

Involvement of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in water treatment sludge dewatering: A potential benefit in disposal and reuse

Y. Q. Zhao

*Centre for Water Resources Research, School of Architecture, Landscape and Civil Engineering,
University College Dublin, Earlsfort Terrace, Dublin 2, Ireland*

* Corresponding detail: Tel: +353-1-716 7284; Fax: +353-1-716 7399;
E-mail: yaqian.zhao@ucd.ie

Abstract

This research assessed the use of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) as a skeleton builder for sludge dewatering since polymer conditioning of sludge affected only the rate of water release, not the extent of dewatering. The use of gypsum as a physical conditioner, in association with a polymer, could improve sludge filterability. More significantly, 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 micro-passages through which water is expressed. Experiments using a high pressure cell apparatus showed that a further decrease of two to seven percent of the equilibrium moisture content of the sludge cake was achieved, for sludge thicknesses for dewatering of 1 to 10 cm, by the addition of gypsum with 60% of the original sludge solids when compared to the single polymer conditioning. The importance of the addition of gypsum in alum sludge dewatering is not only the improvement in the extent of dewatering, but also the potential application of transforming dewatered alum sludge from 'waste' for landfill to useful 'fertilizer' or to be used as filter medium/adsorbent for wastewater treatment engineering.

Keywords: Alum sludge, constructed wetlands, dewatering, disposal, gypsum, skeleton builder

INTRODUCTION

Water treatment sludge refers to the by-product from the processing of drinking water in Water Treatment Works where aluminum sulfate is most widely used as the primary coagulant in Ireland. For this reason, water treatment sludge is commonly known as alum sludge. During alum sludge treatment, an organic polymer is often used as a chemical conditioner to improve sludge filterability by flocculating small gel-like sludge particles into large aggregates with less affinity for water. Ideally, the flocs are porous, permeable to water flow and incompressible, so that the pores will not be blocked under pressure during filtration and dewatering. However, it is evident that polymer conditioning of sludge affects only the rate of water release but not the extent of dewatering and makes the sludge more compressible (1-3).

Keeping these factors in mind, it is reasonable to assume that the target of conditioning should include both an improvement in the extent of dewatering and a reduction in cake compressibility. To achieve these objectives, an alternative approach may be the addition of a skeleton builder or physical conditioners. Physical conditioners are often inorganic admixtures, which are generally inert materials and part of the waste stream from industry. As reported in the literature, fly ash, cement kiln dust, quicklime, hydrated lime, fine coal, bagasse, wood chips and wheat dregs have been used in sludge dewatering (4, 5). Previous studies by Zhao and Bache (3) and Zhao (6) have demonstrated that the use of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) as a skeleton builder in association with a polymer for water treatment sludge conditioning and dewatering could form a permeable and rigid lattice sludge structure that can remain porous under high positive pressure during the

compression step after the cake growth of the filtration, thus sustaining the size of the micro-passages through which water is expressed.

This paper presents an experimental study aimed at demonstrating the effectiveness of a water treatment sludge dewatering after a combined dual conditioning with gypsum and an organic polymer. In this study, a laboratory scale high pressure cell apparatus was used for dewatering tests. Thereafter, the possible applications and benefits of dewatered alum sludge are briefly highlighted. The importance of its potential application lies in transforming dewatered alum sludge from 'waste' for landfill to useful 'material' which may be used as an adsorbent for pollutant immobilization in wastewater treatment.

MATERIALS AND METHODS

Experimental Materials

The alum sludge used in this study was collected from a sludge holding tank of a water treatment works treating a low-turbidity, coloured water with aluminum sulfate as primary coagulant. The sludge with solids concentration of 8,453 mg/l and pH of 6.7 was conditioned using polymer PW 85 (*from OCL Ltd, UK.*), this being an anionic organic polymer with molecular weight in the range 1.2×10^7 and charge density of 5 %. A 0.01 % stock solution was prepared using nanopure water and allowed to stand for 24 h prior to use. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) (supplied by *Tioxide Europe Ltd*) with a density of 1,400 – 1,600 kg/m^3 and a particle size of 4 - 20 μm (measured using a Galai CIS – 100 particle

size analyser) was used as a skeleton builder in combination with the polymer for sludge conditioning.

