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Influence of Surfactants on Electro-osmotic Dewatering of Sludges

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ABSTRACT

The influence of surfactants $\left[ \text{C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}, \text{C}_{16}\text{H}_{35}\text{N}((\text{CH}_3)_2\text{Br}) \right]$ on the electro-osmotic dewatering of sludges is investigated at various pH values. Under favourable conditions, dewatering rate and final solid content can be increased and energy consumption can be lowered. In this investigation, two metal hydroxide sludges (from galvanotechnical industry), sewage sludge and pig manure have been considered.

INTRODUCTION

The recent increase of prosperity in industrialized countries entails the production of large amounts of wastes. Thus, in The Netherlands about $55 \times 10^9$ kg mud sludge and $25 \times 10^9$ kg manure have been produced in 1986. Other important sludges are: metal hydroxide sludges, sewage clearing sludge and water treatment sludge.

These waste streams are difficult to handle due to their high water content. Current methods for removing this water (filtration, sedimentation) are very energy- and/or time-consuming and therefore expensive. In our laboratory a method has been developed [1-4] for dewatering mortars by electro-osmosis, in which the efficiency of the process was remarkably improved by the addition of a surfactant (sodium dodecyl sulphate, $\text{C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}$).

Electro-osmotic dewatering dates back to the beginning of this century [5,6]. There is still interest in this method, as evidenced by a series of papers and patents ranging up to recent times (see, for example, Refs [7-13]). The method employs the surface charges present near the solid/liquid interfaces in a porous material, causing the liquid to move when an electrical field is applied.

In the present study we investigate the possibility of increasing the efficiency of dewatering sludges by electro-osmosis, through the addition of surfactants. The surfactant added may increase dewatering rate and final solid content,
and lower energy consumption by increasing the absolute value of the zeta potential which reduces the importance of energy dissipation through conduction losses.

Compared with the dewatering of mortars, the present study comprises one additional variable parameter: the pH of the aqueous solution in the pores.

EXPERIMENTAL

Materials

(1) Sodium dodecyl sulphate (SDS, C_{12}H_{25}O\text{SO}_3\text{Na}) from Merck, purity 90%.

(2) Cetyltrimethylammonium bromide [CTAB, C_{16}H_{33}N(\text{CH}_3)_3\text{Br}] from Sigma, purity 99%.

(3) Metal hydroxide sludge A (from TNO, Maatschappelijke Technologie, Apeldoorn, The Netherlands): initial solid content 16.5% (m/m), with 13.8% (m/m) Ni, 10.7% (m/m) Ca, 3.0% (m/m) Fe, 2.6% (m/m) Zn and 2.3% (m/m) Cr of dry solid.

Before the experiments, the sludge was dried at 110°C and ground in a hammer mill (Retsch DR 80 b/29) containing a sieve with 250-μm openings.

For the experiments, 200 g of dry powder (<250 μm) is suspended in 350 ml distilled water or 0.05 M surfactant solution; the pH was adjusted by addition of concentrated sulphuric acid or potassium hydroxide solution. The zeta potential of the sludge after drying and dispersion in distilled water was between 0 and −5 mV, its pH was 8.6 and its electrical conductance was 3.2 S m\(^{-1}\).

(4) Metal hydroxide sludge B (from TNO): initial solid content 34.8% (m/m), with 16.2% (m/m) Fe, 11.6% (m/m) Zn, 0.2% (m/m) Cd and 0.1% (m/m) Ca of dry solid.

The treatment before experiments was the same as with sludge A; 200 g (<250 μm) were suspended in 400 ml distilled water. After homogenization (1 h) the pH was 6.5, the electrical conductance was 0.8 S m\(^{-1}\) and the zeta potential was −46 mV.

(5) Sewage sludge: primary sludge from treatment facility “De Dommel”, Eindhoven, pH 6.0; electrical conductance 0.23 S m\(^{-1}\); zeta potential slightly negative; solid content 5.2% (m/m).

(6) Pig manure: fermented, from NCB Experimental Location, Sterksel, The Netherlands, pH 8.0; electrical conductance 4.0 S m\(^{-1}\); dry solid content 4.3% (m/m).

