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Effect of freeze-thaw process on partitioning of contaminants in ferric precipitate

Wendy A.M. McMinn[a,*], James Keown[a], Stephen J. Allen[a], Michael G. Burnett[b]

[a] *School of Chemical Engineering, Queen's University Belfast, David Keir Building, Stranmillis Road, Belfast BT9 5AG, UK*
[b] *School of Chemistry, Queen's University Belfast, David Keir Building, Stranmillis Road, Belfast BT9 5AG, UK*

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Abstract

The primary interest of this work was to determine the processing conditions which will provide the most water removal from the precipitate after freezing and thawing. The work examined the effect of variables such as freezing time, freezing temperature, and pre-treatment steps, e.g. agitation or concentration, on the freeze thaw process of ferric precipitates. The extent of dewatering of freeze thawed samples was not significantly affected by freezing rate or curing time, provided the floc was completely frozen. However, a pre-concentration step was found to produce a more concentrated residual. The relatively low degree of structure within the ferric flocs makes them particularly suitable for freeze-thaw conditioning. Only a slight increase in leach out of contaminant from the floc was observed. Thus, the experiments indicate that this is a very simple and effective method of dewatering precipitates, which does not require the use of additional additives.
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1. Introduction

Over the past 20 years, wastewater treatment has become more important as more stringent limits have been applied to industrial discharges. As emission levels have become stricter, considerable investment and research has been focused on the improvement of many of the well established technologies.

One group of pollutants, which have shown to be highly toxic and persistent in the environment, are heavy metals. Common technologies for the removal of heavy metals from wastewaters include chemical precipitation as hydroxide, sulphide or carbonate, coagulation, co-precipitation and ion exchange [1]. The process which forms the basis for this work is the precipitation of heavy metal contaminants by flocculation, and the subsequent removal of the floc from the wastewater stream. One of the greatest difficulties with such technologies is that the contaminant is not completely eliminated. The heavy metals are simply separated from the wastewater stream and concentrated into a sludge. This sludge has traditionally been disposed of in landfill sites, or dumped at sea. Disposal of highly toxic waste at sea is no longer permitted, and leach out of toxins from landfill sites must be controlled. It is, therefore, imperative that the sludge retains all the contaminates bound within it, and that it can be reduced to as small a volume as possible. One method utilised to improve water removal involves freezing the sludge and then allowing it to thaw. However, use of such a process must not have a detrimental effect on the leach out of contaminants from the floc.

For many years it has been known that subjecting a wastewater residual sludge to a process of freezing and thawing results in improved conditioning [2]. Simply placing a sample of precipitate in a freezer yields a

*Corresponding author. Tel.: +44-028-90274065; fax: +44-028-90381753.
E-mail address: w.mcminn@qub.ac.uk (W.A.M. McMinn).

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Nomenclature

V_i	initial sediment volume (cm^3)
V_f	final sediment volume (cm^3)

sediment, upon thawing, much more concentrated than the original. During the actual freezing process the pure water fraction freezes and the residuals are either 'entrapped' within the forming ice or rejected and thus, 'migrate' ahead of the growing ice [3].

Freezing a floc sample initially produces a freezing, or ice, 'front', with the free water forming ice. The floc particles are rejected by the moving solid–liquid interface and are pushed together when they are eventually surrounded by the advancing wave. As water freezes it expands and thus, the floc particles are compacted together and more water is extracted from within the structure. This water does not permeate back into the particles upon thawing and this results in granular, more highly dewatered flocs. The residue is also much more porous and can therefore be easily filtered [4].

Much of the research on freeze-thaw has been carried out on biological sludges, which make up a large volume of the waste currently being produced. However, simpler metal hydroxide precipitates systems have been analysed, including alum [5] and ferric [6] precipitates; alum has been studied more extensively due to its greater prevalence as a waste product.

Freezing can be achieved by either a natural or mechanical freezing process. Natural freezing can only be reliably utilised in very cold climates, with limited control. The only parameter which can be easily adjusted is sample volume, which in turn affects freezing rate. Most research has shown that it is advantageous to freeze precipitate in thin layers [5], as this ensures complete freezing. It also reduces the destructive effect of the expanding ice, which can crack bulk freezers. One disadvantage of this approach is that a large surface area is needed, which may not be available in urban sites where treatment works often operate.