Experimental Methods

Initially, gypsum was added to a 200 ml sludge sample with the dose expressed as the percentage of alum sludge solids concentration. After several seconds of rapid mixing to ensure dispersion, the polymer was added with dosage of 20.0 mg/l (excluding the gypsum in the sludge). Following polymer addition the sludge was subjected to 30 s of rapid mixing followed by 1 min slow mixing to promote flocculation. After conditioning, the sludge was then subjected to dewatering tests using a laboratory scale high pressure cell apparatus. Experimental procedures are described schematically in Fig. 1. The high pressure cell apparatus is an air pressure driven piston apparatus, which applies a positive pressure to the sludge sample, as illustrated in Fig. 1. Two Whatman 1# filter papers wetted with distilled water were placed at the base of the piston chamber of the high pressure cell to hold the sludge sample. Conditioned sludge samples were poured into the piston chamber up to depths of 1, 2, 3, 5, 7, and 10 cm, respectively, for the dewatering test at an applied pressure of 5 bar ($1 \text{ bar} = 10^5 \text{ N/m}^2$). During the test, the filtrate volumes and the filtration time were recorded. After the dewatering test (dewatering time being pre-set), moisture content (MC) of the sludge cake was measured using standard method. In each test, the run was repeated in the same way to check the data reproducibility. The data presented below represent the mean values.

[Fig. 1 Schematic illustration of experimental procedure]

RESULTS

Fig. 2 illustrates the volume of filtrate as a function of dewatering time, when conditioned sludge was subjected to dewatering using the high pressure cell apparatus. On the basis of previous work reported in Zhao and Bache (3), the present study focused on a gypsum dose of 60% dry solids (DS) of original alum sludge solids concentration, this having been demonstrated to produce a significant improvement in filterability in term of net sludge solids yields, which takes into consideration the increase of sludge solids concentration by gypsum addition. Applied pressure for the dewatering apparatus of 5 bar was also demonstrated as the suitable pressure for dewatering (7). It was found from Fig. 2 that a polymer dose of 20.0 mg/l resulted in a significant improvement in dewatering; further increase of the polymer dose did not affect dewatering behavior. Thus, optimum polymer dose was set as 20.0 mg/l for the oncoming tests in this study.

[Fig. 2 Effect of polymer dosage on dewatering behavior of 60% DS gypsum pre-added sludge (Conditioned sludge was poured into the piston chamber up to a depth of 2 cm. Applied pressure is 5.0 bar. In the legend, S refers to sludge, G represents gypsum and the values show the polymer dosage)]

Fig. 3 shows plots of sludge cake moisture content with dewatering time at the polymer dose of 20.0 mg/l with gypsum addition of 60% DS or without gypsum addition. It is noted in Fig. 3 that the sludge MC at the beginning of the dewatering is different due to the increase of sludge solids concentration by gypsum addition. Comparing the two plots shown in Fig.3, it is clear that the addition of gypsum improved sludge dewatering

behavior by further decreasing cake moisture content in the range of 16.9 to 4.1 percent, corresponding to the dewatering times of 1 h to 6 h, respectively. It is believed that cake moisture content is an indication of the extent of dewatering for the apparatus used. A lower cake moisture value indicated a higher solid content in the cake and a smaller volume of dewatered sludge for final handling. To interpret the data, a parameter of I , which represents the mass of water release per initial solids in sludge sample, was introduced (7).

$$I = \frac{\theta_0 - \theta_t}{1 - \theta_t} \quad (1)$$

where, θ_0 and θ_t refer to the MC of the dewatering samples at $t=0$ and $t>0$, respectively. Calculation of I in the case of 6 hours dewatering (shown in Fig. 3) shows that the values of I are 0.973 and 0.962 corresponding to the absent and the present of the gypsum in dewatering, respectively. Although the mass of water release caused by the per mass of solids in the sludge sample is lower when gypsum is added, increased mass of gypsum addition leads to a increased amount of water (in mass) to be released from the dewatering process.

