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Review

Moisture distribution in activated sludges: a review

J. Vaxelaire*, P. Cézac

Laboratoire de Thermique, Energétique et Procédés, ENSGTI, Rue Jules Ferry, BP 7511, 64 075 Pau Cedex, France

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Abstract

The dewatering of residual sludges is a current problem due to the huge production of this waste. Activated sludges are generally hard to dewater, and the design and the control of the separation operations are often quite difficult. In order to better understand this problem, pertinent indices are needed. The knowledge of how water is distributed within activated sludge is an interesting approach. Current literature dealing with this topic is, however, relatively difficult to apply. This work presents a review of the problem of moisture distribution classification and measurement within activated sludge. The main techniques used for this analysis are compared and discussed in detail. The estimation of the water binding energy is also extremely commented upon. Finally, the paper discusses the utility of this type of analysis to examine the conditioning and dewatering of activated sludge.

Keywords: Bound water; Binding energy; Sludge dewatering; Sludge conditioning

Contents

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*Corresponding author. Tel.: +33-5-5940-7811; fax: +33-5-5940-7801.
E-mail address: jean.vaxelaire@univ-pau.fr (J. Vaxelaire).

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Nomenclature

a_w^l	thermodynamic activity of liquid water (–)
a_w^s	thermodynamic activity of solid water (–)
$\Delta Cp_{f,w}^*$	heat capacity at constant pressure for pure water freezing ($J\,mol^{-1}\,K^{-1}$)
e	sample thickness (m)
E	coefficient in constitutive equation ($Pa^{-\beta}$)
E_B	binding energy ($J\,mol^{-1}$)
F	frequency (Hz)
G	Gibbs energy (J)
h	equilibrium height of sludge in a centrifugal tube (m)
h_0	initial height of sludge in a centrifugal tube (m)
h_∞	height of sludge in a centrifugal tube under infinite rotational speed (m)
$\Delta H_{f,w}^*$	heat of freezing for pure water ($J\,mol^{-1}$)
$\Delta H^{l \to v}$	sum of the heat of evaporation of pure water and the heat of sorption ($J\,mol^{-1}$)
ΔH_s	heat of sorption ($J\,mol^{-1}$)
ΔH_v	heat of evaporation of pure water ($J\,mol^{-1}$)
m	masse (kg)
n	index in constitutive equation
n_c	total number of species
n_i, n_j	number of moles of the species i and j in the liquid water (mol)
n_w	number of moles of liquid water (mol)
n_{solute}	number of moles of liquid solute (mol)
N	rotational speed (rpm)
P	applied pressure (Pa)
P_s	compressive pressure (Pa)
P_{sat}	pressure at saturation (Pa)
P_{si}	reference pressure (Pa)
P_v	vapour pressure (Pa)
R	gas constant ($J\,mol^{-1}\,K^{-1}$)
R_C	centrifuge arm length (m)
RH	relative humidity (–)
RH_{eq}	relative humidity at the thermodynamic equilibrium (–)
s_w^l	partial molar entropy for water in the liquid phase ($J\,mol^{-1}\,K^{-1}$)
S	entropy ($J\,K^{-1}$)
$\Delta S_{f,w}^*$	entropy of freezing for pure water ($J\,mol^{-1}\,K^{-1}$)
t	time (s)
T	temperature (K)
T_f	freezing temperature (K)
$T_{f,w}$	water standard freezing temperature (K)
V	volume (m^3)
V_l	volume of liquid (m^3)
V_v	volume of vapour (m^3)
W_{C1}	water content at the first transition point ($kg_{H_2O}\,kg_{DS}^{-1}$)
W_{C2}	water content at the second transition point ($kg_{H_2O}\,kg_{DS}^{-1}$)
W_{eq}	water content at the thermodynamic equilibrium ($kg_{H_2O}\,kg_{DS}^{-1}$)
X	weight fraction of solid
x_B	mole fraction of solute
x_i^l	mole fraction of the specie i in liquid phase
z_i^s	mole fraction of the specie i in solid phase
x_w^l	mole fraction of water in liquid phase
α	local specific resistance ($m\,kg^{-1}$)
α_0	reference specific resistance ($m\,kg^{-1}$)
β	index in constitutive equation
ε	porosity
ϕ_w	bound water content ($kg_{H_2O}\,kg_{DS}^{-1}$)
γ_w^l	activity coefficient of water in liquid phase
μ_w^l	chemical potential of water in liquid phase ($J\,mol^{-1}$)
$\mu_w^{*,l}$	chemical potential of pure water in liquid phase ($J\,mol^{-1}$)
μ_w^s	chemical potential of water in solid phase ($J\,mol^{-1}$)
$\mu_w^{*,s}$	chemical potential of pure water in solid phase ($J\,mol^{-1}$)
ρ_{sl}	density of bulk sludge ($kg\,m^{-3}$)
ρ_s	solid density ($kg\,m^{-3}$)
ρ_w	water density ($kg\,m^{-3}$)
Ω	angular velocity ($rad\,s^{-1}$)
ω	weight fraction of solid in the sludge ($kg_{DS}\,kg_{sludge}^{-1}$)

1. Introduction

The treatment of effluents from industrial and domestic activities generates large amounts of activated sludge. Due to environmental and economic considerations, the reduction and reuse of this waste are nowadays needed. Many types of processing equipment (filters, centrifuges, dryers, incinerators, etc.) can be used depending on the chosen means of disposal and the sludge dewaterability. Good management of the necessary treatment requires good knowledge of the various types of the sludge. Among these materials, biological sludge issued from wastewater treatment is generally the most difficult to dewater. It is widely complex [1–3], hard to study and many parameters such as particle size, extracellular polymeric substances, cationic salts, filamentous bacteria, conditioning, etc., can influence its dewaterability [4–8]. The representation of the moisture distribution within the sludge has always been (and it is still) considered to be essential for the examination of dewatering problems. However, scientific literature in this field is often hard to apply because of controversial data and definitions.

This paper may help the reader to analyse the results reported in the literature more easily (and perhaps more efficiently). It first presents and compares different types of water classifications. Then, the most commonly used experimental methods are discussed in order to evaluate the accuracy of the results they can offer. The measurement of the binding energy is also discussed as an interesting parameter of water classification. Finally, the paper will discuss the utility of this type of analysis to examine the conditioning and dewatering of activated sludge.

This study only deals with activated sludge. The other residual sludges (organic or mineral) are separate specific cases. Moreover, they are generally easier to dewater and thus cause less problems during their treatment. The interested reader can find current literature on alum water treatment sludge [9,10], $CaCO_3$ [11], $Cu(OH)_2$ [11,12], clay [13], hot rolling mill sludge [14], kaolin [15,16], chemical sludge from tannery [17], lime water treatment sludge [9,15,16], metallic surface treatment sludge [14] and PVC [11].

