IMPACT OF A HIGH LINEAR WEIGHT POLYMER CO-CONDITIONING WITH POLYALUMINIUM CHLORIDE ON DEWATERING AND CONVECTIVE DRYING OF URBAN RESIDUAL SLUDGE.

Y.B PAMBOU, L. FRAIKIN, T. SALMON, M. CRINE, A. LEONARD

Laboratory of Chemical Engineering, Department of Applied Chemistry,
University of Liège, B6c Sart Tilman, 4000 Liège, Belgium

**Corresponding author: Tel.:+324366472, E-mail: yvon-bert.pambou@student.ulg.ac.be*

Abstract: This paper investigated the influence of Polyaluminium chloride (PAX) co-conditioning with a high linear weight polymer on the dewatering performance and the drying behavior of sludge. The CT linear polymer with a high molecular weight was used combined with PAX for sludge flocculation prior to mechanical dewatering and drying.
It was found that sludge conditioned with the couple PAX/ CT led to better flocculation/dewatering process regarding size flocs and specific resistance to filtration.
Concerning drying, it appeared that this chemicals combination led to improved drying rates with effect of a reduction of the drying time, when compared to polyelectrolyte used without PAX adding.

Keywords: Activated sludge flocculation, dewatering, convective drying, linear polymers, PAX

INTRODUCTION

According to the directive of the Council of European Communities concerning urban wastewater treatment [1, 2], municipalities will have to face with growing amounts of wastewater sludges. At the same time, the directive on waste landfill [3] has planned the progressive reduction of sludge disposal in dump sites until 2016 [4, 5]. At the present time, two major issues are used for sludge disposal: energy valorization through incineration and agriculture valorization through landspreading [5]. Excess sludge which is produced by the biological treatment of wastewater still contains more than 99% of water at the bottom of thickeners. Before being valorized, sludge has thus to be dewatered and, more and more often thermally dried
Sludge is a colloidal system in which small sludge particles form a stable suspension in water, making them very difficult to be separated from the water phase. To overcome this problem, the addition of chemical conditioners such as flocculants and/ or coagulants is often necessary to help the sludge particles to agglomerate into larger settleable flocs prior to solid-water separation usually by mechanical dewatering. Polyelectrolytes are often used to induce the formation of flocculated particle networks their most important characteristics are average molecular weight [6, 7] and charge density [8].
Depending on the dewatering technique, the so-called sludge cake reaches around 15 to 35 % DS. Thermal drying can then be used to remove totally or partially the remaining water, depending on sludge final use. This obviously reduces the mass and volume of waste and, consequently, the cost for storage, handling and transport. The removal of water to such a low level increases drastically the lower calorific value, transforming the sludge into an acceptable combustible

Conditioning, dewatering and drying cannot be seen as independent steps. Indeed, some wastewater treatment plant managers have observed that, in some cases, the shear stresses underwent by the sludge in centrifuges will alter its drying behavior. Overdosage of conditioning polymer has also been referred to induce drying slowing down.
Furthermore, a strong decrease of the drying rate was obtained when the sludge was destructured due to pumping [9].
As thermal drying is highly energy consuming, this process still needs to be optimized [10] but considering the whole chain effect including conditioning and dewatering. As just stated before, this effect is known to exist but there is a real lack of scientific paper concerning this issue [11, 12, 13].

In this context, the aim of this work was to study experimentally the influence of Polyaluminium chloride coagulant (PAC or PAX) co-conditioning with high linear weight polymer on dewatering performances and subsequent convective drying behaviour. The effect of wastewater sludge conditioning with PAX was proposed to become a technically feasible and very effective method to enhance sludge dewaterability and to avoid fouling problems during the course of drying [14].

MATERIALS AND METHODS

Experimental design

An experimental design is used to investigate the effect of input factors on a response variable.

To have a better understanding of the dose effect, five points of experiments (Fig. 1) were carried out in order to study the effect of Polyaluminium chloride coagulant combined to polyelectrolyte chemical on both the sludge dewatering process and drying behavior.