[Fig. 3 Comparison of dewatering behavior between polymer dosed and polymer plus gypsum dosed sludge (polymer dosage is 20.0 mg/l; gypsum is 60% DS. Sludge thickness in piston chamber is 2 cm. Applied pressure is 5.0 bar)]

In order to identify the effect of gypsum addition on sludge cake equilibrium moisture content, groups of dewatering tests were designed and performed at the sludge thickness of 1, 2, 3, 5, 7, and 10 cm, respectively, in the piston chamber of the high pressure cell apparatus. At each sludge thickness, a dewatering test was carried out continuously for 8 days, by which time the constant moisture content, which was suggested as equilibrium moisture content, was reached. The results are given in Fig. 4. Fig. 4 demonstrates that, compared with the equilibrium moisture content obtained without the gypsum, the addition of gypsum resulted in lower cake moisture content during the dewatering process, and eventually led to a further decrease of 6.8 percent of the cake equilibrium moisture content at sludge thickness of 1cm and 2.3 percent at sludge thickness of 10 cm. In addition, Fig. 4 indicates that the dewatering behavior can be significantly affected by sludge thickness in the dewatering apparatus; the effects of this factor have been investigated and are reported in Zhao and Bache (7).

[Fig. 4 Effects of thickness of sludge samples on cake equilibrium moisture content with and without gypsum addition (Applied pressure is 5.0 bar)]

DISCUSSION

Gypsum as a Physical Skeleton Builder in Alum Sludge Dewatering

Although gypsum is commonly known in agricultural science as an amendment for ameliorating alkaline soils, there have been no reports from the literature investigating its

use as a physical conditioner in improving sludge dewaterability until the previous studies (3, 6). The results presented in this study provide vital evidence that gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) can be used in combination with a polymer for conditioning an alum sludge. Sludge filterability was improved with the addition of gypsum. The addition of gypsum enhanced the sludge dewatering by further decreasing equilibrium cake moisture content by about 2 to 7 percent, depending on the thickness of sludge being dewatered (see Fig. 4). Therefore, it is reasonable to believe that gypsum functioned as the skeleton builder to help or enhance the interaction between polymer and sludge particles. This has been shown by direct measurement of the polymer residual using size exclusion chromatography in a previous study (3). It has been demonstrated in the past studies (3, 6) that either addition of gypsum itself (without polymer) or addition of other material, such as non-shrinking glass-microspheres, with polymer could hardly improve sludge dewatering. It is the enhanced interaction between gypsum and sludge particles under the function of polymer as a coagulant during the conditioning that makes the sludge form a more compact structure, thereby reducing its compressibility during the dewatering process. The more rigid lattice structure can retain solid particles and allow the water to be transmitted via the micro-passages during dewatering. This view has been supported by the investigation of floc structure (evaluated in terms of fractal dimension, D_F , which is a quantitative measurement of how the original particles in the flocs occupy space) using an image analysis system (6) and has been described schematically by Lai and Liu (8), as shown in Fig. 5.

[Fig. 5 Conceptual description of the role of gypsum as a skeleton builder in sludge dewatering (8)]

The Potential Application of This Study

It is noted that gypsum is neither an inert material nor a waste from industry. Why is it selected as a skeleton builder? The selection of gypsum originated from its common use as an amendment in agricultural science. The use of gypsum in alum sludge treatment leads to a number of possible applications for the dewatered sludge.

Firstly, dewatered alum sludge with the addition of gypsum makes land use a possibility. To date, efficient techniques for utilizing the dewatered sludge are still lacking, and the most economic way to dispose of dewatered sludge is the application to land as a soil fertilizer. However, alum sludge is directly discharged or landfilled in Ireland because of high levels of aluminum and some heavy metal ions, which have been shown to be toxic to aquatic life and provide marginal, if any, benefits to soil fertility. On the other hand, land disposal of alum sludge has advantages; compared with sewage sludge, alum sludge is relatively clean with respect to heavy metals and organics, and poses lower environmental risks (9). It is noted in the literature that some attention has been paid to the assessment of land use of alum sludge (10-12). In particular, according to the study reported by Geertsema et al. (9), there was no long-term adverse effect observed when alum sludge was applied to forest lands at a loading rate of at least 1.5 to 2.5 percent by dry weight. Therefore, it is fair to say that the addition of gypsum in alum sludge will enhance its possible application to land, particularly for ameliorating alkaline soils.

