Available online at www.sciencedirect.com
ScienceDirect
Journal of Environmental Sciences 2011, 23(5) 875–880
JOURNAL OF ENVIRONMENTAL SCIENCES
ISSN 1001-0742
CN 11-2629/X
www.jesc.ac.cn

Moisture distribution in sludges based on different testing methods

Wenyi Deng[1,*], Xiaodong Li[2], Jianhua Yan[2], Fei Wang[2], Yong Chi[2], Kefa Cen[2]

1. School of Environmental Science and Engineering, Donghua University, Shanghai 201620, China. E-mail: dengwy@dhu.edu.cn
2. State Key Laboratory of Clean Energy Utilization, Institute for Thermal Power Engineering, Zhejiang University, Hangzhou 310027, China

Received 10 May 2010; revised 03 August 2010; accepted 16 August 2010

Abstract

Moisture distributions in municipal sewage sludge, printing and dyeing sludge and paper mill sludge were experimentally studied based on four different methods, i.e., drying test, thermogravimetric-differential thermal analysis (TG-DTA) test, thermogravimetric-differential scanning calorimetry (TG-DSC) test and water activity test. The results indicated that the moistures in the mechanically dewatered sludges were interstitial water, surface water and bound water. The interstitial water accounted for more than 50% wet basis (wb) of the total moisture content. The bond strength of sludge moisture increased with decreasing moisture content, especially when the moisture content was lower than 50% wb. Furthermore, the comparison among the four different testing methods was presented. The drying test was advantaged by its ability to quantify free water, interstitial water, surface water and bound water; while TG-DSC test, TG-DTA test and water activity test were capable of determining the bond strength of moisture in sludge. It was found that the results from TG-DSC and TG-DTA test are more persuasive than water activity test.

Key words: moisture distribution; sludge; bond strength

DOI: 10.1016/S1001-0742(10)60518-9

Citation: Deng W Y, Li X D, Yan J H, Wang F, Chi Y, Cen K F, 2011. Study on moisture distribution in sludges based on different testing methods. Journal of Environmental Sciences, 23(5): 875–880

Introduction

Sludge management is an ever-increasing problem in China and many parts of the world. At present, million tons of dry matter of sewage sludge is annually generated in China from municipal and industrial wastewater treatment plants (MIWTP). Most sludge from MIWTPs directly or indirectly is applied to agricultural land or disposed by landfilling (Lin and Zhou, 2004). For sludge treatment, usage, and disposal, low moisture content is usually required. 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 and drying problems. Quantitative measurement methods describing the distribution of water in wet sludges are proposed based on the observation that the physical properties of water adjacent to the particles surface differ from those of bulk water. The commonly used testing methods are drying test (Sato et al., 1982; Robinson and Knocke, 1982; Tsang and Vesilind, 1990; Smollen, 1990), DTA or DSC test (Chen et al., 1997; Chu and Lee, 1999; Ferrasse and Lecomte, 2004), and water activity test (Vaxelaire et al., 2000; Vaxelaire, 2001; Arlabosse et al., 2003; Vaxelaire and Cézac, 2004). However, the conclusions of scientific literature in this field are often hard to apply because of controversial data and definitions. Lee et al. (2006) has given a review report on comparison of different testing methods. The comparison was based on results from different publications, thus the referential value was weakened due to great differences in experimental condition and materials.

In this study, the moisture distribution of three typical sludges, i.e., municipal sewage sludge (MSS), printing and dyeing sludge (PDS) and paper mill sludge (PMS), were studied based on drying test, TG-DSC test, TG-DTA test and water activity test, respectively. The bond strengths of sludge moisture from different testing methods were compared. The advantages and disadvantages of different testing methods were discussed.

1 Materials and methods

1.1 Materials

Three kinds of mechanically dewatered sludges: MSS, PDS and PMS, which were all produced from aeration basins using anaerobic/oxic (A/O) wastewater treating system, were used in this study. The moisture content of MSS, PDS and PDS were 3.6, 2.7 and 4.3 kg moisture/kg dry solid (ds), respectively. MSS was sampled from a municipal sewage treatment plant in Hangzhou City of Zhejiang Province, PDS from an industrial dyeing

* Corresponding author. E-mail: dengwy@dhu.edu.cn

wastewater treatment plant in Yunchen City of Shandong Province, and PMS from a paper-making factory in Pinghu City of Zhejiang Province, China. Sludge samples were stored at 4°C before experiments. The principal characteristics of the sludges are listed in Table 1.

