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BOUND WATER CONTENT AND WATER BINDING STRENGTH ON SLUDGE FLOCS

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Abstract—On the basis of the thermodynamic hypothesis and using the thermodynamic approach, a binding strength was calculated to define the physical meaning of bound water content of sludge as measured by dilatometer. The sludge samples considered in this study included kaolin, alum and biological sludge. The binding strength of bound water at −20°C was calculated as 24.5 kJ/kg, which is close to that of the normal physico-adsorption process. Most of the frozen moisture in a dilatometric measurement should be interstitial water or vicinal water. Results also indicated that moisture with a lower binding strength easily became free water. The release of interstitial water from sludge flocs would cause less bound water. When solid concentration is higher, the expelling strength induced by the compacting action of sludge flocs is increased over the binding strength, thereby forcing out the interstitial water. Lower bound water contents are attained. Accurate measurement of bubble volumes with the calculated stem on the top of the dilatometer could improve the precision of expansion coefficient and bound water content measurement. © 1998 Elsevier Science Ltd. All rights reserved

Key words—bound water content, water binding strength, dilatometer

NOTATION

- n_A water contained in an ideal solution (mole)
- n_B solute contained in an ideal solution (mole)
- T temperature (K)
- T_f freezing temperature (K)
- T_{f0} normal freezing temperature (K)
- E_B binding strength (kJ/kg-dry solid)
- G_s Gibbs free energy for the solid phase (kJ)
- S_s entropy for the solid phase (kJ/K)
- G_L partial molar Gibbs free energy for the bound water phase (kJ)
- S_L partial molar entropy for the bound water phase (kJ/K)
- R: gas constant (J/K mole)
- X_B impurities fraction in solution
- ΔH_f standard enthalpy of ice formation (kJ/mole)

INTRODUCTION

Water in sludge is generally classified as bound water and free water. The bound water has been defined as the portion of moisture that can not be removed via mechanical means (Vesilind, 1994). A precise measurement of the bound water content is desirable for sludge treatment engineering. Several comprehensive studies to measure bound water in sludge are available (Lee, 1994). Although widely employed in estimating the bound water content of sludge, these methods are limited to the operational definition with respect to the measurement methods (Robinson and Knocke, 1992; Lee and Hsu, 1995). An acceptable method with a clear definition of bound water is needed.

The dilatometric measurement of the bound water content in sludges was first conducted by Heukelekian and Weisberg (1956) and was later used by many research groups (Foster, 1993; Barber and Veenstra, 1986; Colin and Gazbar, 1995; Smith and Vesilind, 1995). This method is based upon the assumption that the bound water remaining unfrozen at a temperature below free water's freezing point (−20°C) (Jone and Gortner, 1932). By measuring the change in the sample volume at reduced temperature, the portion of moisture remains unfrozen was estimated and defined as bound water. Robinson and Knocke (1992) have compared the drying and dilatometric tests and concluded that the latter provided more reliable bound water data. The bound water content of sludge can also be reduced using the conditioning and dewatering process. Smith and Vesilind (1995) have published a review paper about this method and have suggested that the freezing temperature, solid concentration, and air bubbles liberated from the sludge all affected the frozen water measurement. The bound water content is a relative measurement of water binding intensity but a true quantity of water existing in a bound form. A theoretical and certifiable definition of the dilatometric test for distinguishing between bound and unbound water has remained from past studies. Lee

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and Lee (1995) have developed a binding strength theory on the basis of thermodynamic hypotheses to interpret the physical meaning of the bound water content measured by differential scanning calorimetry (DSC). The basic assumptions behind the DSC and dilatometric tests are the same. The object of this study is to apply the DSC thermodynamic hypotheses to the dilatometric test to interpret the bound water content and water binding strength of sludge. The effects of solid contents and freezing temperature on bound water content measurements in dilatometric testing are also investigated.