Secondly, alum sludge dewatered with gypsum may be used as the adsorbent for the immobilization of some pollutants, such as phosphorus removal in farmyard and other animal wastewaters as well as agricultural and food industrial wastewaters. The raw alum sludge contains flocs of humic matter and metal hydroxide in which the impurities removed from the natural water are entrapped, adsorbed or chemically bound. More significantly, the dewatered alum sludge is predominantly composed of amorphous aluminum ions. Furthermore, the involvement of gypsum means that the dewatered alum sludge is abundant in calcium ions. Both amorphous aluminum and calcium ions have been shown to play an important role in the treatment of phosphorus-rich wastewater (13-15). Currently, a research project focused on identifying the absorption capacity of a wide range of phosphorus species by dewatered alum sludge is being carried out in the Centre for Water Resources Research (CWRR) of University College Dublin (16). The results derived from this project can be used for further and extensive research towards the possible application of dewatered alum sludge in wastewater treatment engineering. In particular, it has been proposed that the dewatered alum sludge has the potential to be used as the main substrate in constructed wetlands for phosphorus-rich wastewater treatment (17). It has been recognized that constructed wetlands are an effective technique for wastewater treatment and are increasing in popularity. Compared with the other technologies, e.g. activated sludge, tricking filter and biological reactors, constructed wetlands have the advantage of an aesthetically pleasing appearance and lower energy consumption, and are more environmentally friendly (18, 19). It is expected that the reuse of dewatered alum sludge as the filter medium in constructed wetlands will

further reduce the capital cost of engineered wetlands. Moreover, the reuse of alum sludge can transform the sludge from a 'waste' into useful material in accordance with the theme of sustainable development.

CONCLUSIONS

Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was introduced as a physical conditioner in combination with a polymer for alum sludge conditioning. Dewatering tests in a high pressure cell apparatus have demonstrated that water release was significantly enhanced by the addition of gypsum, which served as a skeleton builder. Addition of gypsum by 60% DS (original alum sludge dry solids) can lead to a further decrease of about 7 percent of the cake equilibrium moisture content at sludge thickness of 1cm and 2 percent at sludge thickness of 10 cm, compared with the moisture content achieved with only polymer conditioning. The lower moisture content will benefit the final handling of dewatered sludge. The beneficial effect of gypsum lies in its role as a skeleton builder to help or enhance the interaction between polymer and sludge particles and to build up a more rigid lattice structure. Dewatered alum sludge is thus proposed as a land fertilizer or alternatively as a filter medium in constructed wetlands for wastewater treatment. These possible applications provide a promising prospect for the disposal of alum sludge, but more research work is needed.

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REFERENCES

1. Novak, J.T., O' Brien, J.H. (1975) Polymer conditioning of chemical sludges. *J. WPCF.* 47 (10), 2397 - 2410.
2. Knocke, W.R., Dishman, C.M., Miller, G.F. (1993) Measurement of chemical sludge floc density and implications related to sludge dewatering. *Water Environment Research*, 65 (6), 735-743.
3. Zhao, Y.Q., Bache, D.H. (2001) Conditioning of alum sludge with polymer and gypsum. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 194 (1-3), 213-220.
4. Benitez, J., Rodriguez, A., Suarez, A. (1994) Optimisation technique for sewage sludge conditioning with polymer and skeleton builders. *Wat. Res.* 28 (10), 2067 - 2073.
5. Zouboulis, A.I., Guitonas, A. (1995) Use of fly ash as conditioning agent for improving biological sludge dewaterability by filter press. *Fresenius Envir. Bull.* 4, 387 – 392.

6. Zhao, Y.Q. (2002) Enhancement of alum sludge dewatering capacity by using gypsum as skeleton builder. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 211 (2-3), 205-212
7. Zhao, Y.Q., Bache, D.H. (2002) Integrated effects of applied pressure, time, and polymer doses on alum sludge dewatering behaviour. *Waste Management*, 22 (7), 813-819.
8. Lai, J.Y., Liu, J.C. (2004) Co-conditioning and dewatering of alum sludge and waste activated sludge. *Wat. Sci. & Technol.*, 50 (9), 41-48.
9. Geertsema, W.S., Knocke, W.R., Novak, J.T., Dove, D. (1994) Long term effects of sludge application to land. *J. AWWA*. 86, 64-74.
10. Elliott, H.A., Dempsey, B.A. (1991) Agronomic effects of land application of water treatment sludge. *Journal of American Water Works Association*, 83 (4), 126-131.
11. Titshall, L.W., Hughes, J.C. (2005) Characterization of some South African water treatment residues and implications for land application. *Journal of Water SA*, 31 (3), 299-307.
12. Babatunde, A.O., Zhao, Y.Q. (2006) Constructive approach towards water treatment works sludge management: An international review of beneficial re-uses. *Critical Reviews in Environmental Science and Technology* (in press).
13. de-Bashan, L.E., Bashan, Y. (2004) Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997–2003). *Wat. Res.*, 38 (19), 4222-4246.