2. Bound and free water

Due to the presence of solids, all the water within the sludge does not have similar properties in terms of vapour pressure, enthalpy, entropy, viscosity and density [18,19]. The behaviour of a molecule of water during the dewatering process is widely dependent on its proximity to the solid. Usually, two main types of water are considered: the free water which is not influenced by the solid particles and the bound water whose properties are modified due to the presence of the solid. The estimation of the amount of free water (the bound water being the complement to the whole amount of water) is based on this difference of behaviour. As several properties can change, different techniques have been used to measure the free water content (Table 1). The results presented in scientific literature differ widely due to this large range of experimental techniques. It is often argued that the free water is an operationally defined value depending on the chosen methods of measurement [14,11,9]. Some results of comparative studies are illustrated in Table 2. The measurements carried out by Lee and Lee [12], Chen et al. [24] and Chu and Lee [13] on sludges, sampled in the same plant, also show that a given technique (a drying test in this case) can lead to different values (Table 2). This can be explained by the large variability of materials such as activated sludge and by the different operating conditions used during the test: Chen et al. and Chu and Lee worked at 80°C while Lee and Lee used 40°C. In fact for the different methods, the operating conditions are not universally standardised (Table 1): this also contributes to the difficulty of efficiently putting to use the data supplied by this literature. It is generally admitted that the free water can be (partially or totally) removed by mechanical stress. Smollen [41] supposes that all the free water can be removed by a moderate stress (vacuum filtration under 5×10^4 Pa during 30 min) while Lee [40] considers that high pressures (usually larger than 28 MPa) are necessary to extract the all the free water within activated sludge. Another definition frequently used to describe free and bound water assumes that bound water remains unfrozen at temperatures below the freezing point of free water. The temperature most generally retained is $-20°C$ [14,35,37,9,16]. Other temperatures have also been used, for example $-8°C$ [30], and the impact of this parameter on the bound water measurement was discussed by Smith and Vesilind [32]. In a less usual manner, Herwijn [45] proposes to differentiate bound and free water according to the binding energy. He assumes that the water is bound when its binding energy exceeds 1 kJ kg^{-1}. This value was discussed by Lee and his fellow workers who consider it to be very low [24,16,13].

To evaluate the pertinence of these definitions, it is important to list the different mechanisms which can be involved in liquid–solid bonding and to discuss what different techniques do really measure. Both aspects are the purpose of the following parts of this paper.

3. Water classification

Simply classifying water into two categories is often insufficient to fully understand and predict the mechanisms of dehydration and of the pre-treatments which are usually associated with it (coagulation, flocculation, thermal conditioning). Consequently, supplementary types of water can also be considered. Generally, four kinds of water are proposed but a few slight differences can be noted in their definition (Table 3). The distribution suggested by Vesilind and his fellow workers [32,28,19,30] is often used as a reference which supposes the following four categories:

- Free water: water non-associated with solid particles and including void water not affected by capillary force.
- Interstitial water: water trapped inside crevices and interstitial spaces of flocs and organisms.
- Surface (or vicinal) water: water held on to the surface of solid particles by adsorption and adhesion.
- Bound (or hydration) water.

But, this classification does not fully consider the impact of the polymeric matrix which constitutes activated sludge. On this aspect Legrand [5] states that a large amount of water which is trapped into the polymer network. This idea is also discussed and completed by Mikkelsen and Keiding [6], who have

Table 1
Different techniques used to measure water distribution within activated sludge

Technique	Authors	Operating conditions
Drying test		
Vacuum drying	Smollen [20]	$P = 60$ kPa; $T = 35$°C; e = N.D.
	Halde [21]	P = N.D.; $T = 30$°C; $e = 5$ mm
	Halde [21]	$P = 13$ kPa; $T = 35$°C; e = N.D.
	Kopp and Dichtl [22,23]	RH = N.D.; $T = 35$°C; e = N.D.
Drying at atmospheric pressure	Chu and Lee [13]	RH = N.D.; $T = 80$°C; e = N.D.
	Chen et al. [24]	RH = N.D.; $T = 80$°C; e = N.D.
	Lee [25]	RH = 60%; $T = 40$°C; e = N.D.
	Lee and Hsu [11]	RH = 60%; $T = 40$°C; $e = 1$ mm
	Lee and Lee [12]	RH = 60%; $T = 40$°C; e = N.D.
	Lee [26]	RH = N.D.; $T = 40$°C; $e = 1$ mm
	Matsuda et al. [27]	RH = 11%; $T = 30$°C; $e = 0.7$ mm
	Robinson and Knocke [9]	RH = 50–60%; $T = 35$°C; $e \leqslant 2$ mm
	Tsang and Vesilind [28]	N.D.
	Coackley and Allos [29]	RH = 34%; $T = 30$°C; $e = 10$ mm
Dilatometric test	Wu et al. [16]	Hydraulic oil, $T = -20$°C
	Vesilind and Hsu [30]	Hydraulic oil, $T = -8$°C
	Lee [31]	N.D.
	Smith and Vesilind [32]	Hydraulic oil, $T = -35$°C to -3°C
	Colin and Gazbar [14]	Xylene, $T = -20$°C
	Gazbar [33]	Xylene, $T = -20$°C
	Robinson and Knocke [9]	Hydraulic oil, $T = -20$°C
	Katsiris and Kouzeli-Katsiri [18]	N.D.
	Barber and Veenstra [34]	Crude petroleum, $T = -20$°C
	Forster [35]	Xylene, $T = -20$°C
	Forster and Lewin [36]	Xylene, $T = -20$°C
	Heukelekian and Weisber [37]	Crude petroleum, $T = -20$°C
Centrifugal settling test	Yen and Lee [38]	$R_C = 0.188$ m, $N = 200-500$ rpm (8–51 g), $t = 1400$ s
	Erdincler and Vesilind [39]	R_C = N.D., N = N.D. (2800 g), $t = 1800$ s
	Colin and Gazbar [14]	R_C = N.D., N = N.D. (5–20 g), $t = 7200$ s
	Lee and Hsu [11]	$R_C = 0.135$ m, $N = 0-4000$ rpm (0–2369 g), $t = 3600$ s
	Lee [40]	$R_C = 0.135$ m, $N = 0-4000$ rpm (0–2369 g), $t = 3600$ s
	Gazbar [33]	R_C = N.D., N = N.D. (5–20 g), $t = 7200$ s
	Matsuda et al. [27]	$R_C = 0.134$ m, $N = 1000-3000$ rpm (147–1322 g), $t = 3600$ s
Expression test	Chu and Lee [13]	$P = 20.7$ MPa
	Chen et al. [24]	$P = 31.0$ MPa
	Lee [25]	$P = 31.0$ MPa
	Lee and Hsu [11]	$P = 3.4$–31.0 MPa
Filtration test	Smollen [41]	$P = 0.05$ MPa, $t = 1800$ s
	Lee [25]	N.D.
Differential thermal analysis (DTA)	Katsiris and Kouzeli-Katsiri [18]	$T_{\mathrm{mini}} = -20$°C, cooling rate 2°C min^{-1}, $m_{\mathrm{sample}} = 18-25$ mg
Differential scanning calorimetry (DSC)	Erdincler and Vesilind [39]	T_{mini} = N.C., cooling rate 2°C min^{-1}, $m_{\mathrm{sample}} = 30$ mg
	Lee and Hsu [11]	$T_{\mathrm{mini}} = -60$°C, cooling rate 10°C min^{-1}, $m_{\mathrm{sample}} < 10$ mg