The polyelectrolyte dose range, which covers the underdosing to overdosing area for the polymer ranges from the half to the double g polyelectrolyte per kg sludge dry matter, from the dosage determined as ‘optimum’ (see below).

Concerning Polyaluminium chloride coagulant, a dose ranging above 8 g PAX/ kg_{DS} was shown to be ineffective, allowing to investigate the range below this value.

The tests were performed with sludge samples taken in the same week, stored in a vessel at room temperature of 25 °C and under continuous gentle stirring.

The day 1 served to determine the optimum dosage prior to the measurement campaign by CST. The trials were performed in two weeks in random sequence, except for the central point (C) which was repeated 4 times respectively at the beginning and the end of each week, which secured almost the same sludge characteristics.

The range investigated for each parameter and experimental plan are presented in Table 1 and Fig 1.

Table 1**.** Experiments days design

Monday	CST [s]
Tuesday	C_1
Wednesday	A
Thursday	B
Friday	C_2
Monday	CST [s]
Tuesday	C_3
Wednesday	D
Thursday	E
Friday	C_4

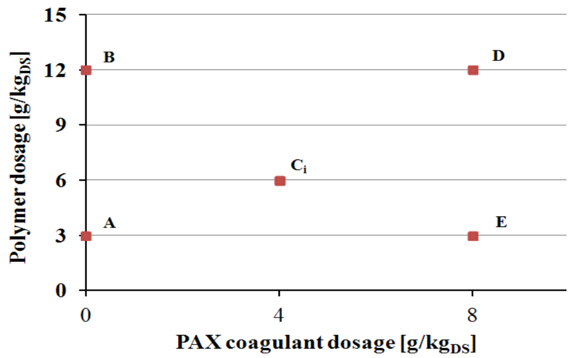

Fig. 1. Design of experiments representation.

Sludge samples characteristics and conditioners

The study was performed on activated sludge samples collected after thickening from the wastewater treatment plant of the Grosses-Battes, located closed to University of Liège (Belgium). The dry solids (DS) and volatile solids (VS) content were respectively determined by drying the wet material at 105 °C during 24 h, and then calcinating the dried residue at 550 °C during 2 hours, and weighing. Table 2 presents dry solids (DS) and volatiles solids (VS) contents characteristics, determined according Standard Methods [15]. Three replicated tests were carried out to evaluate the reliability of the experiments.

The 640 CT cationic polymer was obtained as 40 wt % active substance from the Société Nationale Française supplier (Andrezieux, France) in emulsion form. It was referenced as linear polyelectrolyte with a high molecular weight and high charge density.

These charged organic polymers were gained a large market share over the last decades in sludge treatment, since they can be dosed in much lower quantities than inorganic flocculants such as lime and iron chloride [16]. Furthermore, these organic polyelectrolytes are easily biodegradable and can be obtained at economic costs.

Concerning the Polyaluminium chloride coagulant used in this paper, it was commercially available PAX-14 from Kemira Rotterdam (basicity 26 ± 6%; density of 1.3 kg/L; Al concentration of 7.2 ± 0.3 wt %). PAX solution was characterized by the presence of the highly charged tridecameric polymer or polycation $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$, in short referred to as the Al_{13} polymer [17, 18]. The Al_{13} has the so called Keggin crystal structure composed of a tetrahedral $Al(O)_4$ center surrounded by 12 octahedrally coordinated Al atoms with bridging hydroxides and water molecules.

Table 2. Sludge characteristics

	Week 1	Week 2
Dry solids [%]	0.85±0.01	0.80±0.02
Volatiles solids [%]	39.50±0.5	39.30±0.2

Table 2 showed the Dry solids content obtained for two successive weeks. These values are slightly different, that can be explained by a possible variation of sludge quality from one week to another. The repeatability of the measurements can be considered as constant in regard to standard errors below of 0.05 %.
Concerning the Volatiles solids content, the values were repeatable from the two successive collected weeks.

