IMPROVEMENT OF DEWATERING CAPACITY OF A PETROCHEMICAL SLUDGE

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Abstract

Oily sludge produced from a petrochemical industry was used to investigate the improvement of its dewatering properties. The oil content and the dry solid content 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 \(~5.5\times10^{16}\) 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% and 95% SRF were achieved for CST and SRF respectively when this dosage of cationic polyelectrolyte was used.
Keywords: Sludge, oily sludge, conditioning, petrochemical, oil

1. Introduction

Oily sludge is generated during the treatment of oily wastewaters which are produced in oil production and processing in petroleum, food and oil industries. Oily sludge is also produced from accidental oil spills, such as leakage of oil into rivers. In wastewater treatment plants, although most of the oil floats on the wastewater, a portion is carried into the sludge with settling solids. Oil creates difficulties in the treatment stages of wastewaters, and subsequently in the sludge dewatering processes [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]. Therefore, suitable sludge conditioning processes should be chosen before dewatering operations.

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. Some researchers have reported that the freeze/thaw process could be preferred for oily sludge dewatering [3-5].
Previous research has shown that chemical conditioning of oily sludge with inorganic flocculants improves 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 to 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 between 6% to 10% had to be used to yield favorable characteristics of the sludge for better filterability [1, 6]. 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% to 4% [7].

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. Zall et al. [8] 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 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). Evaluations were done based on the measurement of CST and 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 CST and SRF values were found to be $5.5 \times 10^{16}$ 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 [9].

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 minutes and 30 minutes, respectively.
SRF and CST tests were applied to raw and conditioned sludge samples for comparison of dewatering characteristics [10]. 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:

\[ E(\%) = \left(\frac{X_0 - X}{X_0}\right) \times 100 \]

Where:

\( X_0 \): SRF or CST of the raw sludge

\( X \): SRF or CST of the conditioned sludge

### 2.3 Chemical Conditioners

Six different chemical conditioners were examined for laboratory studies. Less conventional chemicals such as bentonite, fly ash, and gypsum were used in addition to widely used ones such as alum, lime, and polyelectrolyte. Fly ash has been used for oily sludge conditioning [7, 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 [11, 12]. The bentonite, fly ash, and gypsum dosages used in this work ranged from 0.5% to 6%, 2% to 18%, and 2% to 18%, respectively. The chemical compositions of bentonite and fly ash used in this work are given in Table 1.
The amounts of alum \( \text{Al}_2(\text{SO}_4)_{18}\text{H}_2\text{O} \), lime \( \text{Ca(OH)}_2 \), and cationic polyelectrolyte added ranged between 1-12%, 4-14%, and 0.03-0.9%, 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 special type of clay having properties which make it economically important in drilling operations for oil or underground water. It absorbs great amounts of water and increases enormously in volume, acquiring the colloidal property needed for drilling mud [13]. Bentonite was the first conditioner tried in this study.

Chemical conditioning efficiencies obtained using different bentonite concentrations are given in Figure 1. The results indicate that bentonite is not an effective conditioner for the dewatering of petrochemical sludge. Minimum SRF (2.83x10\(^{16}\) 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 (\( R^2 = 0.59 \)).
To our knowledge, there are no other studies on the dewatering of oily sludge by the use of bentonite in the literature. 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 [11].

**Figure 1. Performance of Bentonite as a Petrochemical Sludge Conditioner**

### 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. The conditioning efficiencies obtained by addition of fly ash are given in Figure 2. The optimum fly ash dosage was determined to be 10% based on the SRF results, while this dose was 6% considering CST reductions. At these dosages, minimum SRF and CST values were $4 \times 10^{16}$ 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 [7] have found that the addition of fly ash produced in a municipal solid waste incinerator decreases the specific resistances and capillary suction times of oily sludges containing 1.8% to 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 [14]. The results of gypsum application for petrochemical sludge conditioning are depicted in Figure 3. A maximum of 44% SRF reduction efficiency was obtained when 12% gypsum was used ($SRF_{\text{min}} = 3.1 \times 10^{16}$ m/kg), whereas a maximum of 32% CST reduction was obtained using 10% gypsum ($CST_{\text{min}} = 1362$ s). For this application, the correlation coefficient between SRF and CST was 0.47.

Zhao [12] reported that gypsum helps provide a porous, permeable and rigid lattice sludge cake structure under positive applied pressure when alum sludge conditioned with gypsum is subjected to dewatering. In the same study, it was demonstrated 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%.
3.4 Alum Conditioning

Figure 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 $0.5 \times 10^{16}$ to $2 \times 10^{15}$ m/kg ($E = 92\%$) while CST decreased from 2000 s 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.

Figure 4. Performance of Alum as a Petrochemical Sludge Conditioner

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 Figure 5. Approximately 38.5 % CST ($CST_{\text{min}} = 1232$ s) and 80% SRF ($SRF_{\text{min}} = 1.1 \times 10^{16}$ m/kg) reductions were achieved using 8% and 12% lime, respectively. The correlation coefficient between the two parameters was 0.54 for lime conditioning.

Figure 5. Performance of Lime as a Petrochemical Sludge Conditioner

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% to 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.

3.6 Polyelectrolyte Conditioning

Cationic polyelectrolyte is the most predominant forms of organic additives used in sludge conditioning [15-17]. Cationic polyelectrolyte applications gave better results than other conditioners studied in this work. With polyelectrolyte conditioning, it was possible to obtain up to 95% CST and SRF reductions as given in Figure 6. CST decreased to 22.4 s (E=99%) and SRF was reduced to 0.28x10^{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).

Figure 6. Performance of Cationic Polyelectrolyte as a Petrochemical Sludge Conditioner

4. Conclusions

Based on the results obtained from the above laboratory studies, the concluding remarks can be formulated as follows:
• Conventional chemical conditioners examined in this study, namely alum, cationic polyelectrolyte, and lime, gave better results compared to bentonite, fly ash, and gypsum.

• 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.

Acknowledgement

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References


Figure 1. Performance of Bentonite as a Petrochemical Sludge Conditioner

Dosage of Bentonite

CST, s  SRF x 10^6, m/kg

Optimum dosage range

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Figure 1. Performance of Bentonite as a Petrochemical Sludge Conditioner
Figure 2. Performance of Fly Ash as a Petrochemical Sludge Conditioner
Figure 3. Performance of Gypsum as a Petrochemical Sludge Conditioner
Figure 4. Performance of Alum as a Petrochemical Sludge Conditioner
Figure 5. Performance of Lime as a Petrochemical Sludge Conditioner
Figure 6. Performance of Cationic Polyelectrolyte as a Petrochemical Sludge Conditioner

Dosage of Polyelectrolyte

- CST  - SRF

Optimum dosage range

Figure 6. Performance of Cationic Polyelectrolyte as a Petrochemical Sludge Conditioner
Table 1. The Chemical Compositions of Bentonite and Fly Ash

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<th>Content (%)</th>
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