Available online at www.sciencedirect.com
ScienceDirect
Journal of Hazardous Materials 144 (2007) 323–327
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Improvement of dewatering capacity of a petrochemical sludge

Nurdan Buyukkamaci *, Emrah Kucukselek

Dokuz Eylul University, Engineering Faculty, Environmental Engineering Department, Kaynaklar Campus Buca, 35160 Izmir, Turkey

Received 27 September 2005; received in revised form 10 October 2006; accepted 11 October 2006
Available online 15 October 2006

Abstract

Oily sludge produced from a petrochemical industry was used to investigate the improvement of its dewatering properties. The oil content (OC) and the dry solid content (DS) of the raw sludge were respectively, 15% and 3.6% by weight. The capillary suction time (CST) and the specific resistance to filtration (SRF) of the raw petrochemical industrial sludge were found to be 2000 s and $\sim 5.5 \times 10^{16}$ m/kg, respectively. Conventional chemical conditioners such as alum, lime, and polyelectrolyte, and less conventional ones like fly ash, gypsum, and bentonite were used in the sludge conditioning studies. Conventional chemical conditioners gave better results for the enhancement of the dewatering capacity of the sludge. The best result was obtained by using 0.9% cationic polyelectrolyte by weight, and a decrease of 99%–95% were achieved for CST and SRF, respectively, when this dosage of cationic polyelectrolyte was used.

Keywords: Sludge; Oily sludge; Conditioning; Petrochemical; Oil

1. Introduction

In wastewater treatment plants, oily sludge is especially generated during the treatment of oily industrial wastewaters produced in many industries, such as petrochemical, food processing, and edible oil production. Although most of the oil floats on the wastewater, a portion is carried into the sludge with settling solids [1]. The characteristics of oily sludge can vary depending on the type of industry, the oil, and the wastewater treatment processes used. Oily sludges, frequently present in oil production or processing sites, contain different concentrations of waste oil (40%–60%), wastewater (30%–90%), and mineral particles (5%–40%) [2]. Oily sludge contains a large amount of emulsified, negatively charged oil droplets [3]. Oil creates difficulties in the treatment stages of wastewaters, and subsequently in the sludge dewatering processes [1]. Therefore, suitable sludge conditioning processes should be chosen before dewatering operations.

Some researchers have reported that the freeze/thaw process could be preferred for oily sludge dewatering [3–6]. As a physical sludge conditioning method, the freeze/thaw treatment, which can significantly improve certain sludge dewatering characteristics, change the floc structure into a more compact form, and reduce the sludge-bound water content, is generally accepted.

Previous research has shown that chemical conditioning with inorganic flocculants improves oily sludge dewatering capacity. Hwa and Jeyaseelan [1] have stated that the dewaterability of oily sludges could be enhanced by addition of lime or alum in the sludge conditioning stage. In their study, various digested sludge samples from a wastewater treatment plant were used and the oil contents of some of the samples were adjusted from 1.8% to 8.0% by weight by addition of engine oil. The optimum alum dosage was determined as 4% for these oily sludges and significant decrease in specific resistance to vacuum filtration was observed. The same workers found that lime dosages ranging from 6% to 10% had to be used to yield favorable characteristics of the sludge for better filterability [1,7]. In another study, the same researchers used incinerator fly ash from combustion of municipal solid wastes as a conditioner for the sludge. The optimum fly ash dosage was determined to be 3%–4% [8].

Physical conditioners, which are relatively inert materials and are often referred to as skeleton builders, can also be used to improve the dewatering capacity of oily sludges. Jonathan et al. [9] investigated the effect of industrial hydrated lime and fly ash to condition an oily sludge. By examining the sludge compressibility, these workers pointed out that conditioning with skeleton builders greatly reduced the compressibility and yielded a more

* Corresponding author. Tel.: +90 232 4127129; fax: +90 232 4531153.
E-mail address: nurdan.buyukkamaci@deu.edu.tr (N. Buyukkamaci).