THERMODYNAMIC INTERPRETATION OF BINDING STRENGTH

Lee and Lee (1995) has assumed that the tendency of bound water to remain unfrozen at low temperatures can be attributed to a reduction in the chemical potential of moisture, with some "binding strength" acting on the solid–liquid interface. Bound water is assumed to be an ideal solution containing n_B moles of solute and n_A moles of water. The chemical potential of bound water can be reduced by a binding strength of E_B (kJ/kg-dry solid). In the dilatometric test, unfrozen water is taken to be the bound water at $T = T_f$, or equivalently, the moisture exhibiting a freezing temperature less than T_f is referred to as bound water. An estimate can thereby be made by considering that the ice is in equilibrium with the bound water phase.

The standard state has been defined as the normal freezing temperature $T_{f0} = 273°K$ and the atmospheric pressure P = 1 atm. Changes in the molar Gibbs free energy for the solid phase and partial molar Gibbs free energy for the bound water phase under T_f and atmospheric pressure can therefore be stated as:

$$\frac{dGs}{T} = -\frac{Ss}{T}dT \quad (1)$$

$$\frac{dG_L}{T} = -\frac{S_L}{T}dT - \frac{R}{n_A + n_B}dn_B - \frac{dE_B}{T}, \quad (2)$$

where G_s, and S_s are the Gibbs free energy and entropy for the solid phase, G_L and S_L are the partial molar Gibbs free energy and partial molar entropy for the bound water phase, R a gas constant, and the last term of RHS of equation 2 accounts for the binding strength.

If we assume a solution with dilute concentration and little temperature difference $T_f - T_{f0}$, the threshold temperature T_f can be expressed as (Lee, 1996):

$$T_f - T_{f0} = \left(RX_B + \frac{E_B}{T_{f0}}\right)\frac{T_{f0}^2}{\Delta H_f} \quad (3)$$

where $X_B = n_B/(n_A + n_B)$. Equation (3) states that the freezing temperature of the bound water is affected by the presence of impurities and by the binding strength. In a typical dilatometric test, the freezing point depression owing to impurities is insignificant. An estimate can thereby be made as follows:

$$E_B = \frac{T_f - T_{f0}}{T_{f0}}\Delta H_f. \quad (4)$$

Choosing a freezing temperature for a dilatometric test is equivalent to setting the binding strength used to divide the sludge moisture into the bound and non-bound conditions.

EXPERIMENTAL

Alum sludge was obtained from the Fengyuan water treatment plant (Taichung County, Taiwan). Biological sludge was taken from the wastewater treatment plant in the Taichung Industrial Part (Taichung County, Taiwan). Kaolin sludge was produced by mixing high concentrations of kaolinite with distilled water for 24 h. The samples solid contents were measured by weighing and drying.

Dilatometer with total volume of 50 mL, similar to that used by Robinson and Knocke (1992), was employed to measure the bound water content of our samples. A 15 g sample was introduced into the dilatometer and followed by filling with an indicator fluid. A mineral oil (Shell Donax TG, U.S.A.) was selected as an indicator fluid according to the selection criteria described by Robinson and Knocke (1992). Dry ice with ethanol bath was used to freeze the sludge and to maintain a constant system temperature. The level changes on dilatometer during the cooling period were recorded as a function of temperature. Contraction and expansion curves for the indicator oil and sludge's supernatant were developed over the temperature range for all dilatometers. A contraction curve for the indicator oil without supernatant was also established. Using both the contraction curve for oil and the expansion curve for the supernatant, the contraction coefficient of oil and the expansion coefficient of the supernatant were quantified. The total water content of the sludge was determined by drying at 105°C for 24 h; the free water

Table 1. The expansion coefficient and bound water content of filtrates and distilled water

Filtrate	Expansion coefficient (ml/g°C)	BW_1 (kg H_2O/kg DS)	BW_2 (kg H_2O/kg DS)	ΔBW (%)
Distilled water	0.1012	—	—	—
Alum	0.1021	1.24	1.42	12.6
Biological	0.1018	6.77	7.05	4
Kaolin	0.1017	0.38	0.43	11.6

BW_1: Bound water content calculated using expansion coefficient of distilled water.
BW_2: Bound water content calculated using expansion coefficient of filtrate.
ΔBW: $\Delta BW = BW_2 - BW_1/BW_2 \times 100\%$.
The expansion coefficient of distilled water and filtrates were measured by the same dilatometer.

content under the desired temperature was determined by using equation (5). Hence, the amount of bound water was calculated subtracting the free water content from the total water content.

$$\text{Free water content} = [D + W \times A \times (T_0 - T_1)]/B \quad (5)$$

D is the level difference in the dilatometer from T_0–T_1, W is the weight of the oil used, A is the oil concentration coefficient for each dilatometer, T_0–T_1 is the temperature difference and B is the expansion coefficient of the sludge filtrate for each dilatometer.