Mechanical freezing can be tailored much more effectively to produce the optimum thawed sediment. Several key characteristics have been identified in order to determine what constitutes effective freezing, the most important being the extent of dewatering. This can be measured using methods such as: capillary suction time [3,7]: centrifugation [8]; vacuum filtration [8,9]: settled volume [6], and suspended solids [10]. The freeze-thaw process has also been examined with regard to parameters such as particle size, density and fractal dimension [8]. It is important that the freeze thaw process not only compacts the floc as much as possible, but also leaves a residual which can be easily separated from the melt-water. This is most easily achieved by producing large, dense particles with good mechanical strength, which can then be removed by sedimentation or filtration.

The effect of operating parameters, namely those related to how the floc is actually frozen, have been studied. Studies of freezing rate indicate that the speed at which a floc is frozen can have varying effects on the thawed product, with the effect being strongly dependent on the substrate frozen [5,8]. Thus, it may be considered that the primary constraint on the speed at which freezing can occur is related to the amount of structure within the floc. As the solid–liquid interface moves forward, floc particles will be either enveloped or rejected. The faster the freezing wave moves the greater the likelihood of particles being trapped; this may, in turn, reduce the effectiveness of freezing because particles are isolated, and not concentrated and compacted together [3]. This may be expected to only be important when floc particles are relatively large and immobile; characteristics observed in biological sludges. Therefore, only these should be frozen at a slower rate. Vesilind and Martel [4] differentiated between the variables of freezing rate and temperature by freezing samples at the same temperature and then curing them at different final temperatures, and also freezing samples at different temperatures until completely frozen. It was reported that although dewatering improved with a lower final temperature, the rate of freezing was much more important for producing the most dewatered residual. A slower freezing rate was also found to produce a much more dewatered residue in a mixture of mixed digested and aerobic sludges. Further examination indicated that although both sludge types dewatered better when cured at a lower temperature, mixed digested sludge performed better than aerobic sludge. Before freezing the mixed digested sludge was also shown to contain much larger floc particles than the aerobic sludge. This supports the theory that freezing rate is only critical when the sludge contains large amounts of structure. Parker et al. [3] found freezing rate a less crucial factor, with slower rates giving only slight improvements. A slower rate may be employed for another reason, as it has been shown that smaller thawed particles are produced from fast freezing [5]. Such particles prove to be more difficult to remove by filtration, and are formed when sludge is isolated in small pockets by a fast moving solid–liquid interface which is unable to push a large volume of floc ahead of it.

A more important detail is to ensure that the floc is completely frozen, and to this end freezing temperature is much more significant. Temperature is also closely linked with curing time once frozen so, either low temperature freezing (below $-15°C$) with a shorter curing time, or a higher temperature freezing with a longer curing time, must be employed. Both combinations give complete freezing, which in turn means the maximum compressive force is exerted on the floc particles. Indeed all the conclusions drawn from work on freezing stress the necessity for complete freezing, otherwise little improvement is observed in sludge conditioning. It has also been suggested that reducing the temperature further can result in the freezing of water bound to the surface, which is then released on freezing [11]. This can produce a floc more dewatered than is possible with any physical separation process. Differential scanning calorimetry produced a secondary isotherm at $-30^{\circ}C$ which has been suggested to result from the freezing of surface water. This, however, has been disputed by Vesilind and Hsu [12] who have shown that the surface water and water of hydration remain unfrozen at $-30^{\circ}C$.

Other operating variables which affect the properties of the precipitate prior to freezing have also been investigated. Vesilind and Chen [13] reported that agitation of the floc leads to an improvement in the process. This again is in agreement with the explanation that a smaller, less entangled floc is more likely to migrate under freezing and be concentrated and compacted with other particles. Parker et al. [3] found that increasing the solids concentration of alum precipitates prior to freezing greatly improved the dewaterability of the thawed residual. A pre-concentration step was also suggested as a means of further reducing any detrimental effects which may occur when working at higher rates of freezing. Therefore, in systems where fast freezing rates result in residuals with poor dewaterability, a pre-concentration step can help eliminate any such problems. Martel et al. [5] also observed an improvement in the dewaterability of flocs of higher solids concentration due to the larger particle size produced during freezing. Similar work by Halde [14] investigating the effects of polymeric surfactant addition, revealed enhanced particle migration and improved dewatering.