Table 1 (*continued*)

Technique	Authors	Operating conditions
	Lee and Lee [12]	$T_{\mathrm{mini}} = -60^\circ\mathrm{C}$, cooling rate 1–10°C min^{-1}, $m_{\mathrm{sample}} =$ N.D.
Combined thermal gravimetry analysis and differential thermal analysis (TGA/DTA)	Chu and Lee [13]	$T = 80^\circ\mathrm{C}$, $m_{\mathrm{sample}} = 100\,\mathrm{mg}$
	Chen et al. [24]	$T = 80^\circ\mathrm{C}$, $m_{\mathrm{sample}} = 35\,\mathrm{mg}$
Water vapour sorption	Vaxelaire [42]	Method based on thermodynamic equilibrium
	Ferrasse [43]	Combined TGA/DSC method
	Vaxelaire et al. [44]	Method based on thermodynamic equilibrium
	Herwijn [45]	Method based on thermodynamic equilibrium
Nuclear magnetic resonance	Carberry and Prestowitz [46]	$F = 10.72\,\mathrm{MHz}$

N.D., no data given.

Table 2
Results of some comparative studies carried out on different activated sludges

	Bound water content ($\mathrm{g\,g^{-1}}$ DS)				
	Bread plant sludge	Fibre plant sludge	Municipal sludge	Aerobic digested municipal sludge	Anaerobic digested municipal sludge
Katsiris and Kouzeli-Katsiri [18]			DTA 10.68		
Matsuda et al. [27]			Di 11.4 CS 8.1 Dr 8.5		
Robinson and Knocke [9]				Dr 6.8±1.0 Di 5.2±0.5	Dr 5.3±0.9 Di 3.9±0.4
Lee [26,40]		CS[a] 4.13 Ex[a] 3.43			
Lee and Lee [12]	DSC[a] 6.6 Dr[a] 6.3				
Lee and Hsu [11]		Ex 3.85 Dr 6.70			
Lee [25]		Ex 2.8–3.6 Dr 4.6–5.7 F 7.8-8.5			
Chen et al. [24]	Ex[a] 4.0 Dr[a] 5.1				
Chu and Lee [13]	Ex 3.6 Dr 4.3				

[a] Average data: CS, centrifugal settling; Di, dilatometric method; Dr, drying test; DSC, differential scanning calorimetry; DTA, differential thermal analysis; Ex, expression test; F, filtration test.

introduced the term "water-holding" to cover both surface bound water and osmostic water as well as water trapped within the polymer network. Nevertheless, no data are yet available in current literature concerning the amounts of this new kind of water. Another aspect the above classification does not consider is the nature of intracellular water, which is not well defined either [39].

Taking into account all the previous remarks, it is quite difficult to get a clear picture of the distribution of water within activated sludge. Thus, the choice of the

Table 3
Main classifications of water within activated sludge

Kind of bond	Keey [47] and Halde [21]	Tsang and Vesilind [28], Vesilind [19], Smith and Vesilind [32], Vesilind and Hsu [30]	Smollen [41,20]	Kopp and Dichtl [22,23]	Lee and Lee [12]
Chemical	Ionic: hydration	Bound (or hydration) water	Chemically bound: bound by powerful chemical linkage	Intracellular water	Internal water
	Molecular: crystallisation				
Physical	Adsorptive: hydrogen bonding/ solvatation	Surface (or vicinal) water: held on to the surface of solid particles by adsorption and adhesion	Bound water: adsorbed by individual solid particle	Surface water: bound by adhesive forces	Surface water: physically and/or chemically adsorbed
	Physico-chemical adsorption Osmotic: osmotic imbibition Structural: dissolution in gels				
Mechanical	Microcapillary: capillary condensation	Interstitial water: trapped in crevices and interstitial spaces of flocs and organisms (perhaps water trapped within cells)	Immobilised water: capillary, trapped or adhesive	Interstitial water: bound by capillary forces between the flocs	Interstitial water
	Macrocapillary: capillary condensation				
Unbound	Surface condensation	Free moisture: non-associated with solid particles Include void water not affected by capillary force	Free water	Free water	Free water

best-adapted method of investigation is not easy. However, an extensive discussion about the different methods which are currently applied should facilitate the use of data reported in current literature, as well as provide a better evaluation of the information that each test can offer.

4. Discussion

4.1. Drying test

This technique assumes that the rate of evaporation of the water depends on the type of bond between the water and the solid particles (or within the material structure). This is based on the analysis of a drying curve. According to drying literature [47,48] this curve describes the evolution of the evaporation flux versus the mean moisture content. It classically shows four different phases (Fig. 1):

- A short period of increasing temperature.
- A period of constant rate, this is typical of free water evaporation at the surface of the material.
- A falling rate period, this is typical of the drying boundary progressing into the material. Below this drying boundary there is free water migration. Above it only the bound water (in the case of hygroscopic

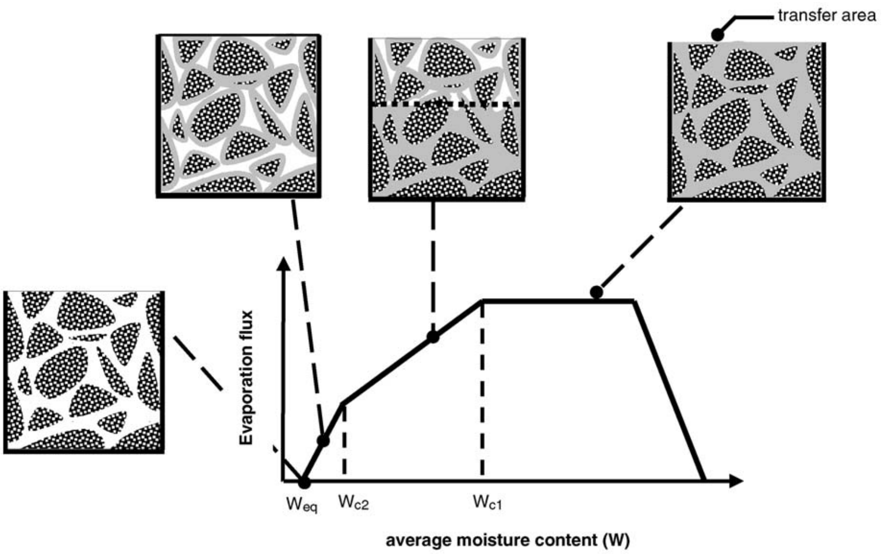

Fig. 1. Classical drying curve.

material) and the vapour are removed. The mass and heat transfer resistance increases as the drying boundary progresses into the material. This results in the decrease of the evaporation flux.
- In the case of hygroscopic materials (such as activated sludge), a second falling rate period appears due to the very slow evaporation of more hardly bound water.

