinite (%)	Bentonite (%)	EBS (Å)	LL based on correlation with EBS (%)
100	0	6.7	51
95	5	7.1	65
90	10	7.5	80
80	20	8.2	109
60	40	9.6	167
40	60	11.1	226
20	80	12.5	284
0	100	13.9	343

Table 4	
The measured liquid limit of the clay mixtures	

	-			
Kaolinite (%)	Bentonite (%)	LL measured by Seed et al. (1964) (%)	LL equi cone (%)	
100	0	45	45	
95	5	72	72	
90	10	90.8	91	
80	20	120.5	108	
60	40	216	170	
40	60	316	228	
20	80	417.6	283	
0	100	526.2	339	

columns, the composition of each sample is given. In the third column, the liquid limit using the Casagrande Cup is given, and, in the fourth column, an estimate of the liquid limit is given using expression (1).

The comparison of the fourth columns of Tables 3 and 4 shows that the predicted value of the liquid limit is very close to the actual measured value. The difference between inert clay mixtures (kaolinite-bentonite) and active clay mixtures (illite-bentonite) is discussed in detail in Schmitz (2004).

# 6. Conclusion

With the concept of equivalent basal spacing, a new tool has been created which provides a direct link between clay mineralogy and geotechnical properties. When, 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 mineralogy can be useful in Engineering practice not only qualitatively but quantitatively as well.

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### Appendix A. Abbreviations and symbols

(10 - 14m)	Illite-smectite mixed layer
(10 - 14c)	Illite-chlorite mixed layer
$BS_{i}^{(001)}$	The basal spacing of an oriented clay sample
	that can be found in literature (e.g., Mitchel, 1993;
	unit length)
CF	The clay mineral fraction (all clay minerals and
	not only the fraction $< 2 \mu m$ ) in mass % of the sample,
	determined from a total random powder XRD plot
	(% total mass sample)
$C_{\rm mc}$	The concentration of monovalent cations (mol/l)
$CF_{i}^{FOA}$	Fraction of a clay mineral species (with respect to the
	total amount of clay minerals) determined during the
	XRD analysis of a forced oriented aggregate (fraction)
EBS	Equivalent basal spacing, determined using formula
	(unit length)
FOA	Forced oriented aggregate, an oriented sample used
	for XRD analysis taking the whole clay fraction into
	account (not only the fraction $<2 \mu m$ )
LL	Liquid limit (% fluid content)
LL <sub>casa</sub>	Liquid limit determined using the Casagrande cup
LL <sub>cone</sub>	Liquid limit determined using the cone penetrometer
LL <sub>equi-cone</sub>	Liquid limit determined using the Casagrande cup but
	corrected for the slightly higher value using this
	method with respect to the value obtained using
	the cone penetrometer
LLs	A standard liquid limit of a clay tested with
	demineralised water (% fluid content)
Sm <sub>Al</sub>	Pillared smectite
TCF <sup>TRP</sup>	Total amount of clay minerals determined during TRP
	(fraction)
TRP	Total random powder, the nonoriented sample used for
	XRD analysis
XRD	X-ray diffraction

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