1.2 Experimental set-up and procedures

1.2.1 Drying test

The apparatus shown schematically in Fig. 1 was used for determining the different types of moisture fractions in sludge. It consists of a thermostatically controlled heating oven inside which was placed a digital balance. The experimental data from the balance was recorded by a computer automatically. Sludge sample of 5 g was introduced to the balance dish. The dish was placed in an oven and the sample was dried slowly at 30°C and at a controlled humidity by sparging the oven with 400 mL/min of compressed dry air. The sludge mass was automatically recorded by the computer at 10 min intervals, until there was no change in sludge mass. When the drying process in the oven was finished, the sludge sample was heated at 105°C for 12 hr to continue drying and the final dried mass was recorded.

1.2.2 TG-DTA and TG-DSC test

By TG-DTA test, a thermal analyzer (Mettler TGA/SDTA 851, Germany) was employed for recording the thermographs with sludge sample of 35 mg. Pure N_2 was used as the carrying gas. Cell temperature of the analyzer was heated from 25 to 80°C with heating rate of 10°C/min, and kept stable at 80°C for 50 min. The TGA and DTA analysis was conducted simultaneously.

By the TG-DSC test, sludge sample of 35 mg was introduced into the thermal analyzer (TA SDT Q600, USA)

Table 1 Proximate and ultimate analysis of MSS, PDS and PMS (on a dry basis)

Species (mass fraction)	MSS	PDS	PMS
Ash content (%)	54.75	64.90	49.73
Volatile content (%)	37.38	32.02	42.37
Fixed carbon (FC) content (%)	6.12	0.12	3.94
Carbon in volatile and FC (%)	25.18	15.42	16.94
Hydrogen in volatile and FC (%)	3.88	3.08	3.64
Nitrogen in volatile and FC (%)	2.56	0.98	1.07
Sulfur in volatile and FC (%)	1.59	4.75	1.66
Oxygen in volatile and FC (%)	9.29	7.91	23.00

MSS: municipal sewage sludge; PDS: printing and dyeing sludge; PMS: paper mill sludge.

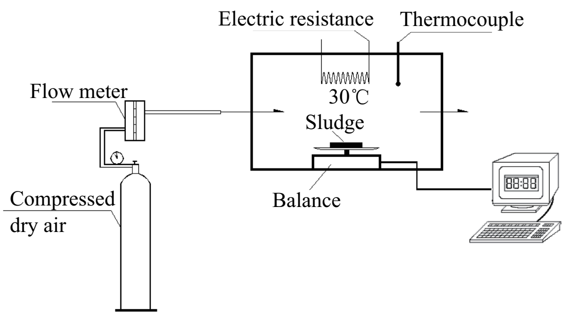

Fig. 1 Schematic diagram of drying test.

with carrying gas of pure N_2. Cell temperature was heated from 25 to 90°C with heating rate of 10°C/min, and kept stable at 90°C for 45 min.

1.2.3 Water activity test

In water activity test, each kind of the dewatered sludges was divided into seven groups which were pre-dried to different moisture contents. Each group of the pre-dried sludge samples was 10–15 g, and was ground into particles with diameter less than 3 mm. Thereafter, the pre-treated sludge samples were introduced into a water activity meter (Rotronic HygroPalm AW1, Switzerland) for fast determination of water activity.

2 Results and discussion

2.1 Drying test

The method of drying test was first proposed by Tang and Vesilind (1990). By this method, a typical drying curve (Fig. 2) can be divided into a constant-rate period (line AB), first falling-rate period (line BC), second falling-rate period (line CD), and equilibrium stage. The first critical point B is the transition from the constant-rate period to the first falling-rate period, while the second critical point C is the transition from the first falling-rate period to the second falling-rate period. The moisture content removed during the constant-rate period, the first falling-rate period and the second falling-rate period are regarded as free water, interstitial water, and surface water, respectively. The residual moisture content in equilibrium stage is regarded as bound water.