The transition between the period of the constant rate and the falling rate period is a typical point of the drying rate curve. It is often used to quantify the amount of bound (not free) water [11,9,28,22,23]. It represents the transition from a period where the process of drying is controlled by external conditions (for a convective drying test the external conditions are temperature, relative humidity and air velocity) to a period where the transfer properties inside the product control the process. The moisture content at this point (W_{C1}) depends both on the material being dried and the drying conditions. Consequently, it cannot be considered to be an intrinsic parameter of the sludge.

Similarly, the use of the equilibrium moisture content (W_{eq}) as a parameter used to identify the amount of chemically bound water [20,28], internal water [12,11] or intracellular water [22,23] is worthy of discussion. Indeed, it represents the moisture content at the thermodynamic equilibrium under the operational conditions of the drying test (relative humidity and temperature). So it not only depends on the nature of a given solid, but on the operating conditions (the evolution of the equilibrium moisture content combined with temperature and air humidity can be described by sorption isotherms [45,44,43,42]. Besides, in the case of shrinkable materials (such as activated sludge) a good analysis of drying curves has to be based on evaporation flux data (g water s^{-1} m^{-2}). Consequently, it is necessary to follow both sample mass and sample size during the test. Contrary to what it is implicitly supposed in most of the studies using the drying method, the size of activated sludge samples widely decreases during the test and thus the decrease of the transfer surface area cannot generally be neglected [49,50]. Moreover, the thickness of the sample also influences the drying curve and the position of the transition points [21]. As shown in Fig. 1a "dry zone" appears at the exposed surfaces at the beginning of the first falling period and it advances progressively through the cake. Consequently, some moisture gradients, related to the permeability of the material and to the external transfer resistances, may appear within the sample. An average moisture content is no longer representative of the sludge behaviour. This phenomenon can be limited by using thick samples. Finally, some recent studies have described the formation of a crust [51] and cracks [49] appearing at the surface and within the sample, respectively. Both phenomena can also perturb the analysis of the drying curves, which again proves the inadequacy of using the drying test for water classification purposes.

4.2. Techniques based on freezing properties

4.2.1. Dilatometric test

In this method, bound water is defined as the water which does not freeze at the same temperature as that of free water, which is typically −20°C. The amount of free water is determined by observing the expansion of a given sludge sample, due to the transformation of free water to ice. The bound water content is calculated by the difference between the amount of free water and the total amount of water (usually measured by drying at 105°C for 24 h). The sample of sludge is immersed into an indicator fluid in order to measure its expansion under freezing conditions. Different schemes of dilatometer can be found in the literature [14,37,9,32,30]. An important step in the test is the selection of the indicator fluid. Heukelekian and Weisber [37] suggest the following criteria in selecting the fluid:

- it must be immiscible in water,
- it must have a specific gravity less than water,
- it must not freeze at the lowest temperature employed,
- it must have a linear expansion/contraction over the temperature range in question.

Several relatively common fluids meet these criteria and can be used for the test (see Table 1). The value of the water expansion coefficient is also a main parameter for the analysis of the experimental data. Wu et al. [16] show some differences between the bound water content calculated using the expansion coefficient of distilled water and the expansion coefficient of a filtrate.

According to Robinson and Knocke [9] the dilatometric technique is preferable to the drying test because it is rapid and it allows an easier analysis of experimental raw data. On the contrary, Katsiris and Kouzeli-Katsiri [18] report some difficulty in using this method. In order to improve the quality of the measurement and to better analyse the experimental data, Smith and Vesilind [32] propose a detailed review of the parameters which can influence (or perturb) the results. They show that gas bubbles liberated from the sludge, freezing temperature and solid concentration can all affect frozen water measurements. Moreover, they point out that "the amount of unfrozen water in the sludge is a combination of the effects of trapping of water in between the particles of the floc, the quantity of the ordered layers at the particle surface as well as the extent of intracellular ice formation". Since all these mechanisms cannot be separated during experimental measurements, the interpretation of the results can be debatable. A similar problem also exits with the other methods which measure the amount of unfrozen water, such as in differential thermal analysis (DTA) and differential scanning calorimetry (DSC) tests.

4.2.2. DTA and DSC tests

Similarly to the dilatometric test, these techniques are based on the assumption that bound water does not freeze when the sample is cooled to below the threshold temperature, for example −20°C. DTA measures the difference of temperature between the sample and a reference sample (which is a thermally inert material: alumina powder, for example) in relation to imposed temperatures. Plotting the temperature differences against several fixed temperatures shows increasing or decreasing peaks characteristic, respectively, of exothermic or endothermic transformations in the sample. By measuring the area of the peaks and by considering the heat of water freezing, Katsiris and Kouzeli-Katsiri [18] convert the temperature data into the amount of heat required for transformation and then finally into the mass of unfrozen water. This analysis in terms of heat (instead of temperature) is close to the DSC approach. The latter technique measures the variation of the heat absorbed or released by a sample placed in a controlled atmosphere and submitted to temperature scanning. Any transformation in the sample induced by the evolution of the temperature, such as water freezing, can be observed (this is the peak of the heat) and described by direct thermal analysis. If it is assumed that bound water does not freeze at the given threshold temperature, the heat released by the sample during measurement is proportional to the free water amount. The bound water content can be determined by its difference to the total water content, which is measured by drying at 105°C.

According to Katsiris and Kouzeli-Katsiri [18], such tests are fast and can be considered as a valuable tool for the determination of bound water. However, Lee and Hsu [11] indicate that they are not well adapted for the measurement of the bound water content within activated sludge because the sample uniformity cannot be guaranteed. Indeed, these sludges generally contain large particles or flocs and the sample quantity is usually small (10–30 mg). Moreover, the choice of the threshold temperature is very important because it is equivalent to define a threshold binding energy used for distinguishing free and bound water [12]. However, the freezing water temperature depends of many combined phenomena (adsorption, capillary strengths, non-ideality of the aqueous phase, etc.) and the choice of the threshold temperature is not really obvious.