The objective of this work is to investigate the effect of freezing time, freezing temperature and pre-treatment steps, including pre-agitation and pre-concentration, on the dewaterability of freeze thawed ferric residuals.

2. Materials and methods

2.1. Floc synthesis and dewatering

A 100 ppm iron (III) nitrate solution was prepared and continuously stirred (at 250 rpm) in a baffled beaker. During agitation, the pH was monitored (Metrohm 691 pH meter) and 1 M sodium hydroxide solution added to attain a stable pH of 7.00 ± 0.05. Raising the pH causes iron to precipitate out of solution as an iron hydroxide floc. The solution was stirred at 250 rpm for 10 min, before the speed was reduced to 60 rpm for a further 30 min; pH adjustments were made throughout using microlitre amounts of either sodium hydroxide (1 M) or nitric acid (1 M). The sample was then transferred to a laboratory scale filtration unit for dewatering to the required concentration.

2.2. Effect of time and temperature on floc dewatering

A 25 ml sample of ~20000 ppm iron hydroxide floc was placed in a covered plastic dish (diameter 85 mm) and floated on top of a bath of ethylene glycol in a freezer (Tricity Bendix, model CF400W) at $-27 \pm 1^{\circ}C$. After freezing for a specified time period, the sample was removed and allowed to thaw at room temperature ($19 \pm 2^{\circ}C$) for 2 h. The solid floc residue was examined under a Perkin Elmer auto image microscope, and the final sediment volume determined. The effect of freezing time was assessed by freezing samples for various time periods (60, 90, 120, 180, 300 and 720 min). The effect of freezing temperature was also examined by freezing multiple samples at −13, −18 and $-27 \pm 1^{\circ}C$. Once again samples were removed at time intervals ranging from 60 to 720 min, thawed at room temperature, and the final volume fraction of solids measured.

2.3. Effect of initial solids content of the frozen sample on floc dewatering

A volume of concentrated ferric floc (30, 35, 40, 45 and 55 ml) was placed in centrifuge tube and spun (in a BTL bench centrifuge) at 3000 rpm until the floc layer settled to a volume of 25 ml. A further un-centrifuged sample (25 ml) acted as a control. The samples were then placed in a freezer for 12 h at $-18 \pm 1^{\circ}C$, before being thawed at room temperature. The final floc volume fraction was then measured. In order to ensure the effect of centrifugation did not mask any effect of concentration, two further samples were centrifuged from 50 to 30 ml. One of the samples was then heavily sheared in a Griffen automated flask shaker for 20 min until free flowing and then both samples were frozen for 12 h at $-18 \pm 1^{\circ}C$, before thawing at room temperature. The final floc volume fraction was calculated in each case.

2.4. Effect of shearing prior to freezing on floc dewatering

Concentrated floc samples (~20 000 ppm iron) were stirred at 250 rpm for 5, 10, 20, 40 or 90 min, prior to being frozen at $-25 \pm 1^{\circ}C$ for 12 h. The final volume fraction of the thawed sample was then determined.

2.5. Effect of the freeze-thaw process on contaminant binding

A 1000 ppm iron (III) nitrate solution was prepared containing 100 ppm of cadmium nitrate. The solution was flocculated, allowed to settle under gravity and then centrifuged at 2500 rpm for 15 min. Spinning the sample caused further settling, leaving a layer of clear supernatant water above a concentrated suspension or floc pellet. A sample of supernatant was removed and the cadmium content determined by ICP atomic emission spectroscopy. The floc pellet formed, was placed in a freezer at $-25 \pm 1°C$ for 12 h and then allowed to thaw for 2 h. A sample of supernatant was then removed and the cadmium content determined.

