Freeze-Thaw Conditioning of Activated Sludge: Effect of Monovalent, Divalent, and Trivalent Cations

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ABSTRACT: This study investigates the effect of monovalent (Na\(^+\) and K\(^+\)), divalent (Ca\(^{2+}\) and Mg\(^{2+}\)), and trivalent (Al\(^{3+}\) and Fe\(^{3+}\)) cations on freeze-thaw conditioning of activated sludge. Effects of cations on sludge characteristics and bioflocculation have been studied heavily, but few studies have investigated the effect of cations on freeze-thaw conditioning of sludges. This study evaluated the changes in the dewaterability, settleability, turbidity, and solids content of freeze-thawed activated sludge aggregates after the addition of NaCl, KCl, CaCl\(_2\), MgCl\(_2\), FeCl\(_3\), and AlCl\(_3\). The results showed that addition of cations does not improve the freeze-thaw conditioning of activated sludge. The improvement in the dewaterability and settleability of activated sludge after freeze-thaw conditioning decreases with increasing concentrations of cations, and the type of cation seems to be a factor in determining the overall effectiveness of freeze-thaw conditioning.

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INTRODUCTION

Physical, chemical, and biological properties of activated sludge are influenced by changes in ionic strength and ionic composition of sludge. Many studies have investigated the effects of various cations on sludge characteristics [e.g. 1–6] and concluded that cations, particularly divalent cations, play a crucial role in the formation of flocs, influence floc properties such as size, density, and strength, and directly affect sludge settleability and dewaterability.

On the other hand, few studies have investigated the effect of cations on freeze-thaw conditioning of sludges [7–11]. Vesilind et al. [8] hypothesized that increased compression of double layer in the presence of sodium chloride may promote particle aggregation during freeze-thaw conditioning which would lead to better dewaterability. They found no significant improvement in sludge dewaterability, and concluded double layer compression is not an influential mechanism in freeze-thaw treatment. Chu et al [9] also studied the effect of sodium chloride on freeze-thaw conditioning and they concluded presence of sodium chloride retarded the gross migration of sludge particles, and thus reduced the effectiveness of freeze-thaw conditioning.

Volkhin and Zolotavin [7] suggested that complete freezing of ferric hydroxide coagulants can only be achieved at freezing temperatures lower than the eutectic temperature of the water/electrolyte system, and higher freezing temperatures would cause incomplete freezing of coagulants which would reduce the freeze-thaw effectiveness. Jean et al. [11] investigated the formation of eutectics in clay slurry and activated sludge and reported that eutectic peak disappears in activated sludge possibly due to the presence of particles. They also reported significant improvement in sludge dewaterability after freeze-thaw conditioning even if the freezing temperature was higher than the eutectic temperature.

Addition of cations directly affects activated sludge properties and the freezing conditions. Depending on the type of the cation added, floc size, shape, and density thus sludge dewaterability and settleability changes. In addition, cations lower the freezing temperature which would change the freezing conditions altogether. Some of these changes may improve, and others may hinder the effectiveness of freeze-thaw conditioning. For example, monovalent cations (such as Na\(^+\) and K\(^+\)) may replace divalent cations (Ca\(^{2+}\) and Mg\(^{2+}\)) which are known to aid in flocculation by forming cation bridges in the floc structure [3, 4, 12]. Replacement of cations is likely to decrease the average floc size and improve freeze-thaw conditioning. On the other hand,
monovalent cations may also compress the double layer around the particles, promote flocculation, and hinder freeze-thaw conditioning by increasing the average floc size and lowering the freezing point of sludge. Which one of these mechanisms prevails will depend on the type and concentration of the cation added to sludge. Previous research mainly focused on the effect of NaCl on freezing of alum and activated sludges, and the effect of other cations has not been studied. In addition to sodium, activated sludge contains relatively large amounts of potassium, calcium, magnesium, iron, and aluminum, either present as part of the wastewater or added in the form of salts during treatment. Therefore, it is important to study how presence of these ions affects the dewaterability and settleability of activated sludge after freeze-thaw conditioning.

MATERIALS AND METHODS

The return activated sludge used in this research was collected from North Durham Wastewater Treatment Facility, Durham, NC. The sludge was taken to the laboratory within 30 minutes, and was kept aerated throughout the experiments. All experiments in a particular group were finished on the same day to avoid differences in results that may be caused by the changing characteristics of sludge.