RESULTS AND DISCUSSION

Measurement precision

Table 1 shows the expansion coefficient values of filtrates and distilled water. These filtrates were obtained by filtering the various kinds of sludge including alum sludge, biological sludge, and kaolin sludge. The calculated bound water content of solids with respect to the expansion coefficient values of either filtrates or distilled water are also included in the Table. It is clear that the expansion coefficient values for the filtrates are larger than the value for distilled water and that small differences exist among them. A suitable choice of expansion coefficient can significantly affect the calculated quantity of bound water content. Table 1 also shows differences of 4 ~ 12.6% in the bound water content (BW_1, BW_2) as calculated using different expansion coefficient values for the three kinds of sludge. Bound water content in most previous studies was determined using the expansion coefficient of distilled water. However, a reasonable bound water content should be calculated using the measured expansion coefficient of filtrate or supernatant. Bubble formation caused by dissolved gases was also found in the dilatometer during the biological sludge freezing. This phenomenon would produce a corresponding overestimation of the expansion coefficient, and therefore, an overestimation of bound water content. A number of solutions for eliminating the formation of bubbles have been proposed, but none of the researchers could give a suitable solution that avoids destruction of the sludge sample (Smith and Vesilind, 1995). Smith and Vesilind (1995) chose an expansion coefficient of 0.11 mg/g/°C, taking into consideration the extra expansion due to the formation of bubbles, for their biological sludge filtrate. In their study, this bubble volume was estimated by observing a side-calibrated stem fused onto their modified dilatometer. We also estimated the bubble volume by observing bubbles that appeared in the calibrated stem on the dilatometer. Unlike the modified dilatometer used by Smith and Vesilind (1995), our calibrated stem was connected directly to the top of dilatometer. During the freezing in our dilatometric tests, bubbles floated toward the calibrated stem rather than floating into the top space of the vessel as in Smith and Vesilind's work. Hence, the volume of space occupied by the bubbles could be determined more easily and accurately. The freezing of activated sludge used in Smith and Vesilind's work would generate more bubbles than the alum sludge and kaolin sludge we used due to aeration in the biological treatment.

Figure 1 shows the relationships between the solid content of kaolin sludge and the bound water content of kaolin particles. Smith and Vesilind (1995) have demonstrated changes in bound water content by varying the solid contents ranging from 0.28–4.0%. In this study, we examined the bound water content taking into consideration solid concentration up to 10% to investigate the data precision. Figure 1 also indicates that the difference between the duplicate data for the 1% solid concentration is quite large. This difference was markedly reduced when the solids concentration increased from 1–2.5%; the duplicate data then keeps closely

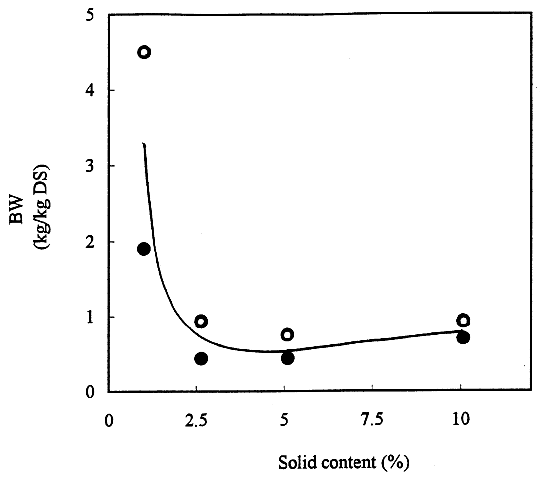

Fig. 1. Relationship between bound water content and solids content of kaolin sludge. The two symbols indicate two separate analysis from the same sample of kaolin sludge. The freezing temperature is −20°C.