A solution of 1000 ppm iron (III) nitrate was flocculated and allowed to settle under gravity. The supernatant was removed and the floc centrifuged at 2500 rpm for 15 min. 1 g of iron powder was then added to the floc and the sample shaken for 5 minutes in an automated shaker. The suspension was frozen at $-25°C \pm 1°C$ for 12 h and then allowed to thaw at room temperature. The interaction of the sample with a magnetic field was then analysed.

2.6. Determination of final volume fraction

In order to determine the final residue volume, the layer of supernatant water (melt-water), which forms as the floc thaws and the particles settle, was decanted off. The solid was then placed in a graduated measuring cylinder and the dish rinsed with the previously decanted supernatant. These rinsings were also added to the cylinder, and the particles allowed to settle under gravity to a constant volume. The final volume of sediment (V_f) was expressed as a fraction of the initial volume of floc frozen (V_i), giving the final volume fraction, V_f/V_i.

Each of the aforementioned experiments were carried out in triplicate, with the results discussed in the following section representing average values.

3. Results and discussion

Visual observation of the sample during freezing show indicated the formation of ridges and veins, separated by layers of clear ice, during solidification. The presence of veins indicate that particle migration occurs. As the temperature drops, pure water around the floc freezes, forming an interface. This interface continues to grow by freezing more pure water and rejecting floc particles by pushing them in front of the boundary. In order to continue growing, the ice must extract water from around the floc but eventually floc builds up to such an extent, water cannot reach the interface. At this point a layer of floc is incorporated into the ice and trapped. The freezing of water then occurs again, and the process is repeated, forming another layer of clear ice followed by a ridge of floc.

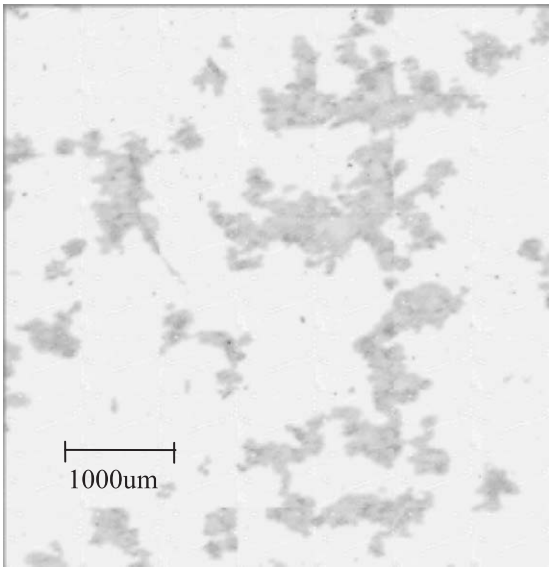

Fig. 1. Optical microscope image of floc particles.

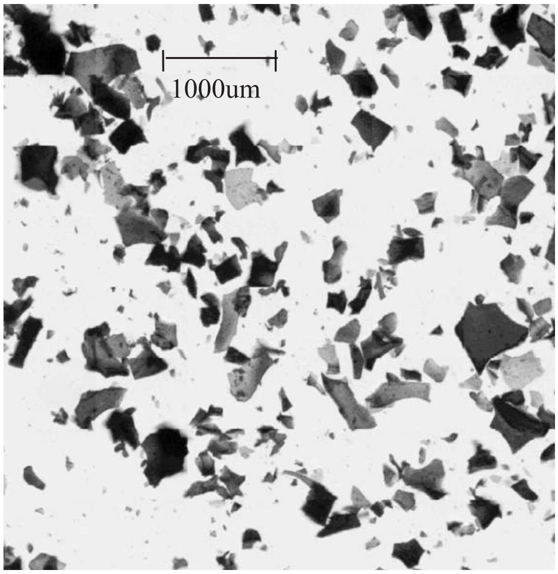

Fig. 2. Optical microscope image of frozen and thawed floc particles.