Figure 3 shows the drying rate curves of MSS, PDS and PMS. It is obvious that the constant-rate period does not exist in the drying curves, which indicates that the free water was completely removed during mechanical dewatering process of sludge. As shown in Fig. 3, the first falling-rate period and the second falling-rate can be clearly identified. The moisture contents of the second critical point C for MSS, PDS and PMS are 61.0% wet basis (wb), 52.5% wb, and 53.0% wb, respectively. Therefore, the interstitial water contents were calculated to be 2.1 kg moisture/kg dry solid (ds) for MSS, 1.6 kg moisture/kg ds for PDS, and 3.1 kg moisture/kg ds for PMS. The interstitial water accounted for 56.9% wb of the total moisture content in the MSS, 58.6% wb in the PDS and 73.5% wb in the PMS. The

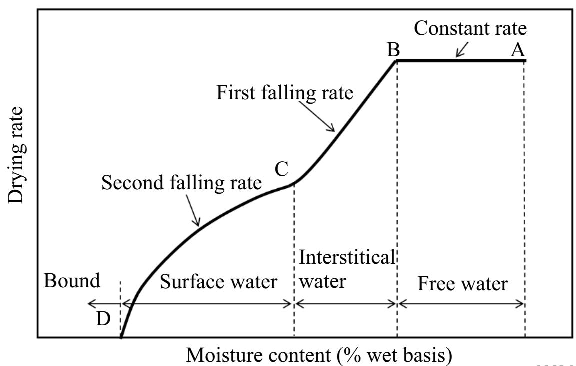

Fig. 2 Typical sludge drying curve.

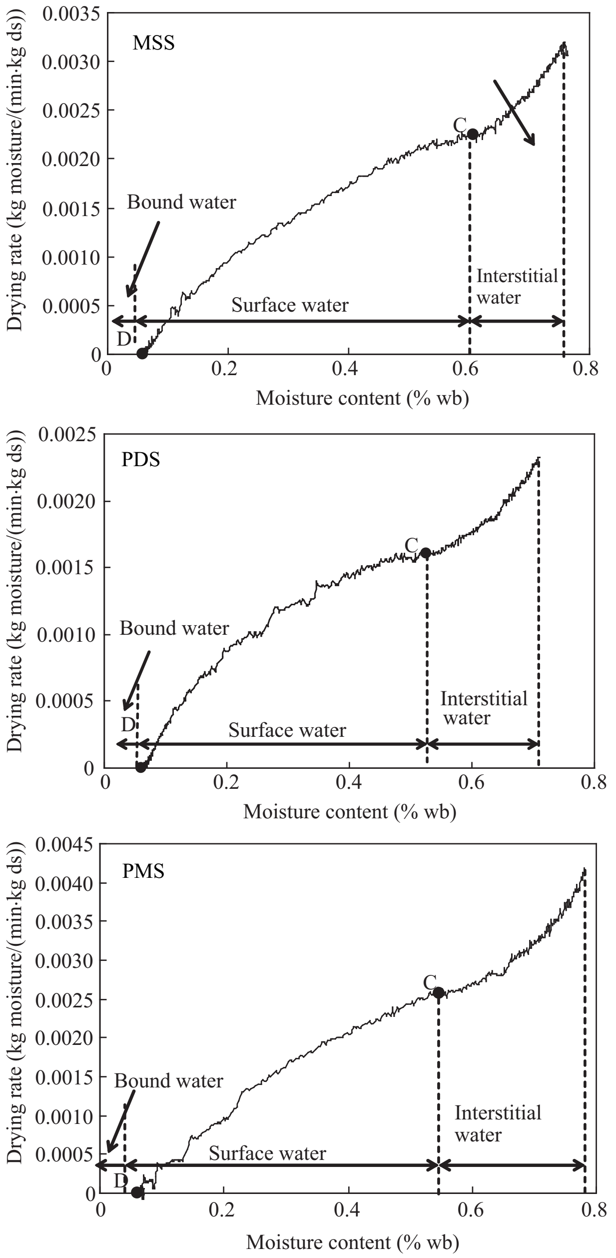

Fig. 3 Drying rate curves of MSS, PDS, and PMS. ds: dry solid; wb: web basis.

higher interstitial water content in the PMS was mainly due to its high original moisture content.