4.3. Mechanical strain tests

4.3.1. Centrifugal settling test

This method assumes that a sample centrifuged under an infinite rotational speed ($N \to \infty$) tends towards an equilibrium height (h_∞) which corresponds to a sediment composed of only dry solid and bound water. All the free water is removed and the bound water is not affected. According to this uncertain hypothesis, the bound water content per mass of dry solid (ϕ_w) can be derived from a mass balance [27]:

$$\phi_w = \left(\frac{\rho_s - \rho_w}{\rho_{sl} - \rho_w}\frac{h_\infty}{h_0} - 1\right)\frac{\rho_w}{\rho_s}. \quad (1)$$

The problem is now to estimate h_∞. Matsuda et al. [27] defined h_∞ at the ordinate intercept in the linear dependency of h/h_0 versus $1/N$. However, Lee [40,11] has shown that this approach fails with activated sludge, due to significant non-linearity when the rotational speed is high. He proposes to combine the equation describing the evolution of the compressive pressure acting on particles with a constitutive equation (empirical equation) to compute h_∞ from the h/h_∞ versus $1/N$ data [40]:

$$\frac{h}{h_0} = \frac{h_\infty}{h_0 E(1-\beta)}\left(\frac{\rho_{\mathrm{sl}}}{\rho_{\mathrm{s}}}\omega(\rho_{\mathrm{s}}-\rho_{\mathrm{w}})R_{\mathrm{C}}h_0\right)^{-\beta}\Omega^{-2\beta}. \tag{2}$$

This equation includes three unknown variables (h_∞, E and β). The plot of $\log(h/h_0)$ versus $\log \Omega$ shows a linear relationship but enables only the estimation of β. Complementary experiments are thus needed to access h_∞. Lee [40] uses some vacuum filtration tests to estimate E and finally h_∞. His filtration approach requires the use of the average specific resistance of filtration (SRF) of the cake. However, few authors [52,53] have described, in the case of extremely compressible material such as activated sludge, the formation of a skin with a very low permeability at the cake/filter medium interface, during filtration. Consequently, the real meaning (or validity) of the average SRF can be discussed [54] and its use criticised. Besides, the use of filtration tests to estimate the parameters E and β is questionable. Other devices are generally preferred: the most frequently employed is the compression–permeability cell [55,56] but its use with activated sludge can also be criticised because of a too long testing time (few days) which can modify the sludge properties of dewatering [57]. A new type of compression–permeation cell was recently proposed by Wu et al. [57], but until now little information on using this device is available in the literature.

Besides, Lee [40] considers the following constitutive equations:

$$\begin{aligned} 1-\varepsilon &= EP_{\mathrm{s}}^{\beta} \text{ and } \alpha = \alpha_0 P_{\mathrm{s}}^{n} \quad \text{if } P_{\mathrm{s}} \geqslant P_{\mathrm{si}}, \\ 1-\varepsilon &= EP_{\mathrm{si}}^{\beta} \text{ and } \alpha = \alpha_0 P_{\mathrm{si}}^{n} \quad \text{if } P_{\mathrm{s}} \geqslant P_{\mathrm{si}}. \end{aligned} \tag{3}$$

Some other mathematical relationships could also be retained as constitutive equations [58] and perhaps lead to different values of h_∞. Moreover, all these constitutive equations implicitly assume that the activated sludge is an elastic material; this is an approximation [59,60] which can also influence the analysis of the results [38].

All these remarks could perhaps explain why the centrifugal settling test is not extensively used. Moreover, this method is essentially based on a widely questionable hypothesis which considers that the sediment resulting of a centrifugation carried out under an infinite rotational speed is composed of only dry solid and bound water.

Colin and Gazbar [14] give another approach to analysing experiments carried out in a centrifuge to describe the distribution of water within sludge. They define a new classification which separates water into different categories (free water, bound water removable by moderate mechanical strain, bound water removable by maximum mechanical strain (60 000 g during 120 min), bound water not mechanically removable), depending on its behaviour during mechanical dewatering. This method seems to be an interesting way to estimate, for a given sludge, the expected efficiency of mechanical dewatering processes, in terms of solid concentration. Nevertheless, it requires a very powerful equipment.

4.3.2. *Filtration test*

This test measures the moisture content of the sludge after a vacuum filtration. Smollen [41] and Lee [25] suppose that the water remaining in the cake after the filtration is the bound water. However, they observed a constant rate period during the drying of the filtrated samples, that they assume to represent the evaporation of interstitial water. This interpretation of the drying curve is rather different from the classical analysis proposed by many other authors (see drying test section) and raises doubts about the pertinence of this test.

4.3.3. *Expression test*

This technique assumes that the final moisture content of sludge expressed under a very high constant pressure (generally around 31 MPa) corresponds to the bound water content [11]; but this main assumption is not verified. Consequently, the validity of this method to measure bound water content can be criticised. Lee et al. [11,13] have shown, from experimental data, that the bound water content is significantly higher when it is estimated by drying, than by the expression test. From experimental comparisons between both methods, Chen et al. [24] concludes that "the water removable by expression should include some surface (physically adsorbed) water as discussed in Tsang and Vesilind [28] or the vicinal water in Dick and Drainville [61]", but nothing was proved. In fact this technique does not seem to be well adapted to the classification of water into the categories defined in the previous paragraphs. However, it is an interesting method to evaluate the upper limits of any conventional mechanical dewatering device (which works under much lower strain). In this aspect, the expression test can be compared to the approach proposed by Colin and Gazbar [14] with their centrifugal test.

4.4. *Sorption isotherms*

This technique allows one to describe the changes of the moisture content within the sample in relation to the thermodynamic activity of the water, at a fixed temperature. From thermodynamic considerations and under some assumptions [44,51] the water activity (a_w^l) is defined by the following ratio:

$$a_w^l = \frac{P_v}{P_{sat}(T)} = RH_{eq}. \tag{4}$$

Experimentally speaking, samples of sludge are placed in containers where the relative humidity is fixed thanks to mixtures of water and sulphuric acid (or salts) of different compositions. The containers are set inside a chamber under controlled temperature. The samples are weighed at the thermodynamic equilibrium (which is reached when the weight remains constant over time). The mass of dry solid is measured at the end of the experiment by drying at 105°C for 24 h. The classical shape of the sorption isotherm curve in the case of water vapour is composed of three parts (Fig. 2):

- AB: the solid surface is covered with a mono-layer of adsorbed water molecules. The interaction forces are short-ranged and very intense.
- BC: the interaction forces decrease and multiple layers of water molecules are held to the solid surface.
- CD: the layers of water molecules coalesce within the micro-pores of the solid structure, and the water is bound due to capillary forces. The free water content can be estimated at $a_w = 1$, but this determination is generally not accurate due to the experimental difficulty of fixing a high relative humidity value (or corresponding water activity). In fact this technique is more adapted for a continuous characterisation of the bound water. However, the length of the measurement (a few weeks) can be a barrier to its use. Arlabosse et al. [62] state that this long testing time is not adapted to biological materials since their properties changes with time. It is indeed usually accepted that the micro-organisms activity significantly decreases with the reduction of the water activity. Consequently, the evolution of the biomass should not have a significant impact on the results obtained at low water activities (below 0.5). To avoid this discussion Ferrasse et al. [63] have recently proposed a faster method (only a few hours) based on a coupled TGA/DSC techniques to determine the water sorption isotherms. They tested it on activated sludge [43]. However, this approach requires several assumptions, which are often too complex to verify, such as the local equilibrium at the surface of the sample or the ability of using the model of the stagnant film [64]. Consequently, some complementary studies are needed to validate this recent technique.