Observation of the floc particles under the microscope clearly show the effect of freezing. As shown in Fig. 1, before freezing the flocs consist of tangled, extended particles which are branched and adhere to each other. After treatment, however, the particles are much more defined, showing crystalline structure (Fig. 2). These crystals are also considerably more compact and concentrated than in the original floc. The crystalline structure produced by freezing occurs when the flocs are placed under pressure and in effect dehydrated. This extraction process occurs as water is drawn out of the particles by the advancing ice–water interface [4]. Intersitial water gives floc particles their mechanical strength and resistance to movement [12], and when this water is removed the structure collapses into itself under the pressure of the expanding ice.

Freezing alum precipitates produced residues which displayed similar crystalline structures [5] as did freezing of most other coagulated metal hydroxide suspensions. Thawed biological sludge residues, however, displayed less compaction and were much more fragile. Knocke and Trahern [10] also found the freezing of biological sludges to give only limited improvement insludge dewaterability. These results indicate that freezing is more effective in more uniform systems which exhibit less structure.

3.1. Effect of freezing time and temperature on floc dewatering

Fig. 3 shows that partially freezing a floc produces very little dewatering. Freezing for 60 min produces a final sediment 1.5 times more concentrated than that of the original precipitate prior to freezing. The concentration effect improves with time; when a sample is frozen for 120 min, it thaws to leave a final sediment over ten times more concentrated than the floc prior to freezing. However, freezing for more than 120 min, produces very little improvement in dewatering. This would indicate that at this stage the floc is completely frozen, and all particles have become trapped and compacted in the ice. This suggests that floc freezing the is a purely mechanical process, and once a certain level of compaction is achieved no further dewatering can be obtained.

Wilhelm and Silverblatt [2] suggested that leaving between 10% and 20% of the precipitate sample unfrozen has virtually no effect with most suspensions, and that observation is borne out in these results. Once complete freezing has occurred, curing the sample at a low temperature has no beneficial effect, and so the optimum time for freezing at $-27°C$ is 2 h, upon which time the sample can then be removed and thawed. Martel et al. [5] found there was no improvement in floc dewaterability produced by curing alum precipitate samples after they were completely frozen, while Parker et al. [3] found no beneficial effect of allowing alum precipitate samples to remain frozen for prolonged periods of time. This is, however, in contrast to the work by Vesilind and Martel [4] which showed a marked improvement in the dewaterability of activated sludge samples when subjected to several days curing. The distinction, however, which should be made between these two studies is the substrate which was frozen in each investigation; differing degrees of internal structure were present in each sludge sample. Improvements with curing time are only observed with activated sludges which contain large amounts of biological matter.

Freezing of other metal hydroxides, namely alum precipitate, provide the best comparison for the ferric hydroxide suspension under investigation in this study. The fact, however, that biological sludges behave differently gives quite a good insight into the mechanism of the actual process. It clearly demonstrates how migration of floc particles to form more concentrated aggregates is essential; this is observed in all freeze-thaw studies. This process has also been shown to occur more slowly in biological sludges, and therefore an increased curing time in these systems may realise beneficial effects.

Samples were frozen at $-13°C$, $-18°C$, $-27°C$ and the thawed floc volumes determined at specified times throughout the freezing process, as shown in Fig. 4. At $-13°C$, the floc required 5 h of freezing before sufficient dewatering had occurred to allow the settled volume (after freezing) to be measured accurately. Before this time, thawed samples still retained much of the character of unfrozen flocs, resulting in very little settling of particles. Similarly at $-18°C$, up to 2.5 h of freezing was required in order to have a significant effect, compared with only 2 h at $-27°C$. Freezing times of 5, 2.5 and 2 h

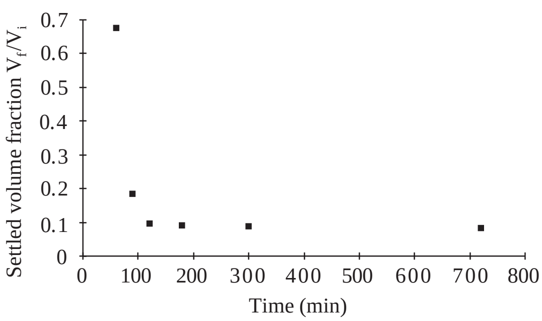

Fig. 3. Effect of freezing time on dewatering of freeze-thawed samples; ~20 000 ppm ferric floc frozen at $-27 \pm 1°C$.