Despite of the marked difference in the interstitial water contents, the surface water contents of the three sludges were more or less the same. The surface water content of MSS was 1.5 kg moisture/kg ds, which was only 0.4 kg moisture/kg ds higher than that of PDS and PMS. Moreover, the residual bound water content was only 0.1 kg moisture/kg ds for the three sludges.

It can be found from Fig. 3 that the drying rates of the three sludges were different under the same drying conditions. The average drying rate of the interstitial water was 2.8 g moisture/(min·kg ds) for MSS, 2.0 g moisture/(min·kg ds) for PDS, and 3.2 g moisture/(min·kg ds) for PMS, which indicated that the interstitial water in PMS was most easily removed during the drying process. The average drying rate of the surface water was 1.2 g moisture/(min·kg ds) for MSS, 0.7 g moisture/(min·kg ds) for PDS, and 1.0 g moisture/(min·kg ds) for PMS. Since the experimental data were all from the same drying conditions, it is reasonable to infer that the drying rate was strongly correlated with the physical properties of the sludges, including thermal conductivity, apparent density, particle diameter, specific heat, etc. (Arlabosse and Chitu, 2007; Deng et al., 2009; Yan et al., 2009). It is well known that MSS is a residue resulting from the treatment of wastewater released from various sources including homes, industries, medical facilities, street runoff and businesses, while PDS and PMS are from treatment of wastewater released from textile industry and paper manufacturing respectively. The major organic loading of MSS is a complex mixture of fats, proteins, carbohydrates, humic material and fatty acids (Rogers, 1996). Differently, PDS mainly contains dyestuff, slurry, dyeing aid, acid or alkali, fiber and inorganic compound, and PMS mainly contains cellulose, varying amounts of highly lignified materials, and molecules of anthropogenic origin depending on the paper manufacturing practices used (Marche et al., 2003; Zheng and Liu, 2006). The high drying rate of PMS may due to its high cellulose content which will produce a capillary force and remove water from inside to outside of sludge.

2.2 TG-DTA and TG-DSC test

The TG-DTA method was developed by Chen et al. (1997) for continuous classification of moisture content in activated sludge. The heat flow (Q, kJ/sec) into the sample cell can thereby be estimated by Eq.(1):

$$Q = Ah(T_{\text{ref}} - T_{\text{cell}}) \tag{1}$$

where, A (m^2), h (w/(m^2·K)), T_{ref} (K) and T_{cell} (K) are the effective heat transfer area, the average heat transfer coefficient, the reference temperature and the cell temperature, respectively. The group Ah and ($T_{\text{ref}} - T_{\text{cell}}$) were determined by pure water test and DTA test, respectively. In the pure water test, the Q in Eq. (1) was the latent heat of pure water, and the ($T_{\text{ref}} - T_{\text{cell}}$) can be derived from the DTA test of the pure water, thus the group Ah can be determined through Eq. (1). It is assumed that the group Ah is a constant in both the pure water test and the sludge test. When the heat flow into the sample cell is completely utilized in moisture evaporation, the following Eq. (2) holds:

$$Q = \dot{m}H_{\text{S}} \tag{2}$$

where, $\dot{m}$ (kg/sec) and H_{S} (kJ/kg) are the drying rate and the evaporation heat of moisture in sludge at 80°C, respectively, and $\dot{m}$ was estimated by the TGA data. Therefore, by combining Eqs. (1) with (2), the evaporation heat of sludge water can be determined. The bond strength H_{B} (kJ/kg) between the moisture and the solid phase can thereby be calculated as follows:

$$H_{\text{B}} = H_{\text{S}} - H_{\text{W}} \tag{3}$$

where, H_{W} is the evaporation heat of pure water at 80°C.