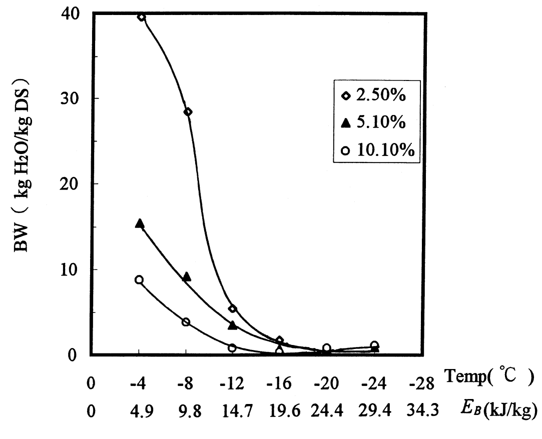

Fig. 2. Typical relationship between bound water content (BW) and freezing temperature (T_f) of kaolin sludge. Reported contents are the average of two samples.

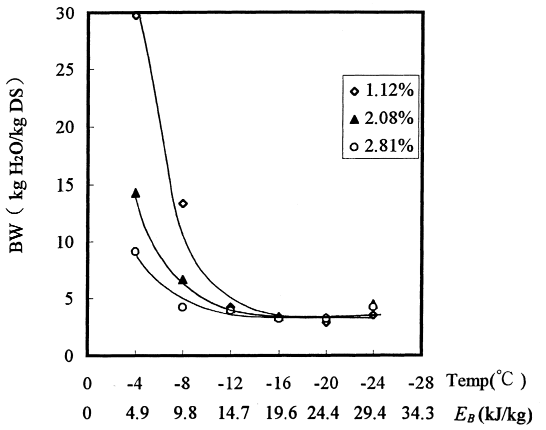

Fig. 3. Typical relationship between bound water content (BW) and freezing temperature (T_f) of alum sludge. Reported contents are the average of two samples.

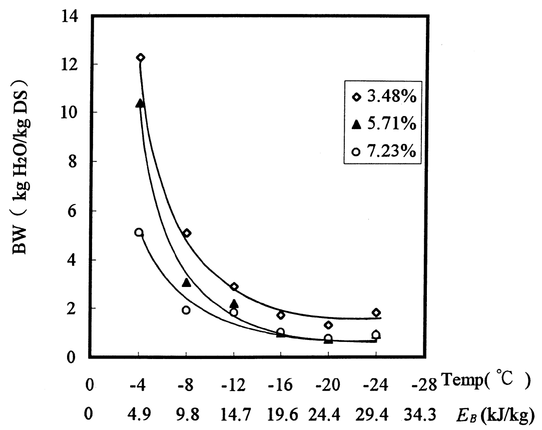

Fig. 4. Typical relationship between bound water content (BW) and freezing temperature (T_f) of biological sludge. Reported contents are the average of two samples.

as the solid concentration was increased to 10.1%. These results parallel the findings of Smith and Vesilind (1995) in that the dilatometric test is not precise at low solids concentration. Therefore, the dilatometric test can most likely be regarded as an effective tool for determining bound water contents on thickened or dewatered sludges. The effect of sampling deviation on the result of duplicate test needed to be considered. Because total water content in dilatometric test is calculated from an average solid content, a divergence between the true solid content in the dilatometer vessel and the average solid content calculated by the dry solid analysis can affect the measured bound water content. In our study, the average solids concentration was obtained by the triplicate of dry solid analysis, therefore sampling deviation occurred accordingly. This means that the differences in solids concentration will exist among sludge samples from the same sludge source in different dilatometers. In our experiment, the solids concentration of kaolin sludge was controlled between 2.2 and 2.7%; the corresponding bound water contents were then calculated to be 1.22 and 0.81 kg/kg, respectively. The sampling deviation noticeably affects the precision of dilatometric bound water measurement. This deviation caused by sampling also occurs in other measurement methods when the solids concentration is low (Lee and Lee, 1995).