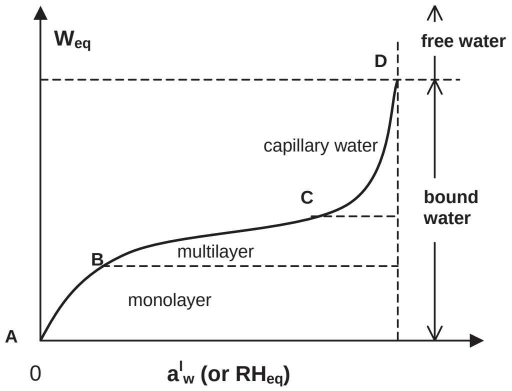

Fig. 2. Classical isotherm curve for water.

5. Binding energy

Due to the "operational character" of the different techniques used to represent the water distribution and to the difficulty in proposing a single classification, the measurement of the water–solid binding energy may be an interesting means to characterise sludge for dewatering purposes. All the research dealing with this approach try to describe the non-ideal behaviour of bound water. According to Lee and Lee [12], the freezing temperature of bound water is decreased due to the reduction of the chemical potential of the water. They suppose this to be linked to the energy of interaction between solid and liquid. Assuming bound water to be an ideal binary solution, with a large excess of water, they derive a simple analytic relationship between the freezing temperature of the sludge, the molar concentration for a given solute and an energy (E_B) that they suppose to be a binding energy. In addition, few relatively strong assumptions (bound water is supposed to be an ideal binary solution with a large excess of water, the entropy of the liquid phase (multi-components) is assimilated to the entropy of pure water, the binding energy is not dependent on temperature) it seems that the approach proposed by Lee and Lee [12] does not measure only the binding energy. Indeed, if one compares the equation they use to calculate the chemical potential of bound water:

$$d\,\mu_w^l = -s_w^l\, dT - \frac{RT}{n_w + n_{solute}}\, dn_{solute} - dE_B \tag{5}$$

with the classical relationship of the chemical potential:

$$dG = \underbrace{\left(\frac{\partial G}{\partial T}\right)_{P,n_i}}_{-S} dT + \underbrace{\left(\frac{\partial G}{\partial P}\right)_{T,n_i}}_{V} dP + \sum_{i=1}^{n_c} \underbrace{\left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j \neq n_i}}_{\mu_i} dn_i \tag{6}$$

it appears that E_B may be considered to be a term of non-ideality. To better discuss this point the thermodynamic equilibrium between the two phases can be established under the following assumptions:

- the uniformity of both phases,
- that no transfer of heat, mass and volume occur between the two phases.

As the two phases are condensed, the influence of the pressure can be neglected and the equality of the chemical potentials can be written as

$$\mu_w^{liq}(T, x_i^{liq}) = \mu_w^{solid}(T, z_i^{solid}). \tag{7}$$

Assuming that the calorific capacities are constant in the range of temperature considered, that $T - T_{f,w}$ is weak and that the ice is a pure solid, Eq. (7) can be rewritten under the following form:

$$RT \ln(x_w^l) + \underbrace{RT \ln(\gamma_w^l)}_{\text{excess term}} = \Delta H^*_{f,w}(T_{f,w})\left[1 - \frac{T_f}{T_{f,w}}\right]. \tag{8}$$

This relationship enables the calculation of an excess term which characterises the non-ideal behaviour of the aqueous solution. This is induced by both the chemical and the physical contributions. Its value for different freezing temperatures can be calculated at a given molar concentration for solute (x_B). Table 4 presents a comparison between this excess term and the binding energy measured by Lee and Lee [12] for $x_B = 5 \times 10^{-2}$. It reveals a good agreement between both the compared values, which tends to indicate that the results proposed by Lee and Lee should not be strictly considered as solid–liquid binding energy. Similar comparisons carried out with the other concentrations for solute reported by Lee and Lee lead to an analogous result.

Comparable comments may also be made on the results presented by Wu et al. [16]. These authors apply the thermodynamic approach proposed by Lee and Lee to dilatometry tests and assume, in this particular case, that the solute has no significant impact on bound water freezing. Consequently, they can derive a simple equation to relate the binding energy to the freezing temperature:

$$E_B = \frac{T_f - T_{f,w}}{T_{f,w}} \Delta H_f^*(T_{f,w}). \tag{9}$$

From this relationship and their experimental results, they report binding energies ranging between 4.9 kJ kg^{-1} (at $T = -4°C$) and 29.4 kJ kg^{-1} (at $T = -24°C$). However, according to Eq. (8) the concentration for solute tends to decrease the freezing temperature. Consequently, the accuracy of the assumption (and the equation) proposed by Wu et al. is not apparent and their results are contestable.

Another method, based on combined DTA/TGA tests, can also be considered to evaluate the binding energy [24,13]. It defines bound water as water having a heat of evaporation greater than that of pure water. The flux of heat and the heat of vaporisation can be obtained from a relatively simple analysis of experimental data [24]. The binding energy is finally calculated by the difference between the heat of evaporation of the sample water and of the pure water. This approach assumes essentially:

1. that thermodynamic equilibrium exists at the surface of the sample,
2. that the product of the mass transfer conductance multiplied by the transfer area and by a parameter characteristic of the apparatus is constant for both pure water and sludge,
3. that the liquid and the gas phases are ideal.

The operating conditions (in terms of speed of increasing temperatures) reported by Chen et al. tend to validate assumption (1). However, the validity of assumption (2) remains questionable according to sample shrinkage. This was discussed previously in the section concerning drying techniques. Assumption (3) can also be validated according to the thermodynamic discussion just above.

The results reported by Chen et al. show a smooth variation of the binding energy followed by a steep increase, reaching maximal values of around 800–1000 kJ kg^{-1} for a moisture content close to 0.3 kg kg^{-1}. The moisture content at the transition point is about 0.5 kg kg^{-1}. For higher moisture contents the binding energy is below 100 kJ kg^{-1}. Due to the accuracy of these results (±30 kJ kg^{-1} is reported by Chen et al.), the binding energy in this part of the curve is of the same magnitude than the excess term calculated previously. Chen et al. comment their results in an equivalent way: they consider that the energy, which they present as binding energy, might not only take into account the real chemical and physical bonds but other contributions as well.