14. Huang, S.G., Chiswell, B. (2000) Phosphate removal from wastewater using spent alum sludge, *Wat. Sci. and Tech.*, 42 (3-4), 295-300.
15. Kim, J.G., Kim, J.H., Moon, H.S., Chon, C.M., Ahn, J.S. (2003) Removal capacity of water plant alum sludge for phosphorus in aqueous solutions, *Chemical Speciation and Bioavailability*, 14, 67-73.
16. Yang, Y., Tomlinson, D., Kenned, Y S., Zhao, Y.Q. (2005) Dewatered alum aludge: A potential adsorbent for phosphorus removal, In: Proceedings of the specialist conference on management of residues emanating from water and wastewater treatment, Sandton Convention Centre, Johannesburg, South Africa, 2005.
17. Babatunde, Akintunde., Yang, Yongzhe., Zhao, Yaqian. (2005) Towards the development of a novel wastewater treatment system incorporating drinking water residual: Preliminary results, In: Proceedings of 10th European biosolids and biowastes conference, workshop and exhibition, Wakefield, West Yorkshire, UK.
18. Verhoeven, Jos T.A., Meuleman, Arthur F.M. (1999) Wetlands for wastewater treatment: opportunities and limitations. *Ecological Engineering*, 12 (1-2), 5-12.
19. Kivaisi, Amelia K. (2001) The potential for constructed wetlands for wastewater treatment and reuse in developing countries: a review, *Ecological Engineering*, 16 (4), 545-560.