0304-3894/$ – see front matter
doi:10.1016/j.jhazmat.2006.10.034

rigid and incompressible structure, capable of maintaining high porosity during high-pressure filtration.

The present study focuses on the improvement of the dewatering properties of an oily sludge, produced at a wastewater treatment plant of a petrochemical industry, by the addition of various chemical conditioners at different dosages. The experimental approach is to compare the effectiveness of conventional conditioners (alum, lime, and cationic polyelectrolyte) versus rather less conventional ones (fly ash, gypsum, and bentonite). The efficiency of each conditioner is discussed based on the measurement of capillary suction time (CST) and specific resistance to filtration (SRF).

2. Materials and methods

2.1. The sludge and its properties

Oily sludge was taken from a wastewater treatment plant of a petrochemical industry located in Aliaga, Izmir. The sludge sample was analyzed for oil content (OC), dry solids content (DS), CST, and SRF. The dry solids content and the oil content in the original raw sludge were 3.6% and 15%, respectively, and the SRF and CST values were found to be 5.5×10^{16} m/kg and 2000 s, respectively.

2.2. Analytical methods

Oil content of the raw sludge was determined according to the Soxhlet extraction method for sludge samples in standard methods [10].

Raw sludge samples were conditioned using classical jar test method. After the addition of a certain amount of chemical conditioner, rapid mixing at 200 rpm, and slow mixing at 25 rpm were applied for 2 min and 30 min, respectively.

SRF and CST tests were applied to raw and conditioned sludge samples for comparison of dewatering characteristics [11]. SRF test was performed using a Buchner Funnel equipped with a piece of Whatman # 2 filter paper and 2 bars of vacuum suction were applied. CST measurements were carried out by using a TRITON Type 304M CST-meter. SRF and CST reduction efficiencies (E(%)) were calculated by using following formula:

$$E(\%) = [(X_0 - X)/X_0] \times 100$$

where X_0 stands for SRF or CST of the raw sludge; X stands for SRF or CST of the conditioned sludge.

2.3. Chemical conditioners

During the conditioning processes, small and amorphous gel-like particles are transformed into larger and stronger aggregates and flocs get more porous and permeable to water flow structure [12]. Chemical conditioning is the more widespread method and alum, lime and polyelectrolyte are commonly used chemical conditioners. In addition to these widely used conditioners, bentonite, fly ash, and gypsum, which are less conventional chemicals, were tried in this study. In order to increase sludge cake porosity and decrease compressibility, these skeleton builders were added. Fly ash has been used for oily sludge conditioning [8], but bentonite and gypsum have not been used for this purpose before; although some work using bentonite and gypsum has been done on other types of sludges [13–16].

The bentonite, fly ash, and gypsum dosages used in this work ranged between 0.5% and 6%, 2% and 18%, and, 2% and 18%, respectively. The amounts of alum [$Al_2(SO)_4 \cdot 18H_20$], lime [$Ca(OH)_2$], and cationic polyelectrolyte added ranged between 1% and 12%, 4% and 14%, and 0.03% and 0.9%, respectively. Doses were adjusted depending on the improvement of dewaterability of the sludge after the addition of each chemical. When the dewaterability of the conditioned sludge decreased, addition of chemical conditioner was stopped.

3. Results and discussion

3.1. Bentonite conditioning

Bentonite is a highly absorbent clay-like substance generated frequently from the alteration of volcanic ash, consisting predominantly of smectite minerals. Bentonite's adsorption/absorption properties are very useful for wastewater purification. Another conventional use of bentonite is as a mud constituent for oil and water well drilling [17,18]. The only study using bentonite for sludge dewatering is about the affect of low temperature and additives on the dewaterability of coagulated water treatment sludges [16]. To our knowledge, there are no studies on the dewatering of oily sludge by the use of bentonite in the literature.