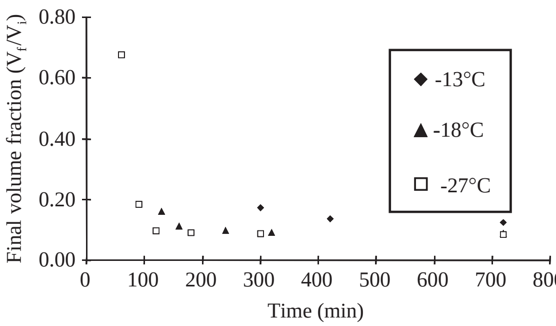

Fig. 4. Effect of freezing temperature on dewatering of freeze-thawed samples; ~20 000 ppm ferric floc.

represented those necessary to achieve a completely frozen sample at −13, −18 and −27°C, respectively. Curing time had little, or no, effect on the final concentration after complete freezing was observed. Freezing at −18°C, or below, did give a slightly more dewatered residual, approximately 1.35 times more concentrated than that frozen at −13°C. Again these results show that the most important factor is ensuring complete freezing and this state is obviously achieved more rapidly at lower temperatures.

These results also show that freezing rate is not a crucial factor for ferric floc precipitates. Freezing samples at a lower temperature has the effect of increasing the rate at which the sample freezes. Faster freezing at −27°C is comparable, in terms of final freezing volume fraction, with freezing at −18°C, and these results probably only show an improvement in comparison to freezing at −13°C because the lower temperature ensures more thorough freezing. It may also be true that a temperature lower than −18°C results in the freezing of water that is more closely bound to the surface.

The results are in agreement with freeze-thaw studies on similar metal hydroxide suspensions. Parker et al. [3] found that freezing rate had no effect on the dewaterability of alum precipitates, with a similar conclusion being reached by Martel et al [5]. The latter study did, however, note that a faster freezing rate produced smaller particles within the thawed residue which could pose a problem in any subsequent separation processes. In the present study, the settling rate of samples frozen at a lower temperature (faster rate) was comparable with that of samples frozen at a higher temperature (slower rate).

Studies examining the dewaterability of biological substrates did report a high dependency on freezing rate. Vesilind and Martel [4] found that freezing rate was an important parameter when dewatering biological sludges containing large amounts of internal structure. This again supports the suggestion that freezing rate is only important when the sludge contains particles with extended structure.

It may be slightly advantageous to freeze at as low a temperature as possible because this produces a slightly more dewatered floc and the processing time is also reduced. However, the actual cost of maintaining a lower temperature, for a shorter period of time, would have to be compared to the cost of adopting a higher temperature, for a longer time, in order to determine the most efficient method.

3.2. Effect of initial solids content of the frozen sample on floc dewatering

Increasing the initial solids concentration of the precipitate sample to be frozen was found to give a slight improvement in the amount of water that can be removed after freezing and thawing due to more particles being trapped together. More pressure is exerted in compacting particles together, leaving a more dewatered product. The experimental results depicted in Fig. 5 show that the final volume forms an increasingly smaller fraction of the original volume used prior to the centrifugation-freezing treatment. This suggests that in order to produce the least volume of waste possible, the sludge should be pre-concentrated before freezing. These findings are in agreement with the work of Parker et al. [3] and Martel et al. [5] who both concluded that more concentrated sludges produced more concentrated residuals after the freeze-thaw process.

The actual improvement, however, may not justify the pre-concentration step. For a precipitate containing approximately 20 000 ppm iron, freezing and thawing produced a floc about 12 times more concentrated than the original precipitate. A similar precipitate sample, concentrated by centrifugation to an iron content of approximately 50 000 ppm, when frozen and thawed had a final volume of waste only 14 times more concentrated. Although the savings would be made by producing less residuals, these may not justify the pre-concentration step. A further factor which must be taken into consideration is the reduced volume to be frozen. The greatest single obstacle to the widespread utilisation of the freeze-thaw process is the current cost of freezing. Therefore, a balance must be reached between the cost of pre-concentration and the savings on freezing costs and ultimate disposal of the waste.