Herwijn [45] and Vaxelaire [42] propose a third way, using sorption isotherm data, to evaluate the binding

Table 4
Comparison, for $x_B = 5 \times 10^{-2}$, of the binding energy measured by Lee and Lee [12] and the excess term calculated from Eq. (8)

Data reported by Lee and Lee [12]		Excess term calculated from Eq. (8)
Freezing temperature (°C)	Binding energy: E_B (kJ kg^{-1})	
−5.17	0	0.04
−13.36	10	10.14
−21.56	20	20.32
−29.75	30	30.51
−37.95	40	40.69
−46.14	50	50.87

energy. It is based on the Clausius–Clapeyron equation:

$$\frac{dP_v}{dT} = \frac{\Delta H^{l \to v}}{T(V_v - V_l)}, \qquad (10)$$

where $\Delta H^{l \to v}$ is the sum of the heat of evaporation of pure water (ΔH_v) and the heat of sorption (ΔH_s). Assuming the gas phase to be an ideal gas and considering ΔH_s to be constant over the range of temperature studied, a linear relationship between ΔH_s and the logarithm of the water activity can be established. Vaxelaire [42] estimates from this approach the heat of sorption ranging between 0 and 200 kJ kg^{-1} and compares it to the binding energy evaluated by the previously discussed methods. In the latter case, the thermodynamic approach used does not take into consideration the non-ideal behaviour of the bound water. Like the other methods the proposed results may include in a unique parameter the impact of different physical and chemical phenomena. A perspective to improve the characterisation of the water distribution within activated sludge could be to carry out a chemical analysis of the surrounding water in terms of species and concentration in order to calculate the energy due to the non-ideality. Then this value should be considered during the determination of the binding energy, measured on the same sample of sludge by DTA/TGA tests or by sorption isotherms determination.

6. Implication to sludge conditioning and dewatering

The representation of the water distribution within sludges is theoretically an interesting parameter for studying sludge conditioning or for predicting its dewatering. However, it is not always of practical use. In terms of conditioning, all the studies published in the current literature show a significant reduction of the bound water content under thermal treatment (freezing/thawing or heating) (Table 5). Neyens and Baeyens [7] have recently published a review paper which discusses the impact of such pre-treatments on the sludge structure. The impact of a chemical treatment (polymer or inorganic coagulant) on the distribution of the water within the sludge is reviewed in Table 5. The majority of authors report an increase of the amount of free water when some chemical conditioners are added to the slurry [21,18,46,14,9]. Even if the impact of chemical conditioning is quite largely admitted, different explanations are proposed to describe this behaviour. Few authors suggest that chemical conditioners act either by replacing water molecules adsorbed on the particle surface or by affecting the water binding capacity to the particle [18,9]. Chu and Lee [13] agree with this explanation when the dose of conditioner is below the charge neutralisation point. For overdosed conditioning they observe an increase in bound water, and they assume that an ‘‘absorption of moisture onto the polymer segments may be responsible for this subsequent increase’’. Smollen [20] also observes an increase of the bound water content under chemical conditioning and explains it in the same way. The action of inorganic coagulants is less discussed. Halde [21] and Katsiris and Katsiris-Kouzeli [18] assume that conditioning by metal salts may be governed by electrostatic forces, but no detailed mechanism is proposed to explain the increase of the free water content. This is damageable because the presence of salts in aqueous systems tends to reduce the freezing temperature of the water. Consequently, one could expected, in this case, more unfrozen water (for a given threshold temperature) and thus an increase of the bound water content (which is estimated from the difference between total water and frozen water).

In regard to the possible correlation between the water distribution within the sludge and its ability to dewater, current literature it is divided (Table 6). The difference in results is explained by some doubts concerning the meaning and/or validity of the measurements of the water distribution (cf. Section 4) and the meaning of the characteristic parameters of the dewatering efficiency such as the SFR or the capillary suction time (CST). About the pertinence of SFR in the case of activated sludge, a discussion is proposed in the mechanical strain test part. Concerning the validity of CST measurements, several investigators [45,59] have criticised the use of this parameter to characterise dewatering ability and have pointed out few experimental problems (influence of the sludge concentration and of the filter paper structure, theoretical model describing the filtration process for CST apparatus).

Besides, many parameters such as particle size and surface characteristics, floc structure, etc. can simultaneously influence sludge dewatering [4–6,8]. Consequently, a single index such as bound water content (or water distribution within the sludge) may not be sufficient to describe all the acting phenomena during the solid–liquid separation and may not correlate well with the true sludge ability to dewater.

The continuous classification of moisture content seems to be an interesting approach if the real meaning of the measured binding energy is known and if the energy provided by each separation process can be evaluated. Chu and Lee [65] have recently proposed a model to estimate the disruption (or binding) energy exerted on the sludge under a centrifugal field. This approach which takes into account the pressure–volume work (considering the volume change of the sludge) and the friction loss, induced by the filtrate, gives a binding energy in the range of 1–13 kJ kg^{-1}. For conventional mechanical dewatering devices, Chen et al. [24] consider a low binding energy, close to 1 kJ kg^{-1} and estimate that 70–80 kJ kg^{-1} can be considered as the upper limit for any mechanical device. The latter value is determined

Table 5
Impact of the conditioning on water distribution

Type of conditioning	Impact on water distribution	Test used	Authors
Polymer	+ +	Drying	Halde [21]
	+ +	DTA	Katsiris and Katsiris-Kouzeli [18]
	+ +	NMR	Carberry and Prestowitz [46]
	+ +	Drying	Smollen [20]
	+	Drying	Tsang and Vesilind [28]
	+ +	Dilatometry	Robinson and Knocke [9]
	+ +	Centrifugation	Colin and Gazbar [14]
	+ +	ATG/ATD	Chu and Lee [13]
	–	Drying	Kopp and Dichtl [22]
	–	Sorption isotherm	Vaxelaire et al. [44]
	+	Expression	Chang et al. [17]
Inorganic coagulant	+ +	Drying	Halde [21]
	+ +	DTA	Katsiris and Katsiris-Kouzeli [18]
	–	Sorption isotherm	Herwijn [45]
Freezing–thawing	+ +	Drying	Halde [21]
	+ +	DTA	Katsiris and Katsiris-Kouzeli [18]
	+ +	Dilatometry	Robinson and Knocke [9]
	+ +	Drying	Lee [26]
	+ +	ATG/ATD	Chen et al. [24]
Heating	+ +	DTA	Katsiris and Katsiris-Kouzeli [18]
	+ +	DCS and centrifugation	Erdincler and Vesilind [39]

Note: + +, significant impact; +, weak impact; –, no impact.

Table 6
Correlation between water distribution and some parameters measuring dewatering efficiency

Parameter characterising solid–liquid separation	Correlation with water distribution	Test used	Authors
Capillary suction time (CST)	–	Drying	Smollen [20]
Specific resistance of filtration (SRF)	+ +	Dilatometry	Robinson and Knocke [9]
Sludge volume index (SVI)	–	Dilatometry	Barber and Veenstra [34]
Solid content after dewatering in full scale processes (centrifuge, press filter)	–	Drying	Smollen [20]
	+ +	Dilatometry	Heukelekian and Weisber [37]
	+ +	Dilatometry	Forster and Lewin [36]
	+	Dilatometry	Barber and Veenstra [34]
	+ +	Drying	Kopp and Ditchlt [22]

Note: + +, significant correlation; +, weak correlation; –, no correlation.

from measurements carried out in a laboratory constant head piston press working under very high pressure (generally around 31 MPa). In classical industrial processes such as belt filter or press filter the applied pressure is much lower; it generally ranges between 0.2 and 1.5 MPa. For drying, they suggest a binding energy of 40 kJ kg^{-1} which is, according to them, close to the heat of physisorption. Some different values are reported the literature dedicated to drying technology. Keey [47] considers that water is attached by capillary condensation with binding energy being lower than 5 kJ kg^{-1} in macro-capillaries ($r > 10^7$ m) and being higher than this value in micro-capillaries ($r < 10^7$ m). In fact, the binding energy associated with drying depends on the residual moisture content required. Keey [47] suggests binding energy to be around 170 kJ kg^{-1} to remove the adsorpted water (physiochemical adsorption, hydrogen bonding/solvatation) and around

280 kJ kg^{-1} to remove the water chemically attached by molecular bonding.