Bentonite was the first conditioner tried in this study. Chemical conditioning efficiencies obtained using different bentonite concentrations are given in Fig. 1. The results indicate that bentonite is not an actually effective conditioner for the dewatering of petrochemical sludge. Minimum SRF (2.83×10^{16} m/kg) was obtained using 2%, while the minimum CST (1460 s) was obtained using 1.5% bentonite; in other words, the decrease in SRF and CST was 49% and 27%, respectively. Correlation coefficients were calculated using MicroSoft Excel correlation function. The correlation coefficient between SRF and CST results was found to be very low ($R^2 = 0.59$). Although high SRF and CST reductions were not achieved, bentonite could be preferred as an auxiliary material to increase sludge cake porosity and reduce compressibility. However, increases in the amount of waste sludge with the addition of bentonite should be taken into consideration [3].

3.2. Fly ash conditioning

Fly ash is the residual waste of incineration processes and if it can be used as a conditioner, it can serve as a zero-cost raw material; and also the elimination of this waste would be possible in this way. However, the use of fly ash carries the risk of a heavy metal release [3].

The conditioning efficiencies obtained by addition of fly ash are given in Fig. 2. The optimum fly ash dosage was determined to be 10% based on the SRF results, while this dose was

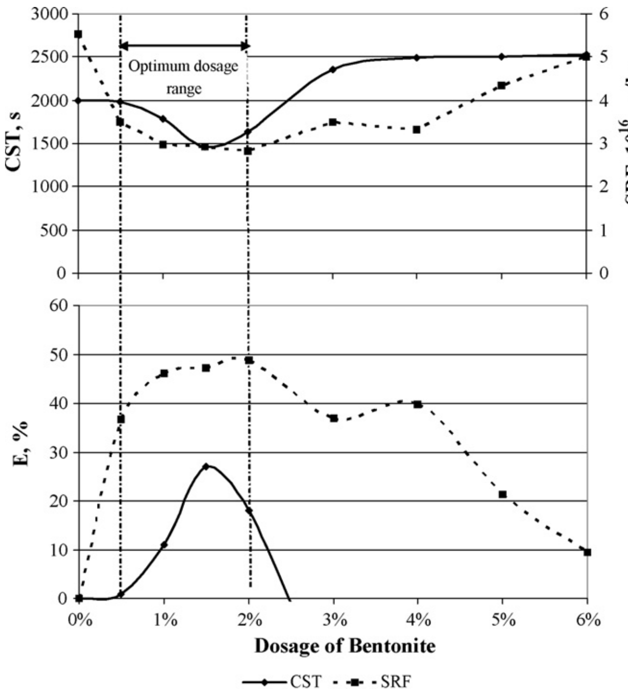

Fig. 1. Performance of bentonite as a petrochemical sludge conditioner.

6% considering CST reductions. At these dosages, minimum SRF and CST values were 4×10^{16} m/kg ($E = 26\%$) and 1476 s ($E = 26\%$), respectively. The correlation coefficient between SRF and CST in this case was 0.69. This is a little higher than the case of bentonite application.

Hwa and Jeyaseelan [8] have found that the addition of fly ash produced in a municipal solid waste incinerator decreases the specific resistances and CST values of oily sludges containing 1.8%–12% oil when 3% fly ash was added. According to their studies, use of more than 3% fly ash, does not improve dewaterability. They also obtained a decrease in the total suspended solids, and an increase in the concentrations of toxic heavy metals in the filtrate upon fly ash addition.

3.3. Gypsum conditioning

Gypsum is another material used for sludge conditioning and it is a common mineral in sedimentary environments. It is a major rock forming mineral that produces massive beds, usually by precipitating out of highly saline waters [19]. As reported in the literature, gypsum serves as a skeleton builder, forming a permeable and rigid lattice structure that can remain porous under high positive pressure during the compression step after the cake growth of the filtration, thereby maintaining the size of the micropassages through which water is expressed [14,15].

The results of gypsum application for petrochemical sludge conditioning are depicted in Fig. 3. A maximum of 44% SRF reduction efficiency was obtained when 12% gypsum was used ($SRF_{min} = 3.1 \times 10^{16}$ m/kg), whereas a maximum of 32% CST reduction was obtained using 10% gypsum ($CST_{min} = 1362$ s). For this application, the correlation coefficient between SRF and CST was 0.47.