Bound water content and water binding strength

Figures 2, 3 and 4 show the relationship between BW and T_f (and E_B) of kaolin sludge, alum sludge, and biological sludge, respectively. The results for kaolin sludge shown in Fig. 1 indicate that the bound water content of kaolin sludge decreases sharply as freezing temperature drops from 0 to -12°C. When the temperatures were lowered to -24°C, the trend of measured bound water contents under various freezing temperatures flattened out. The sharp reduction in bound water content from 0 to -12°C can be interpreted by the analysis of E_B. When the freezing temperature is close to the normal freezing point, only the portion with zero E_B (i.e. bulk water) can be frozen. Consequently, moisture having a lower binding strength easily become free water. At further reductions in temperature, the portion of moisture with a greater E_B remains unfrozen and a corresponding but insignificant reduction in bound water content is then found. In the cases of alum sludge and biological sludge (Figs 3 and 4), a trend similar to that for kaolin sludge was found. We suggest that a clear physical meaning of bound and non-bound water as measured by dilatometer can be defined in terms of the binding strength of the biological and chemical sludge.

Table 2 presents BW and E_B values obtained from three different sludge samples. The binding

Table 2. Bound water content and binding strength (E_B) values of three kinds of sludges

		Bound water content (kg H_2O/kg DS)								
Temperature (°C)	E_B (kJ/kg)	Kaolin			Alum			Biological		
−4	4.9	39.61	15.42	8.81	12.28	10.37	5.12	29.72	14.29	9.13
−8	9.8	28.36	9.21	3.85	5.11	3.08	1.93	13.37	6.66	4.23
−12	14.7	5.47	3.47	0.78	2.91	2.21	1.84	4.22	4.06	3.94
−16	19.6	1.71	0.65	0.31	1.73	0.99	1.01	3.31	3.36	3.22
−20	24.5	0.68	0.59	0.80	1.31	0.72	0.75	2.89	3.24	3.20
−24	29.4	1.01	0.82	1.10	1.82	0.92	0.90	3.51	4.48	4.22
Solid content	%	2.50	5.10	10.10	3.48	5.71	7.23	1.12	2.08	2.81

strength of bound water −20°C can be calculated as 24.5 kJ/kg, which is close to that of the normal physico-adsorption process. Therefore, most of the frozen moisture in a dilatometric measurement should be interstitial water or vicinal water. This interpretation is in harmony with that indicated by Smith and Vesilind (1995) as to what portion of moisture is frozen in the dilatometric test. Figures 2–4 also demonstrate the effects of solid concentration on bound water content. The results indicate that measured bound water content decreases as the solid concentrations increase in all samples. Therefore, a higher solid content produces a lower bound water content. These results agree with the result of Smith and Vesilind (1995) and confirm that solids concentration do affect the bound water content measurement. Table 2 shows that when the binding strength is 24.5 kJ/kg, the difference in bound water content for each sludge samples caused by the differing solid concentration are insignificant. When the binding strength is lower than 24.5 kJ/kg, these differences become significant and higher solid concentration leads to lower bound water contents. The release of interstitial water from sludge flocs would cause less bound water. When solid concentration is higher, the expelling strength induced by the compacting action of sludge flocs is increased over the binding strength, thereby forcing out the interstitial water. Studies by Robinson and Knocke (1992), and Colin and Gazbar (1995) have both concluded that bound water content of biological and chemical sludge decreases significantly following mechanical dewatering, which apparent supports the above hypothesis. As found in other studies (Sato *et al.*, 1982; Pramanik *et al.*, 1993), the bound water content in biological sludge was the highest among three samples with comparable amounts of solid concentration (3%) at −20°C.

CONCLUSIONS

An accurate determination of bubble volume from a calculated stem on the top of dilatometer can improve the precision of expansion coefficient and bound water content measurement. The dilatometric test is not very precise at low solids concentration. In the cases of thickened and dewatered sludges, the dilatometric test can most likely be regarded as an effective tool for determining the bound water content. On the basis of the thermodynamic hypothesis, the binding strength of bound water at −20°C can be calculated as 24.5 kJ/kg, which is close to that of the normal physico-adsorption process. Most of the frozen moisture in a dilatometric measurement should be the interstitial water or vicinal water. The moisture having a lower binding strength easily becomes free water. The release of interstitial water from sludge flocs would cause less bound water. When solid concentration is higher, the expelling strength induced by the compacting action of sludge flocs is increased over the binding strength, thereby forcing out the interstitial water. Lower bound water contents are attained.

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