3.3. Effect of shearing prior to freezing on floc dewatering

As shown in Fig. 6, increasing the amount of shear applied to a floc, i.e. increasing agitation time, appeared to have no effect on the final volume of the freeze-thawed residual.

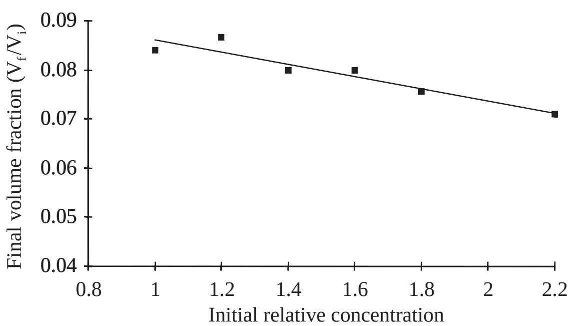

Fig. 5. Effect of initial solids concentration on dewatering of freeze-thawed samples; initial sample ∼20 000 ppm ferric floc was centrifuged to produce up to ∼50 000 ppm flocs prior to freezing.

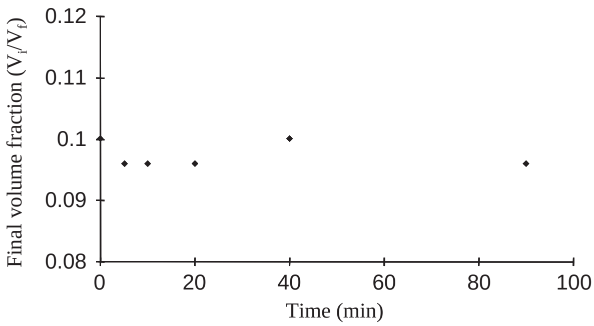

Fig. 6. Effect of pre-agitation time on dewatering of freeze-thawed samples; ~20 000 ppm ferric floc sample.

An increase in dewatering with agitation was reported when treating sewage sludge, which has considerably more internal structure than ferric hydroxide waste [13]. Agitation breaks down much of this structure, making the sludge particles more mobile. This mobility allows the floc particles to migrate ahead of the ice–water interface where they are concentrated. Eventually a large number of particles are trapped together in the ice, where further compaction and concentration occurs. This behaviour is not observed with ferric floc precipitates due to the fact that the precipitate particles are already sufficiently mobile to make further shearing unnecessary.

This is further confirmed by the fact that centrifuging the floc prior to freezing (during the pre-concentration step) did not have a detrimental effect on dewatering. If floc mobility was a critical factor in the system, the effect of increased compression of the precipitate prior to freezing would reduce dewatering. This, however, is not observed and in fact, the reverse was observed. For further verification, the final volume fractions of a heavily sheared, and an unsheared, pre-concentrated freeze thawed sample were compared. Centrifuging the sample prior to freezing produced a semi-solid gel which did not flow and in which particles were relatively immobile. However, this had no impact on floc dewatering as comparable quantities of water were removed from the two samples by the freeze-thaw process.

3.4. Effect of the freeze-thaw process on contaminant binding

As previously mentioned, it is important that the freeze-thaw process, which results in improved dewatering, does not lead to significant increases in leach out of contaminants from the floc. Cadmium metal is poorly retained by ferric flocs and therefore was selected as a contaminant for this study.

The supernatant of a 1000 ppm ferric floc containing 100 ppm cadmium was analysed using ICP atomic absorption spectroscopy and found to contain 5 ppm cadmium. However, after allowing the freeze thaw residual to settle out, the free water (melt-water) produced was found to contain 15 ppm cadmium. This indicates that the freeze thaw process causes a slight increase in the leach out of contaminants from the floc. However, the increase in metal loss is small compared to that remaining bound within the significantly dewatered floc. Mechanical shear was also found to produce a slight increase in the amount of cadmium leached into the supernatant. Again this supports the explanation that the freezing process is an entirely mechanical process, which does not affect the floc at a molecular level. Instead, the changes within the floc occur at a macro-molecular level resulting in extensive compression of floc particles to produce a compact residue.