Zhao [14] reported that addition of gypsum as a skeleton builder can enhance dewatering capacity of the alum sludge by decreasing the cake equilibrium moisture content by 7.1%. In another study of this researcher, gypsum ($CaSO_4 \cdot 2H_2O$) was introduced as a physical conditioner in combination with a polymer for alum sludge conditioning. The study demonstrated that

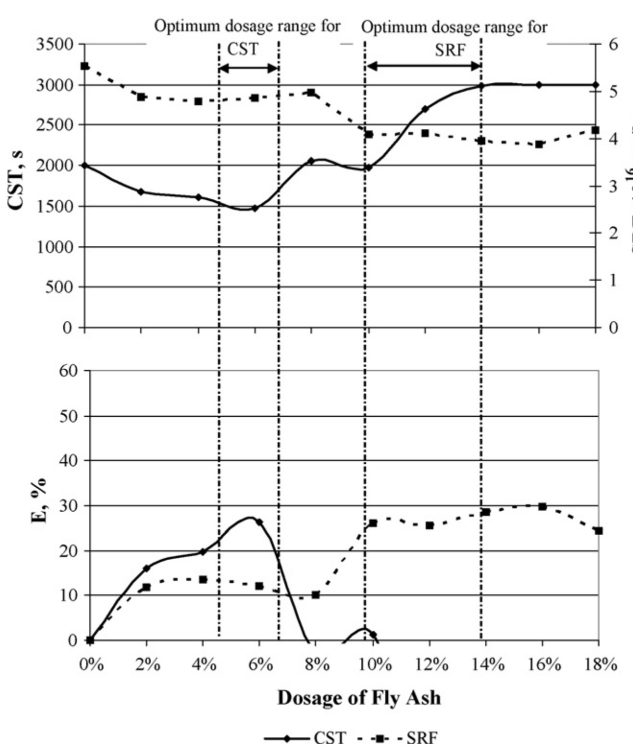

Fig. 2. Performance of fly ash as a petrochemical sludge conditioner.

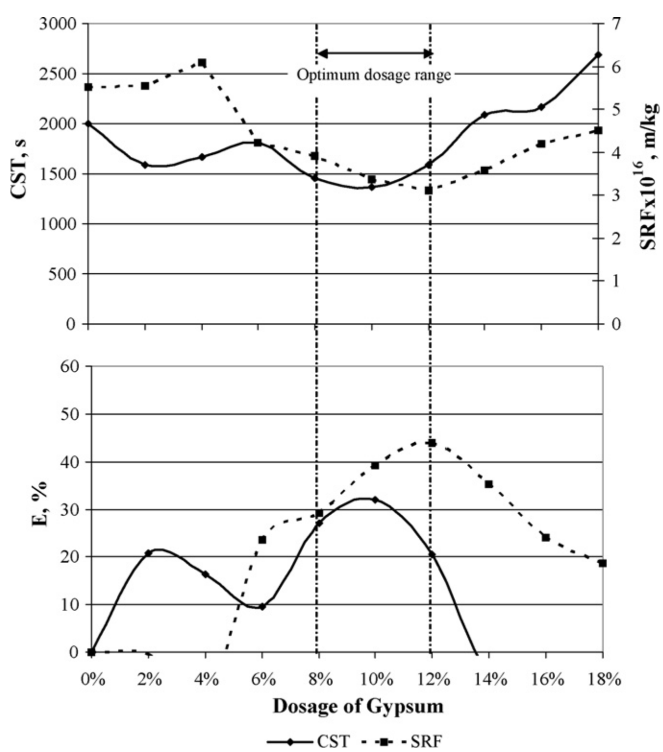

Fig. 3. Performance of gypsum as a petrochemical sludge conditioner.