Freeze-Thaw Conditioning

Untreated activated sludge samples of 100 mL were frozen in a digital freezer (ScienTemp Corp., MI) at −8°C. Samples with higher cation concentrations were frozen at −12°C. Transparent glass bottles, which enabled visual examination of aggregates after freeze-thaw conditioning, were used to freeze the sludge samples. All samples were kept frozen for 36 hours in the freezer, and thawed for 10 hours at room temperature.

Measurement of Sludge Characteristics

Previously it has been shown that capillary suction time (CST) test is not reliable to measure the dewaterability of freeze-thawed sludges due to their high free-water content [13]. The escape of water from the sludge is too fast in freeze-thawed sludges, and the CST test simply measures the movement of water from the filter paper instead of the release of water from the sludge. Specific resistance to filtration (SRF) test [14] with the omission of vacuum was used to measure the dewaterability of freeze-thawed conditioned sludges in this study. The entire freeze-thawed sample in the bottle (100 mL) was used for each of the SRF test due to the difficulties in taking representative sub-samples from freeze-thawed sludge which are likely to differ in their solids and water content. Dewaterability of the samples was reported in terms of specific resistance to filtration constant (b). The filtration constant was obtained from the specific resistance to filtration test, and it is the slope of line of plot of \( t/V \) against \( V \) where \( V \) is the volume of filtrate collected at time \( t \).

Settling tests were conducted in 100 mL graduated cylinders, and the sediment height was recorded after 4 minutes of settling. Although the use of small cylinders for settling tests has been shown to affect the results [15, 16], the results in this study were used for comparative purposes only and the use of the small cylinders is justified. A Hach 2100 turbidimeter was used to measure the turbidity of the sludge supernatant following 4 minutes of settling.

Solids content of freeze-thawed aggregates were measured according to the Standard Methods [14] after 3 minutes of vacuum filtration.

Visual Observation of Aggregates

Sludge samples were frozen in clear glass bottles that enabled the visual examination of aggregates after thawing. In addition, aggregates were examined under Meiji ML 2000 series (Meiji Techno Co Ltd.) microscope. Photomicrographs were taken when needed.

Addition of Cations

The amount of cations added to samples was based on the concentrations of these ions generally found in activated sludge. For the particular activated sludge used in this study, the following initial concentrations, prior to addition of cations, were measured: \( \text{Na}^+ = 40 \text{ mg/L}, \text{K}^+ = 20 \text{ mg/L}, \text{Ca}^{2+} = 16 \text{ mg/L}, \text{Mg}^{2+} = 4 \text{ mg/L}, \text{Fe}^{3+} = 0.3 \text{ mg/L}, \) and \( \text{Al}^{3+} = 0.2 \text{ mg/L} \). \( \text{Na}^+ \) and \( \text{K}^+ \) were added to sludge samples from 3.4 M \( \text{NaCl} \) and 2.68 M \( \text{KCl} \) solutions. \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \) were added from 1 M of \( \text{CaCl}_2 \) and \( \text{MgCl}_2\cdot6\text{H}_2\text{O} \) solutions, and \( \text{Fe}^{3+} \) and \( \text{Al}^{3+} \) were added from 1 M of \( \text{FeCl}_3\cdot4\text{H}_2\text{O} \) and \( \text{AlCl}_3\cdot6\text{H}_2\text{O} \) solutions. After the addition of cations, sludge samples were stirred slowly on a horizontal stirrer for 15 minutes at room temperature, and the samples were
freeze-thawed. The pH of the samples was monitored before and after the addition of cations, and no significant change was observed.

**Measurement of Cations**

Spectra Span 7 DCP Spectrometer (Applied Research Laboratories) was used to determine the cation concentrations in sludge samples.

**Data Reporting**

The data points reported in the results section are the mean of three replicates, and the error bars show one standard deviation from the mean.

**RESULTS AND DISCUSSION**

**Effect of monovalent cations**

Na\(^+\) and K\(^+\) concentration of the samples were increased in 35 mM increments between concentrations of 0 and 175 mM. Figure 1a illustrates a linear increase between the filtration constant (b) and the amount of Na\(^+\) and K\(^+\) added to activated sludge before freeze-thaw conditioning. An increase in the filtration constant indicates deterioration in the dewaterability of sludge. Filtration constant was lowest for untreated sludge in both cases, and after the addition of either of Na\(^+\) or K\(^+\) the filtration constant exhibited a steady increase. The filtration constant increased by 1130% and 550% after the addition of 175 mM Na\(^+\) and K\(^+\) respectively. The increase caused by Na\(^+\) was approximately twice as much as the increase caused by K\(^+\) at all concentrations.