7. Conclusion

The representation of the water distribution within activated sludge seems to be an interesting means of characterising its ability to dewater. Considering the different properties of water, many techniques are suggested to accomplish its identification. Consequently, the data supplied by current literature is widespread and difficult to use. Moreover, in several studies some implicit hypotheses are assumed without discussion (or verification), so the analysis of the data is uncertain. The discussion concerning the principal measurement techniques shows that no technique may be automatically preferred to another. The drying test is contestable because it depends greatly on the operating conditions and it cannot measure the water distribution as an intrinsic parameter of the sludge. The methods based on the freezing properties of water give a very global result which limits a detailed analysis of the sludge conditioning or dewatering. The measurement performed under the centrifugal field does not seem well adapted to extremely compressible and viscoelastic materials such as activated sludge. Nevertheless, mechanical tests carried out under very high strain (very powerful centrifugation or expression under very high constant pressure) may be interesting methods to evaluate the upper limits of any conventional mechanical dewatering device. The continuous classification of moisture based on the determination of the binding energy seems to be a pertinent way of accomplishing the characterisation. The main problem in this approach is to clearly identify the type of energy effectively considered during the measurement.

Even if the distribution of water within activated sludge might be accurately and consistently described, its use as a single index to predict dewatering performances would remain questionable: the solid–liquid separation is indeed controlled by numerous phenomena, and a single index is generally not sufficient to fully describe the whole operation.

8. Uncited reference

[66].

Appendix A

As the two phases are condensed, the thermodynamic equilibrium can be written as

$$\mu_{\mathrm{w}}^{\mathrm{l}}(T, x_i^{\mathrm{l}}) = \mu_{\mathrm{w}}^{\mathrm{s}}(T, z_i^{\mathrm{s}}), \tag{A.1}$$

where

$$\mu_{\mathrm{w}}^{\mathrm{l}}(T, x_i^{\mathrm{l}}) = \mu_{\mathrm{w}}^{*,\mathrm{l}}(T) + RT\ln(a_{\mathrm{w}}^{\mathrm{l}}), \tag{A.2}$$

$$\mu_{\mathrm{w}}^{\mathrm{s}}(T, z_i^{\mathrm{s}}) = \mu_{\mathrm{w}}^{*,\mathrm{s}}(T) + RT\ln(a_{\mathrm{w}}^{\mathrm{s}}). \tag{A.3}$$

Consequently

$$RT\ln\left(\frac{a_{\mathrm{w}}^{\mathrm{l}}}{a_{\mathrm{w}}^{\mathrm{s}}}\right) = \mu_{\mathrm{w}}^{*,\mathrm{s}}(T) - \mu_{\mathrm{w}}^{*,\mathrm{l}}(T). \tag{A.4}$$

From the expression of the chemical potential, Eq. (A.4) can be rewritten as

$$RT\ln\left(\frac{a_{\mathrm{w}}^{\mathrm{l}}}{a_{\mathrm{w}}^{\mathrm{s}}}\right) = \Delta H^*_{\mathrm{f,w}}(T) - T\Delta S^*_{\mathrm{f,w}}(T), \tag{A.5}$$

where

$$\Delta H^*_{\mathrm{f,w}}(T) = \Delta H^*_{\mathrm{f,w}}(T_{\mathrm{f,w}}) + \int_{T_{\mathrm{f,w}}}^{T} \Delta Cp^*_{\mathrm{f,w}}(T)\,\mathrm{d}T \tag{A.6}$$

with

$$\Delta Cp^*_{\mathrm{f,w}}(T) = Cp^{*,\mathrm{s}}_{\mathrm{f,w}} - Cp^{*,\mathrm{l}}_{i} \tag{A.7}$$

and

$$\Delta S^*_{\mathrm{f,w}}(T) = \Delta S^*_{\mathrm{f,w}}(T_{\mathrm{f,w}}) + \int_{T_{\mathrm{f,w}}}^{T} \frac{\Delta Cp^*_{\mathrm{f,w}}(T)}{T}\,\mathrm{d}T. \tag{A.8}$$

At the temperature $T_{\mathrm{f,w}}$

$$\Delta S^*_{\mathrm{f,w}}(T_{\mathrm{f,w}}) = \frac{\Delta H^*_{\mathrm{f,w}}(T_{\mathrm{f,w}})}{T_{\mathrm{f,w}}}. \tag{A.9}$$

Substituting Eqs. (A.6)–(A.9) into Eq. (A.5) leads to

$$RT\ln\left(\frac{a_{\mathrm{w}}^{\mathrm{l}}}{a_{\mathrm{w}}^{\mathrm{s}}}\right) = \Delta H^*_{\mathrm{f,w}}\left[1 - \frac{T}{T_{\mathrm{f,w}}}\right] + \int_{T_{\mathrm{f,w}}}^{T} \Delta Cp^*_{\mathrm{f,w}}\,\mathrm{d}T - T\int_{T_{\mathrm{f,w}}}^{T} \frac{\Delta Cp^*_{\mathrm{f,w}}}{T}\,\mathrm{d}T. \tag{A.10}$$

Assuming the calorific capacities to be constant for the range of temperature considered, yields

$$\ln\left(\frac{a_{\mathrm{w}}^{\mathrm{l}}}{a_{\mathrm{w}}^{\mathrm{s}}}\right) = \frac{\Delta H^*_{\mathrm{f,w}}(T_{\mathrm{f,w}})}{R}\left[\frac{1}{T} - \frac{1}{T_{\mathrm{f,w}}}\right] + \frac{\Delta Cp^*_{\mathrm{f,w}}}{R}\left[\frac{T - T_{\mathrm{f,w}}}{T} - \ln\left(\frac{T}{T_{\mathrm{f,w}}}\right)\right]. \tag{A.11}$$

Assuming that $T - T_{\mathrm{f,w}}$ is weak, the second right term of Eq. (A.11) can be neglected, and leads to

$$\ln\left(\frac{a_{\mathrm{w}}^{\mathrm{l}}}{a_{\mathrm{w}}^{\mathrm{s}}}\right) = \frac{\Delta H^*_{\mathrm{f,w}}(T_{\mathrm{f,w}})}{R}\left[\frac{1}{T} - \frac{1}{T_{\mathrm{f,w}}}\right]. \tag{A.12}$$

Introducing the activity coefficient of water in liquid phase into Eq. (A.12) leads to Eq. (8) in the main text.

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