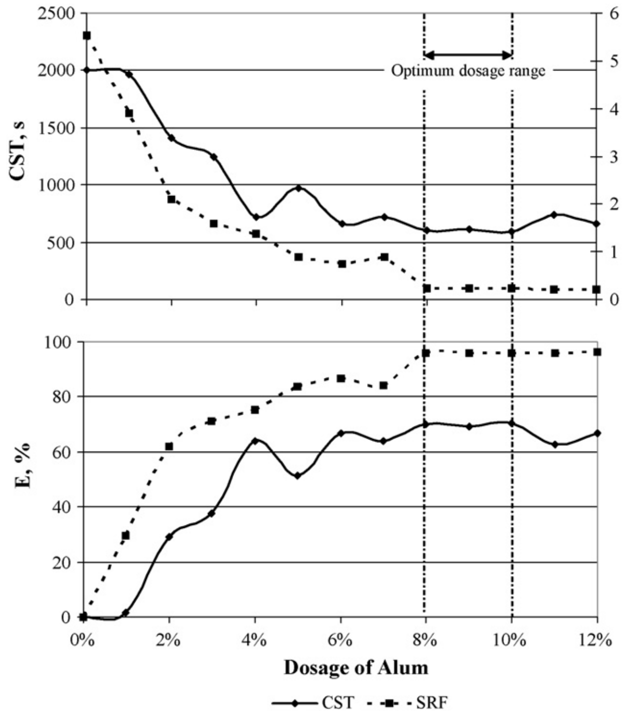

Fig. 4. Performance of alum as a petrochemical sludge conditioner.

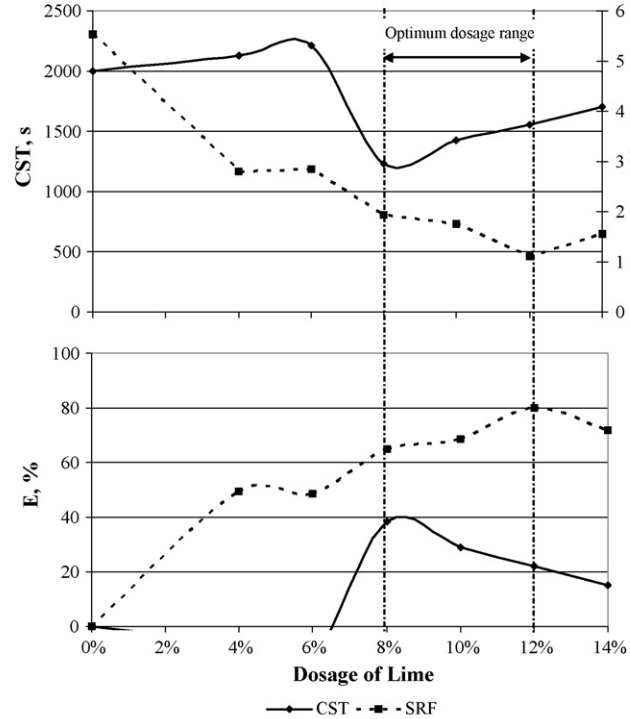

Fig. 5. Performance of lime as a petrochemical sludge conditioner.

water release was significantly enhanced by the addition of gypsum, which help or enhance the interaction between polymer and sludge particles and to build up a more rigid lattice structure [15].

3.4. Alum conditioning

Fig. 4 shows the results of petrochemical sludge conditioning studies when alum was used. Alum was one of the best conditioners and the optimum alum dosage for both SRF and CST was 8%. SRF decreased from 0.5×10^{16} to 2×10^{15} m/kg ($E = 92\%$) while CST decreased from 2000 to 600 s ($E = 70\%$) in this application. The correlation coefficient between SRF and CST was also found to be very high ($R^2 = 0.90$) in this case.

3.5. Lime conditioning

Lime, which is one of the more commonly used chemicals in sludge treatment, since it is quite cheap, gave low SRF and CST reductions as shown in Fig. 5. Approximately 38.5% CST ($CST_{min} = 1232$ s) and 80% SRF ($SRF_{min} = 1.1 \times 10^{16}$ m/kg) reductions were achieved using 8% and 12% lime, respectively. The correlation coefficient between the two parameters was 0.54 for lime conditioning.