Apparatus and procedure

Figure 1 shows the experimental set-up. The filter (2) is a Schott G 1 glass filter, with 100–160 μm pores (radius 5 cm). The electrodes (1) are kept at a
Fig. 1. Experimental set-up: (1) platinum mesh electrodes, (2) Schott G1 glass filter, (3) glass cylinder, (4) sand layer, (5) electronic balance.

constant distance (2 cm) by a glass cylinder of radius 3 cm (3), 230 g of a suspension were introduced and platinum mesh electrodes were used (radius 45 mm). The lower electrode was covered by a layer of ~0.5 cm of sand (4) to depress undesirable electrode reactions.

The water removed was recorded by an electronic balance (5) (Sartorius PRO 32/34P) for 30 min. The voltage was kept constant at 20 V by a Delta SRC 300-S electronic voltage source; the electrical current was registered by a combination of a Nieaf 393219 precision resistance and a Servograph REC 80A recorder.

From the quantities of water removed after 5 min ($G_{eo5}$) in the presence and absence of a voltage between the electrodes, the acceleration number $F$ was calculated by means of

$$F = \frac{G_{eo5}(20 \text{ V})}{G_{o5}(0 \text{ V})}$$  \hspace{1cm} (1)

The energy consumption between $t=0$ min and $t=30$ min was calculated by integration of the current. From this, we calculated the energy consumption per gram of water removed ($\Delta E$), through
where $G_{eo30}$ is the amount of water removed from 230 g sludge in 30 min.

The final solid content is calculated from the initial solid content and the amount of water removed.

Sediment volumes were determined in 10-ml calibrated glass cylinders of cross section $0.75 \cdot 10^{-4} \text{ m}^2$ after one night’s settling.

Zeta potentials were measured in a Rank Brother Mark II electrophoresis apparatus.

RESULTS AND DISCUSSION

Figure 2 shows some typical dewatering experiments for metal hydroxide B in the absence and presence of an electrical field and/or surfactant. In the case concerned, very favourable results can be obtained by the addition of SDS. Thus, $F=6.20$ is reached at pH 3.4 and $F=4.23$ is obtained at pH 4.9. The final solid content can be increased to 47% (without SDS: 35%), and $\Delta E$ can be strongly reduced. The latter quantity is plotted in Fig. 3. Under favourable circumstances, an energy requirement of 13% of the enthalpy of evaporation of water ($2.518 \text{ kJ g}^{-1}$) can be obtained. However, such high efficiencies are restricted to rather specific conditions, as may be seen from Fig. 3: the relatively large $\Delta E$ in SDS solution at pH 6 ($2.15 \text{ kJ g}^{-1}$) is reproducible.

The following factors may impair the efficiency of electro-osmotic dewatering:

1) Reduction of the absolute value of the zeta potential, through approach of the pH to the effective isoelectric point (i.e.p.) of the mixture of solids present.
Fig. 3. Energy consumption during electro-osmosis (30 min) versus pH of metal hydroxide B: (○) without surfactant; (□) with 0.05 M SDS; (△) with 0.05 M CTAB. The horizontal line represents the enthalpy of evaporation of water.

(2) Dissolution of part of the solids leads to an increased electrolyte content which reduces, at given pH, the zeta potential [14], and which increases conduction losses. In addition, partial dissolution makes the method impractical as a means for handling wastes, since effluents containing appreciable amounts of heavy metals cannot be added to surface water without additional purification.

(3) Stabilization of the colloidal system against coagulation by a high surface charge may lead to a dense and impermeable structure of the porous material during dewatering, inhibiting further water removal.

(4) Stabilization of the porous material to be dewatered against coagulation may lead to breaking away of solid particles from the porous body by the flow; if the particles are small, they may block the filter.

Thus, the large $\Delta E$ on electro-osmosis of metal hydroxide sludge B at pH 5.4 in the absence of surfactants (Fig. 3) is due to factor 1. At this pH, dissolution of the metal hydroxides concerned does not yet become important, as shown by the electrical conductivity (Fig. 4); and addition of SDS reduces $\Delta E$ drastically (Fig. 3). In fact, in the absence of SDS or CTAB there is, in this case,
hardly any increase in water removal obtained on application of an electrical field; \( F = 1.02 \) under these circumstances.