Sludge conditioning
Before the sludge was used for dewatering tests, it was conditioned in the laboratory, aimed at mimicking similar operating conditions. The chemical conditioning implies the addition of undiluted amount of PAX in combination with cationic polymer [19].
Classical jar test device was used to mix the PAX/ polymer with the sludge. More specially we gently mixing 600 mL of sludge in a beaker of 800 mL, PAX was added while stirring was applied to the mixture sludge (typically 0; 300; 600 µL depending on the experiment) during 1 minute at 120 rpm, then a defined quantity of the diluted polymer solution (prepared the day before its use) was added rapidly and further shearing was applied at the same rotation speed and time (120 rpm during 1 min) to promote PAX/ polymer dispersion. After this period, the rotation speed was reduced and the sludge was gently shaken at 40 rpm during 3 min to promote flocs growth. Once the supernatant removed, the sludge can be used in dewatering stage.

Capillary Suction Time measurements
The time that the filtrate requires to travel a fixed distance in the filter paper is referred to as Capillary Suction Time (CST). The whole purpose of CST is to determine dewatering characteristics of a given sludge rapidly and easily. A large CST is usually indicator of poor sludge dewaterability.
A sample of conditioned sludge is placed in the sample container. As water migrates through the Whatman filter and reaches the first probe, it activates the timer. When water reaches the second probe, the timer deactivates. The time interval between timer activation and deactivation is the CST [s]. Capillary Suction Time is plotted versus chemical dosage. The dosage that gives the fastest time is called the optimum chemical dosage. CST measurements were done three times each with a Triton Electronics 304 M CSTmeter.

Sludge dewatering
After conditioning, the dewatering process was realized by using a normalized filtration-expression cell (AFNOR 1979). The cell was a 270 mm deep cylindrical stainless steel chamber with an internal diameter of 70 mm (Figure 3). A perforated disk was located at the bottom of the cylinder in order to support the filter medium. Filter medium is polypropylene material with permeability of 8 $L/dm^2/min$ and 0.70 mm of thickness. The pressure on the piston was applied and controlled by pressurized air. It was fixed at 5 bars. The mass of collected filtrate was recorded every 10 seconds on the personal computer linked to a precision balance device that measure collected filtrate. The filtration was stopped after a time fixed at 1 h for all experiments then, the specific resistance to filtration was evaluated by using the Carman-Kozeny equation[20].

Before drying, sludge cakes obtained after mechanical dewatering were extruded through a circular die of 14 mm of diameter and cut at a height of 14 mm, yielding cylindrical samples with mass of approximately 2.5 g, as used in several industrial belt dryers. At the end of drying, the mass sample was weighed and dry matter can be calculated.
The cake dry solids content was finally calculated by an average of two measurements: the one, by using the dry matter value given at convective drying step and the other by dryness performed on the remaining cake placed in an oven at 150° C.

Convective Drying Rig

Convective drying experiments (Fig2) were carried out in a so-called 'micro-drier' specially designed for handling small extruded samples with a mass between 0.5 and 5 g. The micro-drier is a classical convective rig controlled in relative humidity, temperature and air velocity, which has already been described in detail in a previous paper [21]. Drying curves representing the drying rate ($kg\ s^{-1}$) versus the water content on a dry basis W ($kg\ kg^{-1}$) are calculated from these mass versus time data. Dividing the drying rate by the external exchange area yields the so-called Krisher's curves commonly used to study drying, i.e., the mass flux ($kg\ m^{-2}\ s^{-1}$) versus water content ($kg\ kg^{-1}$). Results reported in this study refer to the following operating conditions: temperature of 130°C, superficial velocity of $1\ m.s^{-1}$and the absolute humidity of the air fixed at 0.005 $kg_{water}/\ kg_{DS}$.

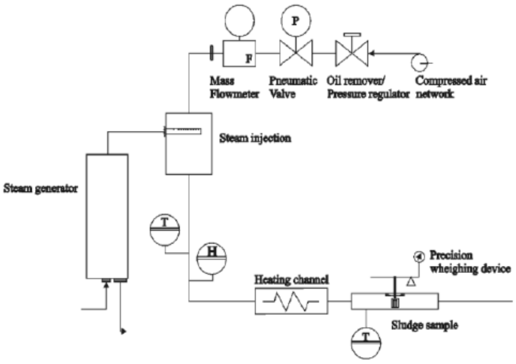

Fig. 2. Scheme of the convective micro-dryer.