The ability of the freezing process to remove entities which are not specifically bound to the precipitate was also assessed. This was carried out to determine if contaminants simply mixed with the concentrated precipitate would be rejected by the freezing wave and compacted together with the floc as it was frozen. Iron powder, mixed with the concentrated precipitate, was used as the example contaminant.

Upon thawing the iron was found to be trapped within the floc particles, and this had the effect of producing a dewatered floc which interacted with a magnetic field. As a result, the thawed floc could rapidly be removed from solution by introducing a magnet to the suspension, or the settling rate of the thawed floc could be increased by placing the suspension in a magnetic field.

This phenomenon indicates two useful properties of the freezing process. Firstly, the freeze-thaw process compacts all solid matter in a wastewater sludge into a single concentrated end product, irrespective of whether the contaminants were aggregated in the unfrozen sludge. Secondly, additives such as finely divided iron powder can be introduced to the unfrozen sludge to aid removal of the thawed residual by magnetic means.

4. Conclusions

On the basis of this work the following conclusions can be drawn.

- Freezing time and temperature were found to have a limited effect on the extent of ferric floc dewatering.
- Complete freezing was required in order to obtain the most effective dewatering.
- Rate at which freezing wave moved through the sample, resulting in rejection or entrapment of particles, was not important for the temperature and concentration ranges investigated.
- Pre-concentration before freezing resulted in a more concentrated sample after thawing due to the fact that more particles were trapped together.
- Pre-agitation, i.e. shear, had no beneficial, or detrimental effect on the floc dewatering; this indicated that dewatering of ferric precipitates does not require highly mobile particles.
- Freezing the floc resulted in a slight increase in the leach out of cadmium into the melt-water.

References

[1] Allen HE, Garrison AW, Luther W. Metals in surface waters. Ann Arbor, MI: Ann Arbor Press, Chelsea, MI, USA; 1997.
[2] Wilhelm JH, Silverblatt CE. Freeze treatment of alum sludges. J Am Waste Water Assoc 1976;68:312–4.
[3] Parker PJ, Collins AG, Dempsey JP. Effects of freezing rate, solids content, and curing time on freeze/thaw conditioning of water treatment residuals. Environ Sci Technol 1998;32:383–7.
[4] Vesilind P, Martel CJ. Freezing of water and wastewater sludges. Journal of Environmental Engineering 1990; 116(5):854–62.
[5] Martel CJ, Affleck R, Yushak M. Operational parameters for mechanical freezing of alum sludge. Water Res 1998;32(9):2646–54.
[6] Zolotavin VL, Vol'khin VV, Rezushkin VV. Effect of freezing on the properties of coagulated metal hydroxides. Colloid J USSR 1960;22(3):305–13.
[7] Gale RS, Baskerville RC. Capillary suction method for determination of the filtration properties of a solid/liquid suspension. Chem Ind 1967;8:355–6.
[8] Lee DJ, Hsu YH. Fast freeze/Thaw treatment on excess activated sludges: floc structure and sludge dewaterability. Environ Sci Technol 1994;28:1444–9.
[9] Parker PJ, Collins AG. Ultra-rapid freezing of water treatment residuals. Water Res 1999;33(10):2239–46.
[10] Knocke WR, Trahern P. Freeze/Thaw conditioning of chemical and biological sludges. Water Res 1989;23(1):35–42.
[11] Anderson DM, Tice AR. The unfrozen interfacial phase in frozen soil water systems. In: Hadas A, editor. Ecological studies, analysis and synthesis, Vol. 4. Berlin: Springer, 1973.
[12] Vesilind PA, Hsu CC. Limits of sludge dewaterability. Water Sci Technol 1997;36(11):87–91.
[13] Vesilind PA, Chen JL. Effect of preagitation on freeze/thaw conditioned sludge dewaterability. J Cold Regions Eng 1994;8(4):113–20.
[14] Halde R. Concentration of impurities by progressive freezing. Water Res 1980;14:575–80.