As shown in Fig. 4, the distribution characteristics of the bond strength are similar for the three sludges. When the moisture content was higher than 1.0 kg moisture/kg ds (50% wb), there was only a little change in the bond strength which increased from 0 to approximately 70 kJ/kg with decreasing moisture content. The moisture content higher than 50% wb was mainly composed of interstitial water (Fig. 3). Thus it can be inferred that the bond strength of the interstitial water in the three sludges fluctuated in the range of 0–70 kJ/kg. The average bond strengths in this moisture range were 38.2, 57.8 and 68.3 kJ/kg for MSS, PDS and PMS, respectively. When the moisture content was lower than 1.0 kg moisture/kg, the bond strength markedly increased from a very low level to more than 1000 kJ/kg with decreasing moisture content. It can be found from Fig. 3 that the moisture content lower than 50% wb was mainly surface water. The average bond strengths in this moisture range were 366.4 kJ/kg for MSS, 505.6 kJ/kg for PDS and 699.6 kJ/kg for PMS. It can be found that the average bond strengths in the low moisture range (moisture content lower than 50% wb) was nearly 10 times higher than that in the high moisture range (moisture content higher than 50% wb). It is obvious that the higher the bond strength, the more energy will be consumed during drying process. Thus surface water evaporation will consume much more energy than interstitial water evaporation.

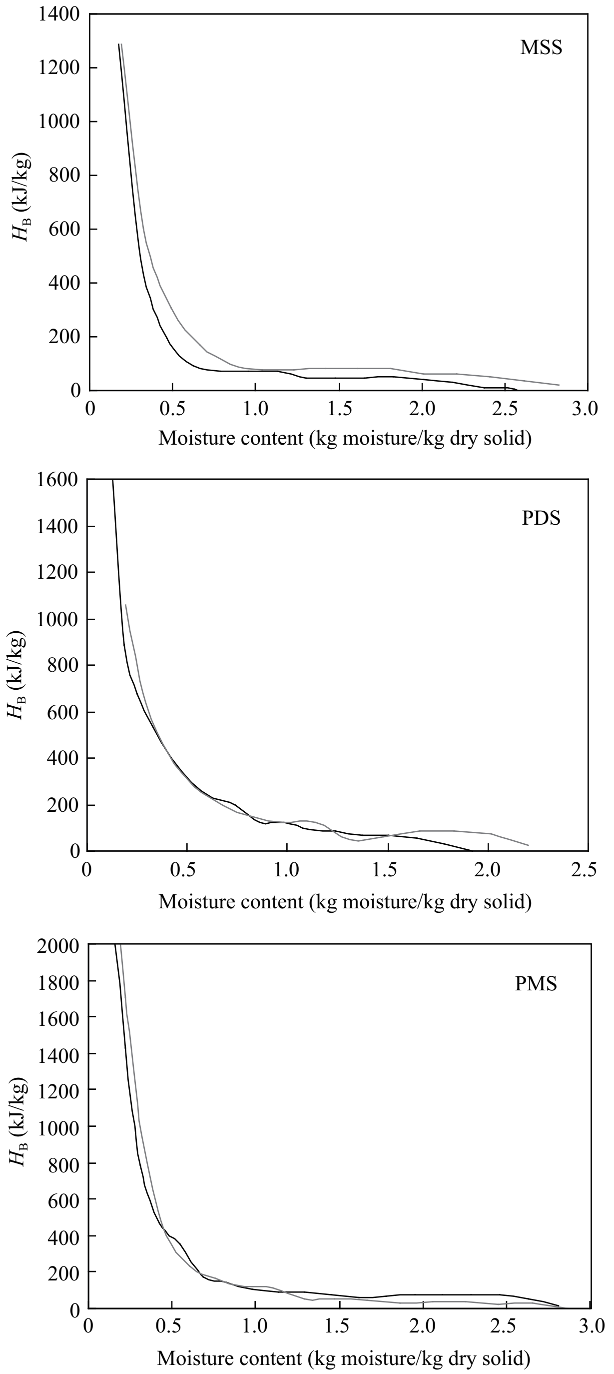

Fig. 4 Bond strength of moisture in MSS, PDS, and PMS through TG-DTA test at 80°C (two replicates). H_B is bond strength.

The TG-DSC method used in this study was proposed by Ferrasse and Lecomte (2004). This method was also developed for continuous classification of moisture content in biological products. In fact, the basic principle of this method is identical with the TG-DTA method, thus it is expected that the bond strength curve from the TG-DSC test is similar with that from the TG-DTA test. Since the heat flow (Q) into the sample cell can be directly measured through the DSC test, the pure water test is not needed in the TG-DSC test. Therefore, the TG-DSC test is more convenient than the TG-DTA test. The evaporation heat of moisture in sludge can be calculated directly through Eq. (2), as well as the bond strength H_B in Eq. (3). Figure 5 shows the experimental results of MSS and PMS. As expected, the bond strength curves are almost identical with that from the TG-DTA tests.