Figure 1b shows the effect of Na\(^+\) and K\(^+\) concentration on the sediment height (H) in a 100 mL graduated cylinder after freeze-thaw conditioning. The sediment height rapidly increased by 77% after the addition of 35 mM Na\(^+\), and 47% after the addition of 35 mM K\(^+\). The increase in the sediment height continued at a slower rate between 35 mM and 105 mM Na\(^+\) and K\(^+\) concentrations. Thereafter, sediment height started to decrease with increasing concentrations of Na\(^+\) and K\(^+\) which can be explained by the increased number of particles in the supernatant due to the increased turbidity (Figure 1c). The overall increase in sediment height and turbidity after freeze-thaw conditioning indicated deterioration in sludge settleability and supernatant quality with increasing concentrations of Na\(^+\) and K\(^+\) in sludge.

Solids percent of the cake from the samples decreased linearly with increasing concentrations of Na\(^+\) and K\(^+\) (Figure 1d). Addition of Na\(^+\) and K\(^+\) produced larger aggregates that held more water compared to the aggregates of the untreated sample. Photomicrographs of an untreated and NaCl treated activated sludge sam-
ple after freeze-thaw conditioning are illustrated in Figure 2. NaCl treated aggregates were larger, and they formed thin layers after freeze-thaw conditioning. Similar formation of layers, also called “rhythmic banding”, were reported previously [17–19] and can be explained by the entrapment of layers of solids by the advancing ice front due to insufficient water transfer to the interface. This can be caused by the high solids content of the sample or the changes in the freezing rate due to the addition of cations. Similar formation of layers was also observed with divalent and trivalent cations in this study.

Effect of Divalent Cations

Ca$^{2+}$ and Mg$^{2+}$ concentration of the samples were increased in 10 mM increments between concentrations of 0 and 50 mM. The effect of the divalent cations on freeze-thaw conditioning of activated sludge was similar to that of monovalent cations. Filtration constant increased with increasing concentrations of Ca$^{2+}$ and Mg$^{2+}$ (Figure 3a). At 50 mM Ca$^{2+}$ and Mg$^{2+}$, the increase in the filtration constant was 121% and 198% respectively. The height of the sludge sediment increased by 117% and 68% after 30 mM Ca$^{2+}$ and Mg$^{2+}$ were added to samples, and beyond that started to decrease slowly (Figure 3b). Mg$^{2+}$ increased the supernatant tur-


Figure 4. The change in the (a) filtration constant, (b) sediment height, (c) turbidity of the supernatant, (d) solids percent of the cake with increasing concentrations of Fe$^{3+}$ and Al$^{3+}$.

bidity more than Ca$^{2+}$ did (Figure 3c). Addition of 50 mM Mg$^{2+}$ increased the turbidity by 55% whereas 50 mM Ca$^{2+}$ increased the turbidity by 129%. Effect of Ca$^{2+}$ and Mg$^{2+}$ on the solids percent of the sludge cake was also different. 50 mM Mg$^{2+}$ caused a decrease of 52% in solids, and 50 mM Ca$^{2+}$ caused a decrease of only 11% (Figure 3d). Overall, addition of divalent cations made the dewaterability and settleability of activated sludge worse after freeze-thaw conditioning, and Mg$^{2+}$ seemed to have a greater impact than Ca$^{2+}$ at corresponding concentrations.

**Effect of Trivalent Cations**

Fe$^{3+}$ and Al$^{3+}$ concentration of the samples were varied between 0 and 25 mM in 5 mM increments. Interestingly at 5 mM Fe$^{3+}$ and Al$^{3+}$, the filtration constant dropped by 53% and 32% respectively indicating an improvement in sludge dewaterability (Figure 4a). However, at higher concentrations of Fe$^{3+}$ and Al$^{3+}$, filtration constant increased steadily indicating an overall deterioration in sludge dewaterability. The height of the sediment increased with increasing Fe$^{3+}$ and Al$^{3+}$ concentration as well (Figure 4b). Although the turbidity of the sludge supernatant stayed same until 10 mM Fe$^{3+}$ and Al$^{3+}$, a significant increase in the turbidity was observed at higher concentrations (Figure 4c). Solids percent in the sludge cake did not show a conclusive change after addition of Fe$^{3+}$ and Al$^{3+}$ (Figure 4d).

The data presented above indicate that increasing the cation concentration, regardless of the charge density, of activated sludge before freeze-thaw conditioning reduces the dewaterability and settleability of sludge after the freeze-thaw. Filtration constant, height of the sediment, and turbidity of the supernatant increase, and the final sludge cake retains more water.