X-ray Microtomography

To determine Krischer's curves, it is necessary to know the exchange surface developed by the sludge sample, assumed to be the external sample surface. Following a method developed inside the laboratory [20-22], it was evaluated by using X-ray microtomography, acting as a medical scanner. This method allows the determination of shrinkage curves from series of 2D cross sections images of the samples. This results in a reduction of the effective surface exchange in course of time. The X-ray microtomographic device used in this study was a "Skyscan-1074 X-ray scanner". The X-ray source operates at 40 kV and 1 mA. The detector is a 2D, 768x576 pixels, and 8-bit X-ray camera giving image with a pixel size of 41µm. The following sequence is repeated several times during a drying experiment: drying interruption- tomographic analysis- drying resumption. These interruptions have been proved to have no impact on the drying kinetics [21].

RESULTS AND DISCUSSION

Optimum polymer dosage estimation

Capillary Suction Time (CST) test was applied to conditioned sludge samples for evaluation of their dewatering capacity. The CST values were plotted in a function of polymer dosage. At low concentration of flocculant the drainage of the filtrate through the filter paper is not favored as the flocculated network is not established, giving high values of CST. Conversely, an overdose of the polymer concentration in the liquid phase increases its viscosity and then, the flow of the filtrate through the filter paper is reduced. The optimum dosage is thus considered to be obtained at the minimum on The CST test results depicted in Figure 3, i.e. closed to 6 g/ kg $_{DS}$.

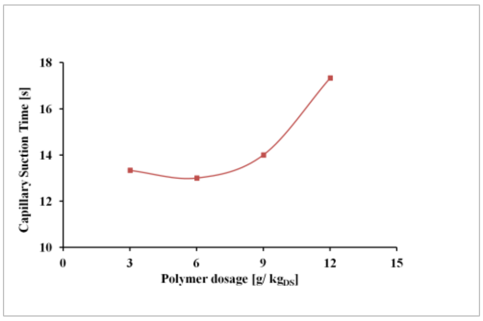

Fig. 3. CST results on activated sludge

Impact of sludge conditioning on the dewatering process

The dewatering of a sludge working under constant pressure is well described by t/V versus V plot [23].The filtration phase is characterized by the linear part (Figure 4). It corresponds to the formation of a cake due to the accumulation of the solid particles on the surface of a filter medium. The second part represents the expression phase. It describes the removal of water by cake squeezing. The ability of the forming cake to let the water go through is commonly characterized, during the filtration phase, by the SRF. This parameter is calculated by the slope of the linear part according to the following equation [24]:

$$\frac{t}{V} = \mu.SRF.\frac{C}{2PA^2}V + \frac{\mu Rf}{PA}$$

Fig. 4 already shows the dewatering repeatability test at the central point of PAX/ 640 CT conditioners. C_3 was one of the replicate of the central point. The dewatering behavior seems to be repeatable. However, negligible differences can be noticed at the dewatering expression phase.

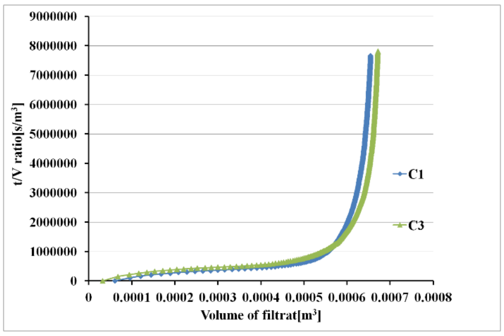

Fig. 4.Dewatering curves of central point's CT

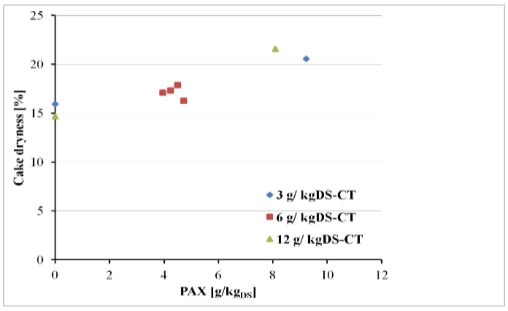

Fig. 5. Impact of PAX/ 640 CT on cake dryness

Sludge cake dryness obtained after a constant pressure filtration is another important parameter than can useful to describe the efficiency of the dewatering performances [25].