2.3 Water activity test

From thermodynamic considerations and under some assumptions (Vaxelaire et al., 2000), the water activity (a_w) was defined by the following Eq. (4):

$$a_w = \frac{P_v}{P_{sat}(T)} \qquad (4)$$

where, P_v (Pa) is the partial pressure of water in the surrounding air, and $P_{sat}(T)$ (Pa) is the saturation pressure of water at the given temperature. It should be noted that Eq. (4) is also the definition of the relative humidity. The water activity test was proposed by Herwijn (1996) and Vaxelaire (2001), based on sorption isotherm data, to

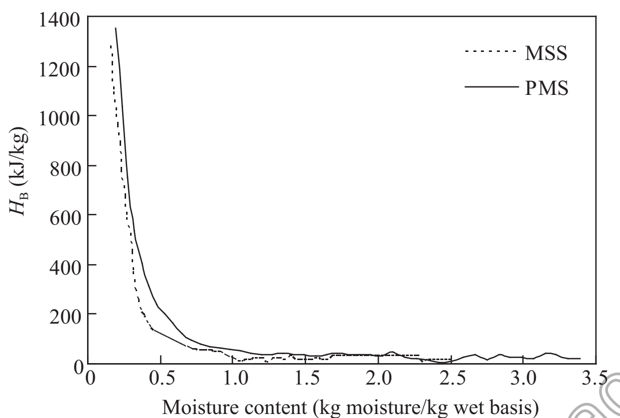

Fig. 5 Bond strength of moisture in MSS and PMS through TG-DSC test at 90°C.

evaluate the bond strength between the moisture and the solid phase. It is based on the Clausius-Clapeyron equation (Zuritz and Singh, 1985; Nunes and Rotstein, 1991) (Eq. (5)):

$$\frac{dP_v}{dT} = \frac{H_S}{T(V_v - V_1)} \quad (5)$$

where, H_S (kJ/kg) is the sum of the heat of evaporation of pure water (H_W) and the bond strength (H_B), and T is the ambient temperature. Neglecting the volume of liquid (V_1) (compare to the volume of vapour (V_v)), Eq. (5) can be rearranged as:

$$\frac{d[\ln(P_v)]}{dT} = \frac{H_S}{RT^2} \quad (6)$$

where, R (kJ/(kg·K)) is universal gas constant. For pure water, the heat of evaporation can be expressed as Eq. (7):

$$\frac{d[\ln(P_{sat})]}{dT} = \frac{H_W}{RT^2} \quad (7)$$

According to Eqs. (4) and (7), the bond strength H_B (kJ/kg) can thereby be determined by Eq. (8) (Vaxelaire, 2001):

$$H_B = -RT\ln(a_w) \quad (8)$$

The water activity can be determined by the saturated salts method, which is widely adopted as a standard method (Vaxelaire et al., 2000). However, several days, or even weeks, may be required to obtain the equilibrium value and, at high relative humidity, this delay can easily lead to bacterial growth or even putrefaction, which consequently invalidates the results. Therefore, the water activity meter, which only takes 4–5 min for the water activity determination with high precision (± 0.015 a_w), was used in this study. Table 2 shows the water activity values of the three sludges at different moisture contents. The results indicate that the water activity decreased with the decrease of moisture content, and that there was no obvious change in the water activity values until the moisture content was lower than 0.4 kg moisture/kg ds.

According to Eq. (8), the bond strength can be determined based on the water activity data in Table 2. Figure 6 shows the calculated results of the bond strength in the three sludges. The bond strength curves from the water activity test have similar shapes with that from the TG-DTA or TG-DSC test. It can be found that the bond strength had a marked increase until the moisture content was lower than 0.2 kg moisture/kg ds. This result was close with those reported by Vaxelaire (2001), but was relatively lower than those from the TG-DTA or TG-DSC test, which was mainly caused by great discrepancies in measuring principles.