Two of the most important factors that directly impact the effectiveness of freeze-thaw conditioning are the freezing speed and the particle size of the sample. When freezing speed is low, particles are rejected by the growing ice front and concentrated at the non-frozen part of the sample. This is called grossmigration [17]. At high freezing speeds however, most particles are trapped in the growing ice resulting in poor conditioning. This is called micromigration. Corte [20] reported that in addition to freezing speed, particle size is also important in determining the effectiveness of freeze-thaw conditioning. He showed that smaller particles are more easily pushed by the advancing ice front compared to larger particles. In addition, it is also easier to replenish the water layer (also called transition layer) between smaller particles and the growing ice layer [8] which is important to sustain grossmigration during freezing.

The interactions of cations with organic and inorganic particles, biopolymers, and sludge bacteria are
very complex. In addition, these interactions greatly influence the freezing of sludge by changing the particle size, freezing speed, and freezing temperature. Some of the possible changes that may take place in the sludge matrix after the addition of cations and during the freezing of sludge are presented below:

1. When cations are added to sludge, cellular water may flow out of the cells and the cells may shrink due to osmotic pressure difference in and out of the cell. At a larger scale, water may move out of the floc structure, leaving a smaller and denser floc behind. Since small particles are more easily pushed by the ice front compared to larger ones, the shrinkage of particles is likely to improve freeze-thaw conditioning of activated sludge.

2. If cation concentration is too high and cells cannot resist the osmotic pressure anymore, cells will rupture and release their cellular content to sludge water. This increases the total area of surfaces, which in turn would increase the vicinal water content. Vicinal water, also known as unfreezeable water, is very difficult to freeze as hydrogen bonds between water molecules are very strong near surfaces. The increase in the vicinal water content of sludge is likely to hinder freeze-thaw conditioning.

3. Another consequence of cell disruption is the release of high molecular weight polymeric substances, such as carbohydrates, proteins, and nucleic acids, to sludge water. These natural polymers are likely to aid flocculation and increase the average particle size. In addition, intracellular material is subject to hydration which increases the vicinal water content further [21]. Both of these factors are likely to decrease freeze-thaw effectiveness. Örmeç and Vesilind [22] reported that freeze-thaw conditioning causes cell disruption and releases intracellular material to the sludge supernatant. Extraction of intracellular and extracellular polymers from the sludge matrix increases the effectiveness of freeze-thaw conditioning on activated sludge [23].

4. Also, addition of cations alone increase the vicinal water content of sludge. When cations are added to activated sludge, they are surrounded by layers of water molecules due to ion-dipole electrostatic pair interaction. The number of water molecules attracted to a cation is dependent upon the charge density of the ion. Monovalent cations are more hydrated than divalent and trivalent cations. The hydrated ions have bigger radii compared to their unhydrated form. For example, the radius of Na+ ion is 0.095 nm whereas its hydrated radius is about 0.36 nm [24]. Degree of hydration of ions decrease in the following order: Na+, K+, Mg+2, Ca+2, Al+3, and Fe+3.

5. Activated sludge consists of mostly negatively charged particles that stay apart due to electrostatic repulsion. These negatively charged particles are surrounded by a tightly bound layer of positively charged particles which is surrounded by another layer of ions that is more diffuse and not as tightly bound. This is called the double layer. Addition of cations decreases the thickness of the double layer surrounding particles and helps particles to overcome repulsive forces. Therefore, an increased ionic strength promotes flocculation. However, increasing the ionic strength too much may cause deflocculation again [3, 25]. In addition to the concentration of ions, their valence number also determines the thickness of the double layer. For example, it takes twice as many monovalent cations than divalent cations to balance a negative surface charge. Therefore, an increase in the thickness of a double layer saturated with monovalent cations (such as Na+ and K+) may also prevent flocculation. As a result, the concentration and valence number of cations added to activated sludge determine whether flocculation or deflocculation would occur. Deflocculation would improve freeze-thaw conditioning whereas flocculation would hinder it.

6. Activated sludge freezes at a lower temperature than its pure solvent, water. This is because various dissolved organic and inorganic materials found in activated sludge lower the freezing temperature due to freezing point depression. The more electrolytes are dissolved in sludge the lower will be the freezing point. On top, freezing process itself lowers the freezing temperature by pushing the ions to the unfrozen part of sludge. This is of particular importance at the ice/water interface. Accumulation of ions lowers the freezing temperature at the interface, and water surrounding the interface freezes first promoting particle entrapment. In addition to the number of moles of an electrolyte, how many ions it dissociates to also affects the freezing temperature. For example, NaCl dissociates to two ions, whereas CaCl2 dissociates three ions. As a result, the change in the freezing temperature caused by CaCl2 is 1.5 times greater than the change caused by NaCl.