In Fig. 5 was represented the cake dryness in function of the dual PAX/ 640 CT added. It was observed that Polyaluminium chloride addition leads to increase cake dryness. It means that PAX was contributed to improve solids capture by releasing much more water contained into flocs. Additional explanation might be found in a higher porosity of sludge, i.e. more cavities in the interface between the sludge were developed after PAX conditioning.

Impact of sludge conditioning on the convective drying behavior

To obtain complete drying curves, two same weight extrudated samples of the same dewatering cake were used: the first one was dried without any interruption which produced the mass loss curves, while the second was removed several times from the dryer for tomographic investigation, allowing to obtain the external surface of dried product. Fig. 6a shows the mass loss of samples versus time obtained for the different points of the experimental design. Classical drying curves were obtained showing the samples mass decreasing. This figure clearly shows the impact of the couple PAX/ polymer on the drying kinetics: the drying time was much longer for curves obtained without PAX adding (A and B).
These results can be well highlighted by analyzing the curves obtained by derivation of mass loss curves which consists at representing the drying flux versus water content, depicted in Figure 6b. The drying flux was calculated by dividing the drying rate by the external exchange area obtained by using X ray microtomography. This illustration of drying flux is called the Krisher's curve commonly used to understand drying phenomena [11].

For sludge such a curve can be divided into three conventional phases [21]: The first phase; is a short period called adaptation period or preheating period during which the product adapts its behavior to the new applied conditions. The second period is called the constant drying flux rate. During this period the supplied heat serves to the evaporation of the product water. The operation was done at constant surface product temperature. The last phase is the falling drying flux period, ending with stabilization in moisture content at an equilibrium value corresponding to the end of drying.
It can be clearly remarked that the dual PAX/ polymer conditioning accelerate the drying process: for a same given water content, the drying kinetic is higher in presence of PAX adding. It means that water is more freely and then more easily removed in the presence of PAX (see Fig. 6b).

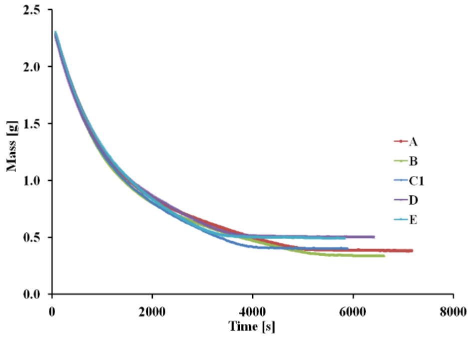

Fig. 6a. Mass curves of experimental points CT

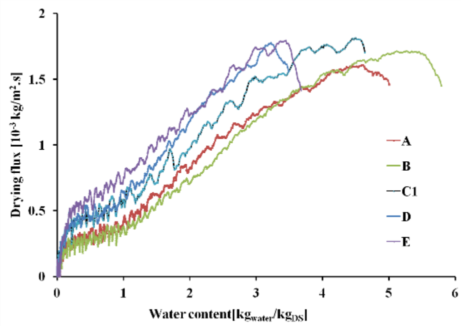

Fig. 6b. Krisher's curves of experimental points CT

We can also mention that, the reliability of the experiment was evaluated on four replicated tests carried out on different central points of the experimental plan. A good repeatability was obtained as shown in Fig. 6a. Thus, the comparison which was made with the other experimental design points can be objective. Figure 6c shows the repeatability test performed on central point.