2.4 Comparison of different methods

Based on the analysis above, the main advantage of the drying test over the other methods is that it is capable of quantifying the contents of free water, interstitial water, surface water and bound water in sludge. However, due to the low drying temperature, 2–3 days are often needed until a constant mass of sludge sample is achieved, which may lead to bacterial growth and quality change of sludges. Besides, under drying, the sludge cake will experience volume shrinkage and surface cracking; both cases have a little effect on sludge drying rate. Unfortunately, due to complexity of sludge composition, it is very difficult to precisely determine the percentage error of the above effects (i.e., bacterial growth, quality change, volume shrinkage and surface cracking) on drying rate.

The experimental results from the TG-DTA test, the TG-DSC test and the water activity test are all lead to the formation of the bond strength curves. As stated above, although the TG-DSC test is more convenient than the TG-DTA test by reducing the pure water test, the TG-DTA test is fundamentally the same with the TG-DTA test. Since the bond strength from the water activity test is lower than those from the TG-DTA or TG-DSC test, it is necessary to ascertain which result is more persuasive. Firstly, it should be noted that there is no bond strength in free water. As can be seen from Fig. 6, the bond strength was

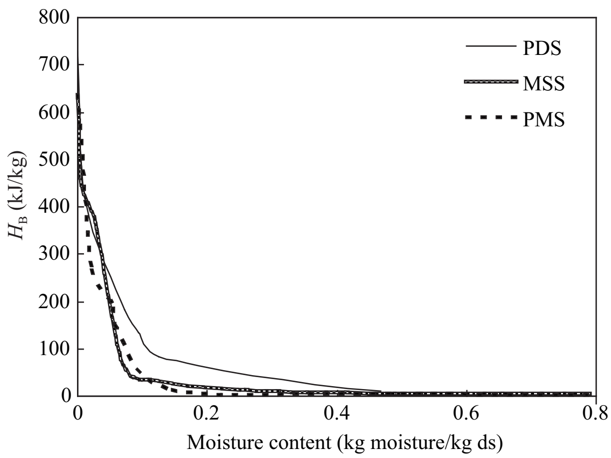

Fig. 6 Bond strength of moisture in MSS, PDS and PMS through water activity test.

Table 2 Water activity of sludges at different moisture contents (ambient temperature of 24°C)

MSS		PDS		PMS	
Moisture content (kg moisture/kg ds)	Water activity	Moisture content (kg moisture/kg ds)	Water activity	Moisture content (kg moisture/kg ds)	Water activity
1.31	0.98	1.46	0.96	1.67	0.99
0.68	0.97	0.93	0.97	1.02	0.98
0.36	0.95	0.47	0.93	0.44	0.97
0.13	0.79	0.13	0.54	0.14	0.88
0.07	0.63	0.09	0.38	0.06	0.35
0.03	0.07	0.07	0.27	0.05	0.23
0.01	0.04	0.01	0.05	0.02	0.13

almost negligible when the moisture content was higher than 0.2 kg moisture/kg ds for PMS, and was higher than 0.5 kg moisture/kg ds for MSS and PDS, which indicates that the moisture with negligible bond strength can be approximately regarded as free water. This is, of course, not consistent with the conclusion that there was no free water in the three sludges (conclusion from the drying test). Chen et al. (1997) also revealed that the bond strength of interstitial water can be estimated as approximately 70 kJ/kg which can be referred to as the upper limit for any mechanical dewatering means. As a conclusion, the bond strengths determined by TG-DTA or TG-DSC test are regarded more persuasive than the water activity test.

3 Conclusions

Continuous classification of moistures in MSS, PDS and PMS were conducted based on drying test, TG-DTA test, TG-DSC test and water activity test, respectively. The contents of free water, interstitial water, surface water and bound water in sludge can be quantified by the drying test. The results indicated that there was no free water in the three kinds of mechanically dewatered sludges. More than 50% of moisture content in the three sludges is the interstitial water. The bond strength of moisture in sludge can be determined by the TG-DTA, TG-DSC and water activity test. The results of the TG-DTA and TG-DSC test indicated that the bond strength had a marked increase until the moisture content was lower than 50% wb. The bond strength determined by the water activity test was lower than the TG-DTA and TG-DSC test due to great discrepancies in measuring principles, and it was proved that results from the water activity test were less persuasive compared with the other two methods.