Factor 3 leads to the expectation that the best dewatering conditions are those in which reasonable values of the zeta potential are combined with relatively large sediment volumes. Thus, for metal hydroxide sludge A, best results are expected at pH 8.8 in 0.05 \( M \) CTAB (compare Figs 5 and 6). This sludge is difficult for electro-osmotic handling because of its appreciable dissolution, even at neutral pH values, presumably due to its high Ca content.
This dissolution is even more pronounced at low pH; it leads to rather low zeta potentials in the absence of surfactants (Fig. 5). Addition of surfactants, especially SDS, increases the zeta potential considerably.

Nevertheless, $\Delta E$ during electro-osmosis is 2.63 kJ g$^{-1}$ at pH 8.8 in 0.05 M SDS solution, which is at the level of the evaporation enthalpy of water. In this solution, the temperature rose to 70–80°C during electro-osmosis because of conduction losses. In addition, in this case, the filter becomes impermeable to water during dewatering due to blocking of the filter; in this case, $F=0.80$. This effect was not observed in the case of metal hydroxide sludge B, because here the primary particles as observed by SEM were 200–250 μm.

In spite of the smaller zeta potentials of metal hydroxide sludge A in CTAB solutions when compared to those in SDS solutions (Fig. 6), electro-osmotic dewatering of this sludge is much better in CTAB containing solutions at pH 8.8. Here $\Delta E$ is low (0.77 kJ g$^{-1}$), $F$ is very large because hardly any water is removed from the sludge in the absence of an electrical field, and a final solid content of 61.8% (m/m) can be reached.

In the case of sewage sludge, $\Delta E$ by electro-osmosis is significantly lower than the enthalpy of evaporation of water (Fig. 7), even in the absence of surfactants. However, $F$ values can be significantly increased by the addition of surfactants. Thus, $F=3.67$ in SDS solution at pH 8.5, while $F=1.43$ in the absence of surfactants. The highest final solid content was 12%, obtained at pH 3 in 0.05 M SDS (in the absence of an electrical field, a solid content of 5% could be reached). Under these circumstances, $\Delta E$ during electro-osmosis is 0.43 kJ g$^{-1}$ (~16% of the evaporation enthalpy of water).

Similar data have been obtained by applying electro-osmosis to pig manure.

![Fig. 7. Energy consumption during electro-osmosis (30 min) versus pH of sewage clearing sludge. Meaning of symbols as in Fig. 3.](image-url)
The $\Delta E$ here is acceptable, even in the absence of surfactants (1.15 kJ g$^{-1}$ at pH 7; 1.81 kJ g$^{-1}$ at pH 8.2). It can be decreased appreciably by adding SDS (0.57 kJ g$^{-1}$ at pH 7.1) or CTAB (0.46 kJ g$^{-1}$ at pH 7.1). Values of $F$ are optimal in SDS solution ($F=3.10$ at pH 7, $F=6.81$ at pH 8.4; in the absence of surfactants, $F=0.95$ and 1.78, respectively). However, the solid content becomes stationary at 8.5% in the presence of surfactants (4% in their absence). Clearly, in this case, a combination of a filter press with electro-osmosis is necessary for obtaining higher solid contents.

CONCLUSIONS

Electro-osmosis of sludges can be performed at reasonable energy requirements ($< 0.5$ kJ g$^{-1}$) if it is performed in the presence of surfactants at carefully chosen pH. Its efficiency is impaired, however, by: dissolution of part of the solids; approach of the pH to the effective i.e.p. of the solids; blocking of the filter by particles broken from the porous material during dewatering; and formation of a dense structure of the solid. The two latter factors are especially important because efficient electro-osmosis requires large zeta potentials which tend to counteract coagulation.

SUMMARY

Favourable circumstances for electro-osmotic dewatering of sludges can be obtained by the addition of surfactants and by a careful choice of pH.

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