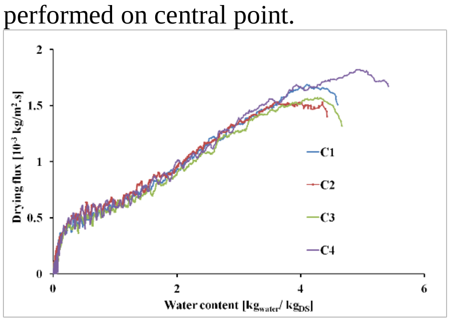

Fig. 6c. Krisher's curves of central point's CT
Repeatability test

Impact of sludge conditioning on the convective drying time

In drying process technology, drying time can be defined like the time required to achieve 95 % of water removed from the sludge samples. This parameter was shown to have a relationship with energy consumption necessary to dry the sludge.
In order to see how the combination of the dual PAX/ polymer dosage can be influence the drying behavior, drying time was plotted versus Polyaluminium chloride and polymer dosages, depicted in Fig. 7.
It can be observed that the drying time decreases when PAX/ flocculant dosage increase.
Particularly, when the polymer concentration is at its low and high level, example for respectively A (0; 3 g/kg_{DS}) and B (0; 12 g/kg_{DS}) points, the drying time is longer as about 5 000 seconds. This time begins to reduce when PAX is added. And then, PAX can improve significantly the drying process when it was combined by linear polymers.

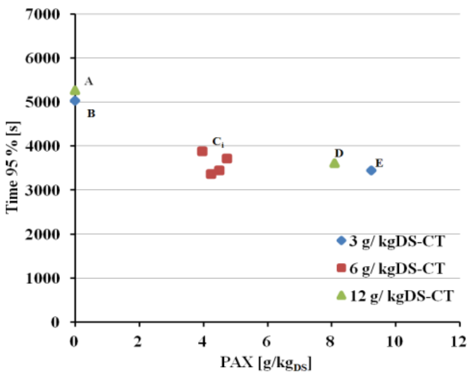

Fig. 7. Impact of PAX/640 CT on drying time

CONCLUSIONS

This article was an attempt to put in evidence the impact of sludge co-conditioning by Polyaluminium chloride and high linear molecular weight polymers on both dewatering and drying behaviours.
It was found that sludge conditioned with the high linear weight polyelectrolyte combined with PAX led to better flocculation/dewatering process regarding size flocs and cake dryness characteristics. PAX appears to be profitable to contribute at this process.
About drying, the positive effect of PAX/ polymers addition was shown on the drying kinetics by improving drying rate, consequently a reduction of the drying time was observed, when compared to polyelectrolyte without PAX adding.
Future work will be done in order to understand the reasons of drying enhancement and to test other PAX/polyelectrolyte structure combinations.

ACKNOWLEDGEMENTS

The authors thank French National Society Company and Kemira for providing the chemicals products and their helpful information.
L. Fraikin is thankful to the FRS-FNRS for its postdoctoral follow positions (FRFC project 2.4596.12)

NOMENCLATURE

A	filter sectional [m^2]
C	Ratio of mass of solid deposited by volume of collected filtrate [$kg.m^{-3}$]
CST	Capillary Suction Time [s]
DS	Dry solids content [%]
Pa	Applied pressure [Pa]
PAX	Polyaluminium chloride
R_{fm}	Resistance of the filter medium [m^{-1}]
SRF	Specific resistance of filtration [$m.kg^{-1}$]
t	Time [s]
V	Volume of filtrate [m^3]
V_0	Initial volume of filtrate [m^3]
VS	Volatile solids content [%]
W	Dry basis water content [kg_{water}/ kg_{DS}]
W_0	Initial dry water content [kg_{water}/ kg_{DS}]
µ	Liquid viscosity [Pa.S]