Acknowledgments

This work was supported by the National Ministry of Education (China) and Technological Department of Zhejiang Province (No. 2007C03003) and the Shanghai Natural Science Foundation (No. 11ZR1400700).

References

Arlabosse P, Chitu T, 2007. Identification of the limiting mechanism in contact drying of agitated sewage sludge. *Drying Technology,* 25(4): 557–567.

Arlabosse P, Rodier E, Ferrasse J H, Chavez S, Lecomte D, 2003. Comparison between static and dynamic methods fro sorption measurements. *Drying Technology*, 21(3): 479–497.

Chen G W, Hung W T, Chang I L, Lee S F, Lee D J, 1997. Continuous classification of moisture content in waste activated sludges. *Journal of Environmental Engineering,* 123(3): 253–258.

Chu C P, Lee D J, 1999. Moisture distribution in sludge: Effects of polymer conditioning. *Journal of Environmental Engineering*, 125(4): 340–345.

Deng W Y, Yan J H, Li X D, Wang F, Lu S Y, Chi Y et al., 2009. Measurement and simulation of the contact drying of sewage sludge in a Nara-type paddle dryer. *Chemical Engineering Science,* 64(24): 5117–5124.

Ferrasse J H, Lecomte D, 2004. Simultaneous heat-flow differential calorimetry and thermogravimetry for fast determination of sorption isotherms and heat of sorption in environmental or food engineering. *Chemical Engineering Science,* 59(6): 1365–1376.

Herwijn A J M, 1996. Fundamental aspects of sludge characterization. Ph.D Thesis. Eindhoven University of Technology, The Netherlands.

Lee D J, Lai J Y, Mujumdar A S, 2006. Moisture distribution and dewatering efficiency for wet materials. *Drying Technology*, 24(10): 1201–1208.

Lin Y Q, Zhou S Q, 2004. Investigation and analysis on the disposal and treatment of sludge in China. *Energy Environment and Protection*, 18(6): 15–18.

Marche T, Schnitzer M, Dinel H, Pare T, Champagne P, Schulten H R et al., 2003. Chemical changes during composting of a paper mill sludge-hardwood sawdust mixture. *Geoderma,* 116(3-4): 345–356.

Nunes R V, Rotstein E, 1991. Thermodynamics of the water-foodstuff equilibrium. *Drying Technology,* 9(1): 113–137.

Robinson J, Knocke W R, 1982. Use of dilatometric and drying techniques for assessing dewatering characteristics. *Water Environment Research*, 64(1): 60–68.

Rogers H R, 1996. Sources, behaviour and fate of organic contaminants during sewage treatment and in sewage sludges. *Science of the Total Environment,* 185(1-3): 3–26.

Sato H, Eto S, Suzuki H, 1982. Dewatering sludges, relationship between amount of bound water and dewatering characteristics of alum sludges. *Filtration & Separation*, (11/12): 492–497.

Smollen M, 1990. Evaluation of municipal sludge drying and dewatering with respect to sludge volume reduction. *Water Science and Technology*, 22(12): 153–161.

Tsang K R, Vesilind P A, 1990. Moisture distribution in sludges. *Water Science and Technology,* 22(12): 135–142.

Vaxelaire J, 2001. Moisture sorption characteristics of waste activated sludge. *Journal of Chemical Technology and Biotechnology,* 76(4): 377–382.

Vaxelaire J, Cézac P, 2004. Moisture distribution in activated sludges: A review. *Water Research*, 38(9): 2215–2230.

Vaxelaire J, Mousques P, Bongiovanni M, Puiggali J R, 2000. Desorption isotherms of domestic activated sludge. *Environmental Technology,* 21(3): 327–335.

Yan J H, Deng W Y, Li X D, Wang F, Chi Y, Lu S Y et al., 2009. Experimental and theoretical study of agitated contact drying of sewage sludge under partial vacuum conditions. *Drying Technology,* 27(6): 787–796.

Zheng X, Liu J X, 2006. Dyeing and printing wastewater treatment using a membrane bioreactor with a gravity drain. *Desalination,* 190(1-3): 277–286.

Zuritz C A, Singh R P, 1985. An equation to compute the heat of evaporation of water for rough rice during drying. *Drying Technology*, 3(3): 421–435.