7. Divalent cations are known to aid in flocculation by forming cation bridges between extracellular poly-
mers and sludge flocs [3, 4, 12]. Therefore, addition of divalent cations, such as Ca\(^{2+}\) and Mg\(^{2+}\), can increase the average floc size and promote particle entrapment during freezing. Trivalent cations, such as Fe\(^{3+}\) and Al\(^{3+}\), have very good flocculating properties, and they might as well increase the average floc size. In fact, ferric ions reacting with extracellular polymers are likely to form stronger bonds than Ca\(^{2+}\) due to their higher valence, higher polarisability, and relatively smaller degree of hydration [26]. Addition of Na\(^+\) and K\(^+\), however, may decrease the average floc size by replacing Ca\(^{2+}\) and Mg\(^{2+}\) within the floc structure and causing deflocculation. Deflocculation prior to freeze-thaw conditioning is likely to increase the effectiveness of freeze-thaw conditioning.

The mechanisms explained above may occur simultaneously during the freeze-thaw conditioning of activated sludge in presence of monovalent, divalent, or trivalent cations. Some of these mechanisms increase and some decrease the freeze-thaw effectiveness on activated sludge. The results of this study show that addition of all cations, even at small concentrations, adversely affect the freeze-thaw conditioning and produce a sludge which is harder to dewater. Therefore, it is concluded that mechanisms that adversely affect freeze-thaw conditioning prevail those that might have a positive influence. Particle entrapment during freezing due to the addition of cations is likely to be the main mechanism that decreases the effectiveness of the freeze-thaw conditioning.

The study by Jean et al. [11] on the effects of electrolytes and curing on freeze-thaw treatment of sludge is of particular importance due to its relevance to this research. Jean et al. [11] studied the effects of four electrolytes (sodium sulfate Na\(_2\)SO\(_4\), potassium nitrate KNO\(_3\), sodium nitrate NaNO\(_3\), and sodium chloride NaCl) on freeze-thaw conditioning of activated sludge, and concluded that the improvement in sludge filterability and settleability are independent of the electrolyte species as well as the addition amount which is not in agreement with the findings of this research. The results of this research show that the improvement in filterability and settleability decreases with increasing concentrations of electrolytes, and the type of electrolyte plays a role in determining the overall effectiveness of freeze-thaw conditioning. Significant differences were observed not only between NaCl, CaCl\(_2\), and AlCl\(_3\), but also between NaCl and KCl, CaCl\(_2\) and MgCl\(_2\), and AlCl\(_3\) and FeCl\(_3\). In addition to the number of moles of an electrolyte, how many ions it dissociates to, degree of hydration of the ions, and how they interact with biopolymers are likely to influence the freezing of sludges. The disagreement in the findings of these two studies may be due to the use of CST test in the Jean et al. [11] study to measure the dewaterability of freeze-thawed sludges. Sludge releases much of its interstitial water to become free water during the freeze-thaw process. When a freeze-thawed sample is placed in the CST reservoir, the free water will immediately begin to be sucked into the filter paper, and the CST test will simply measure the movement of water from the filter paper instead of the release of water from the sludge. Therefore, CST test will not work well to pick up the differences between the freeze-thawed samples. Vesilind and Örmeci [13] reported no significant difference between the CST’s of 1% and 6% solid sludge after freeze-thaw conditioning even though the dewaterability of these sludges were significantly different.

**CONCLUSIONS**

1. Addition of monovalent, divalent, or trivalent cations does not improve freeze-thaw conditioning of activated sludge. Activated sludge, without addition of any ions, exhibited the best dewaterability and settleability in this study.
2. The improvement in the dewaterability and settleability of activated sludge after freeze-thaw conditioning decreases with increasing concentrations of cations.
3. In addition to the concentration, the type of cations used is a factor in determining the effectiveness of freeze-thaw conditioning on activated sludge. Significant differences were observed between the effects of monovalent, divalent, and trivalent cations as well as differences between Na\(^+\) and K\(^+\), Ca\(^{2+}\) and Mg\(^{2+}\), and Al\(^{3+}\) and Fe\(^{3+}\).
4. If freeze-thaw conditioning is chosen as the method of dewatering, excessive use of coagulants such as alum or ferric chloride and other chemicals during treatment should be avoided.

**REFERENCES**