Hwa and Jeyaseelan [1] have also compared lime and alum for the conditioning of oily sludge using CST measurements. They concluded that alum gave better results than lime in all experiments carried out with oily sludge containing 1.8%–8% oil. Similar to our results, alum gave better conditioning performance compared to lime in their study. It is also well known that the use of lime as a conditioning agent increases solids and raises the pH of the final products. Therefore, although lime is a cost-effective reagent, it should not be considered the best and unique solution.

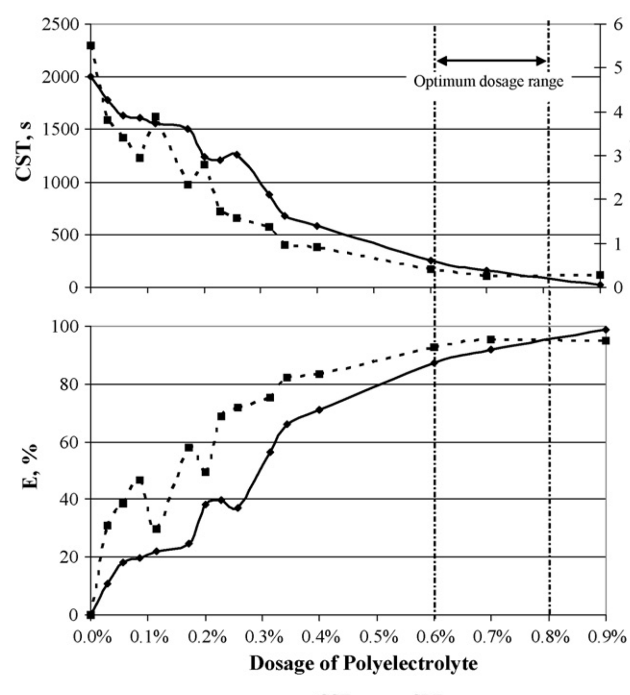

Fig. 6. Performance of cationic polyelectrolyte as a petrochemical sludge conditioner.

3.6. Polyelectrolyte conditioning

Cationic polyelectrolyte is the most predominant forms of organic additives used in sludge conditioning [20–22]. The oily droplet usually carries a negative charge; therefore cationic polyelectrolytes can condition oily sludge by utilizing charge-neutralization mechanisms [3].

In this work, cationic polyelectrolyte applications gave better results than other conditioners studied. With polyelectrolyte conditioning, it was possible to obtain up to 95% CST and SRF reductions as given in Fig. 6. CST decreased to 22.4 s ($E = 99\%$) and SRF was reduced to 0.28×10^{16} m/kg ($E = 95\%$) by the addition of cationic polyelectrolyte. The correlation coefficient between SRF and CST was about the same as the one obtained by addition of alum ($R^2 = 0.89$).

Zhao [15] applied the gypsum as an auxiliary conditioner with a polymer for alum sludge and efficient results were obtained. Similarly, gypsum or other types of skeleton builders with polyelectrolyte can provide better conditioning performances for the petrochemical oily sludge examined in this experiment.

4. Conclusions

Conventional conditioners, namely alum, lime, and cationic polyelectrolyte and less conventional ones, fly ash, gypsum, and bentonite, were examined for petrochemical sludge conditioning. Conventional chemical conditioners gave better results compared to others. Cationic polyelectrolyte gave the best results among all the conditioners examined. Up to 95% CST and SRF reductions were obtained using this conditioner. Alum was another conditioner giving good dewaterability. The optimal alum dosage was 8% based on the SRF and CST results. The correlation coefficients between SRF and CST were very low for bentonite, fly ash, gypsum, and lime applications. However, the correlation coefficients exhibited better agreement for alum and polyelectrolyte applications. Although bentonite, fly ash, and gypsum did not give good dewaterability, they can possibly be used as supplementary reagents together with alum or polyelectrolyte. Hence, the conditioning efficiency of the combination of these chemicals should be examined in further studies.

Acknowledgements

The authors gratefully acknowledge the Research Foundation of Dokuz Eylul University (Project No: 03.KB.FEN.093) for financial support, and PETKIM petrochemical industry for providing the sludge.