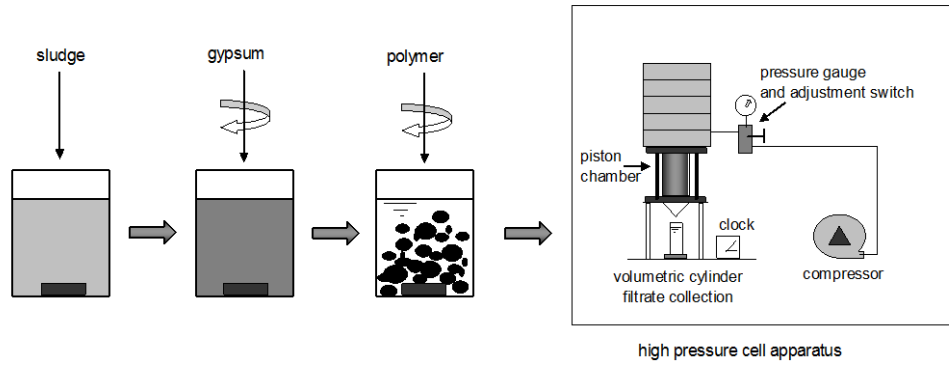


Fig. 1 Schematic illustration of experimental procedure

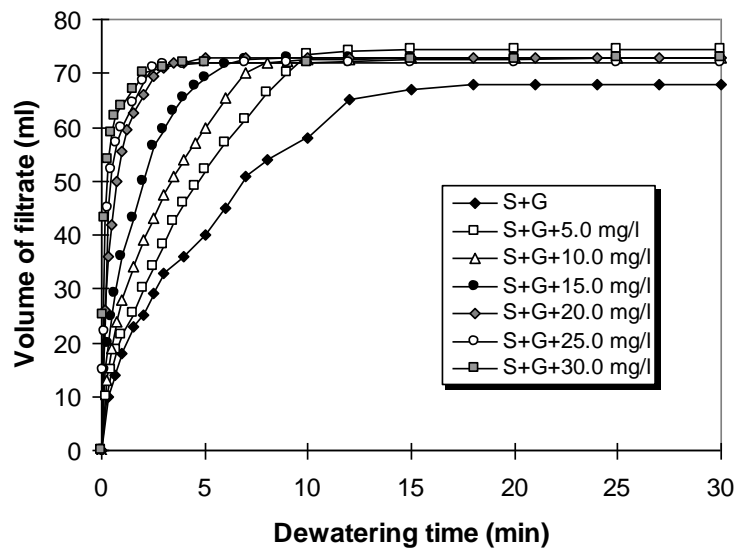


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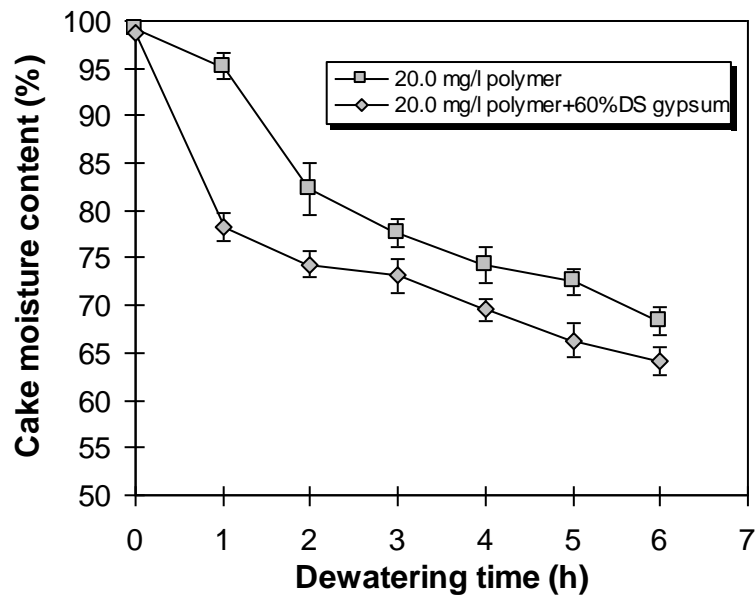


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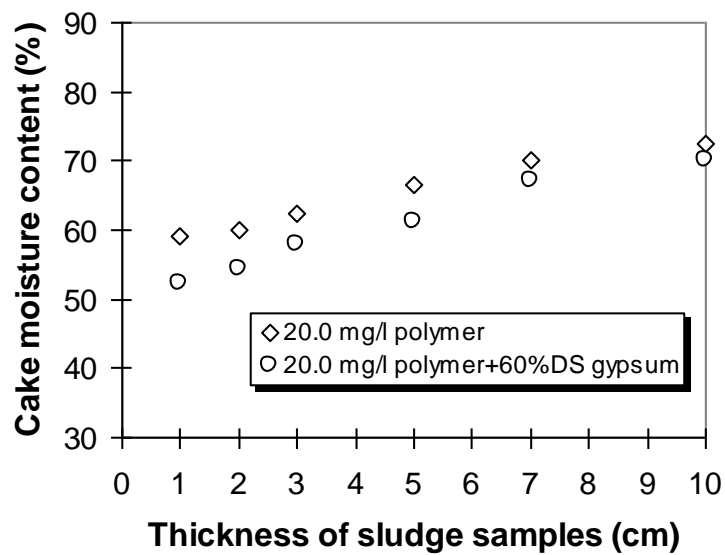


Fig. 4 Effects of thickness of sludge samples on cake equilibrium moisture content with and without gypsum addition (Applied pressure is 5.0 bar)

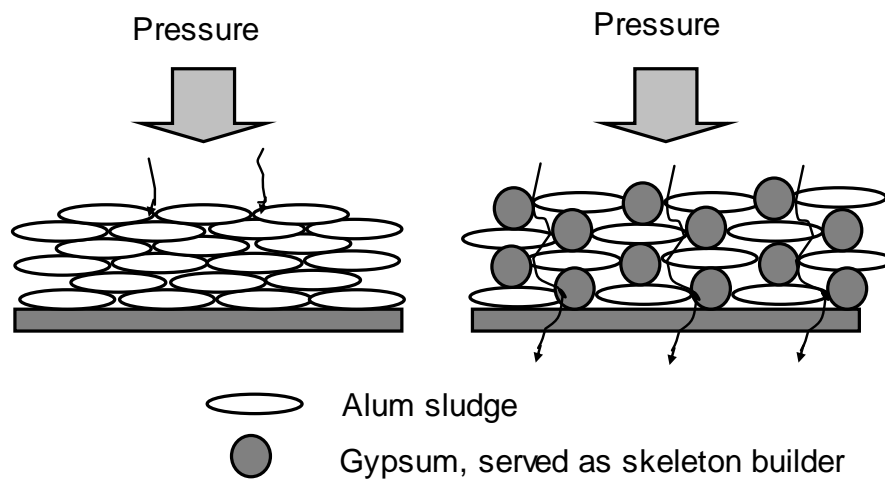


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Figure legends

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