REFERENCES

[1] Conseil de l'Union Européenne. Directive 1991/271/EC du 21 mai 1991 du Conseil relative au traitement des eaux urbaines résiduaires. OJ L 135 30.05.1991. (1991) (1997).
[2] OTV, *Traiter et valoriser les boues*. Infinités Communication, Rennemoulin, 1997.
[3] Conseil de l'Union Européenne. Directive 1999/31/EC du 26 avril 1999 du Conseil relative à la mise en décharge des déchets. OJ L 182 16.07.1999. 1999.
[4] Eléments bibliographiques. Association Pôle Environnement Sud Aquitain, 2000.
[5] ADEME and Cabinet Arthur Andersen., Examen de la situation de la filière de recyclage agricole des boues d'épuration urbaines en Europe et dans divers autres pays du monde. ADEME Eds.; 1999.
[6]:Dentel, S.K., in: Spinosa, P.A. Vesilind (Eds.). Sludge into biosolids, IWA Publishing, London, 2001, Chapter 16.
[7]: Schuster, C., Kotz, J., Kulicke, W.M., Parker, S., Bohm, N., Jaeger, W. Acta Hydrochimy and Hydrobiology. **1993**, 25, 203-212.
[8]: Eriksson, L., Alm. B., Water Science Technology. **1993**, 28, 203-212.
[9] Huron, Y., Salmon, T., Crine, M., Blandin, G., Léonard, A., Effect of liming of the convective drying of urban residual sludges. Asia-Pacific Journal of Chemical Engineering. **2010**, 5 (1) 909-914
[10] Arlabosse, P., Ferrasse, J.-H., Lecomte, D., Crine, M., and Leonard, A. Efficient sludge thermal processing: from drying to thermal valorization.

Modern Drying Technology, Volume 4: Energy savings **2012**, 4, 295-329.
[11] Léonard A. Etude du séchage convectif de boues de station d'épuration - Suivi de la texture par microtomographie à rayons X. PhD Thesis, Université de Liège, Belgique, 2003.
[12] Bazzaoui, R., Fraikin, L., Groslambert, S., Salmon, T., Crine, M., Léonard, A. Impact of sludge conditioning on mechanical dewatering and convective drying. In Proceedings of Euro Drying Conference, Palma Balearic Island, Spain, October 26-28, 2011, 1-3.
[13] Vaxelaire, J., Bongiovanni, J. M., Puiggali, J. R. Mechanical dewatering and thermal drying of residual sludge. Environmental . Technology **1999**, 20 (1), 29-36.
[14] Bart Peeters. Effect of activated sludge composition on its dewaterability and sticky phase. PhD Thesis, Katholieke Universiteit Leuven, Belgique, 2011.
[15] ASAE. ASAE Standard. American Society of Agricultural Engineers; Eds.; Saint. Joseph Michigan.; 1996; 452-464
[16] Dentel, S.K., in: P.A. Vesilind, Sludge into Biosolids, IWA Publishing; Eds. London, 2001, Chapter 16.
[17] Lin, J.L., Huang, C., Pan, J.R., Wang, D. Effect of Al(III) speciation on coagulation of highly turbid water. Chemosphere **2008,** 72, 189-196
[18] Wu, X., Ge, X., Wang, D., Tang, H. Distinct coagulation mechanism and model between alum and high Al_{13}-PACl. Colloids and surfaces. Physicochemical and Engineering **2007,** 305, 89-96
[19] Peeters, B., Dewil, R., Van Impe, J.; Vernimmen, L., and Smets, I. Polyelectrolyte flocculation of waste activated in decanter centrifuge. Applications: Lab evaluation by a centrifugal compaction test. Environmental Engineering Science **2011**, 28(28), 765-773.
[20] Leonard, A., et al., Measurement of shrinkage and cracks associated to convective drying of soft materials by X-ray microtomography. Drying Technology **2004**. 22(7),1695-1708.
[21] Léonard A., Blacher S., Marchot P. and Crine M. Use of X-ray microtomography to follow the convective heat drying of wastewater sludges. Drying. Technology **2002**, 18, 1053-1069.
[22] Léonard, A., et al. Image analysis of X-ray microtomograms of soft materials during convective drying. Journal of Microscopy-Oxford **2003**, 212, 197-204.
[23] Vaxelaire J., Olivier J. Conditioning of municipal sludge dewatering. From filtration compression cell tests to belt press. Drying . Technology **2006**, 24, 1225-1233.
[24] Carman, P.C., Fundamental principles of industrial filtration. Transactions of the institution of chemical engineers, 1938; 168-188.
[25] XP-T97-001:"Essais des boues: Détermination des caractéristiques en liaison avec l'aptitude à la concentration" old French standard.; in AFNOR library, 1979.