References

[1] T.J. Hwa, S. Jeyaseelan, Comparison of lime and alum as oily sludge conditioners, Water Sci. Technol. 36 (12) (1997) 117–124.
[2] I. Lazar, S. Dobrota, A. Voicu, M. Stefanescu, L. Sandulescu, I.G. Petrisor, Microbial degradation of waste hydrocarbons in oily sludge from some Romanian oil fields, J. Petrol. Sci. Eng. 22 (1999) 151–160.
[3] D.S. Jean, C.P. Chu, D.J. Lee, Freeze/thaw treatment of oily sludge from petroleum refinery plant, Sep. Sci. Technol. 36 (2001) 2733–2746.
[4] D.S. Jean, D.J. Lee, J.C.S. Wu, Separation of oil from oily sludge by freezing and thawing, Water Res. 33 (7) (1999) 1756–1759.
[5] C. Guohua, H. Gaohong, Separation of water and oil from water-in-oil emulsion by freeze/thaw method, Sep. Purif. Technol. 31 (1) (2003) 83–89.
[6] L.K. Chun, C. Guohua, L.C. Min, Salinity effect on freeze/thaw conditioning of activated sludge with and without chemical addition, Sep. Purif. Technol. 34 (1–3) (2004) 155–164.
[7] S. Jeyaseelan, T.J. Hwa, Dewatering characteristics of oily sludge, Water Sci. Technol. 28 (1) (1993) 249–256.
[8] T.J. Hwa, S. Jeyaseelan, Conditioning of oily sludges with municipal solid wastes incinerator fly ash, Water Sci. Technol. 35 (8) (1997) 231–238.
[9] Z. Jonathan, G. Noah, R. Menahem, Skeleton builders for conditioning oily sludge, J. Water Pollut. Control Federation 59 (7) (1987) 699–706, ISSN: 0043–1303.
[10] APHA, Standard Methods for the Examination of Water and Waste Water, 19th ed., American Public Health Association, USA, 1995.
[11] EPA, Design Manual: Dewatering Municipal Wastewater Sludges (EPA/625/1–87/014), Cincinnati OH 45268, 1987.
[12] W.W. Eckenfelder Jr., C.J. Santhanam, Sludge Treatment, Marcel Dekker Inc., New York and Basel, 1981.
[13] Y.Q. Zhao, D.H. Bache, Conditioning of alum sludge with polymer and gypsum, Colloids Surf. A: Physicochem. Eng. Aspects 194 (1–3) (2001) 213–220.
[14] Y.Q. Zhao, Enhancement of alum sludge dewatering capacity by using gypsum as skeleton builder, Colloids Surf. A: Physicochem. Eng. Aspects 211 (2–3) (2002) 205–212.
[15] Y.Q. Zhao, Involvement of gypsum ($CaSO_4 \cdot 2H_2O$) in water treatment sludge dewatering: a potential benefit in disposal and reuse, Sep. Sci. Technol. 41 (12) (2006) 2785–2794.
[16] K.A. Northcott, I.S. Peter, J. Scales, G.W. Stevens, Dewatering behaviour of water treatment sludges associated with contaminated site remediation in Antarctica, Chem. Eng. Sci. 60 (24) (2005) 6835–6843.
[17] http://www.ima-na.org, October 10, 2006.
[18] http://www.irantravertine.org, October 10, 2006.
[19] http://mineral.galleries.com, October 10, 2006.
[20] C.C. Wu, J.J. Wu, Effect of charge neutralization on the dewatering performance of alum sludge by polymer conditioning, Water Sci. Technol. 44 (10) (2001) 315–319.
[21] C.F. Lin, Y. Shien, Sludge dewatering using centrifuge with thermal/polymer conditioning, Water Sci Technol. 44 (10) (2001) 321–325.
[22] A.I. Cole, P.C. Singer, Conditioning of anaerobically digested sludge, J. Environ. Eng. 111 (4) (1985) 501–510.