

# Nucleation Seeding to Promote Chemical Precipitation of Hardness and Alkalinity from Mine Pit Lakes

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## ABSTRACT

Several flooded taconite mine pits in northern Minnesota contain circum-neutral water with elevated concentrations of sulfate, hardness (dominated by Mg) and alkalinity, which together contribute to overall total dissolved solids and specific conductivity, and are of increasing local regulatory concern. Two of these mine pit lakes (pit lake "A" and pit lake "B") are meromictic, stratified both thermally and chemically. The deepest and densest water in the pits rarely, if ever, mixes with the overlying, more dilute water. Geochemical modeling suggests that both lakes are increasingly supersaturated with respect to calcite and aragonite with depth; it has been well documented that high concentrations of magnesium can act to kinetically inhibit precipitation of calcium carbonate. Reducing alkalinity and hardness via a passive strategy may be achieved by reducing the barrier to precipitation: nucleation. Nucleation seed crystal precipitation from concentrated bottom waters was initiated via four different processes, including evaporation, heating, lime addition, and salt addition. Precipitated seed crystals were then introduced to more dilute top water while alkalinity and hardness were monitored. Spontaneous precipitation of hardness and alkalinity was successfully achieved by heating deep pit water and exsolution of CO<sub>2</sub>. This process is hypothesized to be responsible for the "white bathtub ring" that edges the pit lakes.

**Keywords:** hardness, carbonate, alkalinity, nucleation

## INTRODUCTION

In some former taconite (iron ore) mine pits on the Mesabi Iron Range in northern Minnesota, oxidation products from trace sulfides are neutralized by relatively abundant carbonates, including siderite and ankerite. The resulting pit lake water quality has circum-neutral pH, but can contain elevated concentrations of sulfate, hardness and alkalinity. Together, these elevated salt concentrations increase total dissolved solids (TDS) and specific conductance, and are of increasing local regulatory concern. Sulfate, specifically, is strongly regulated in the state of Minnesota, where the water quality standard in water used for wild rice production is as low as 10 milligrams per liter (mg/L). The potential may exist to passively reduce salt concentrations by pairing strategies that promote sulfate-reducing bacteria (SRB) to reduce sulfate with strategies that reduce alkalinity and hardness. Non-mechanical strategies that result in reductions in alkalinity and hardness by encouraging chemical precipitation are explored herein.

## BACKGROUND

Hardness and alkalinity in wastewater is typically removed via active processes such as ion exchange, membrane separation or chemical precipitation. Chemical precipitation occurs when the solubility product of calcite increases such that supersaturation occurs (Nancollas and Reddy, 1971). It may be possible to induce chemical precipitation of calcium carbonate in a relatively passive way in mine pit lakes by modulating solution parameters that directly influence saturation state.

The solubility expression and corresponding solubility product for calcite can be represented as:



The driving force, or associated change in Gibbs free energy, of the calcite precipitation reaction is determined by the solubility constant of calcite ( $K_{\text{SP}}$ ) and the ion activity product  $Q$ :

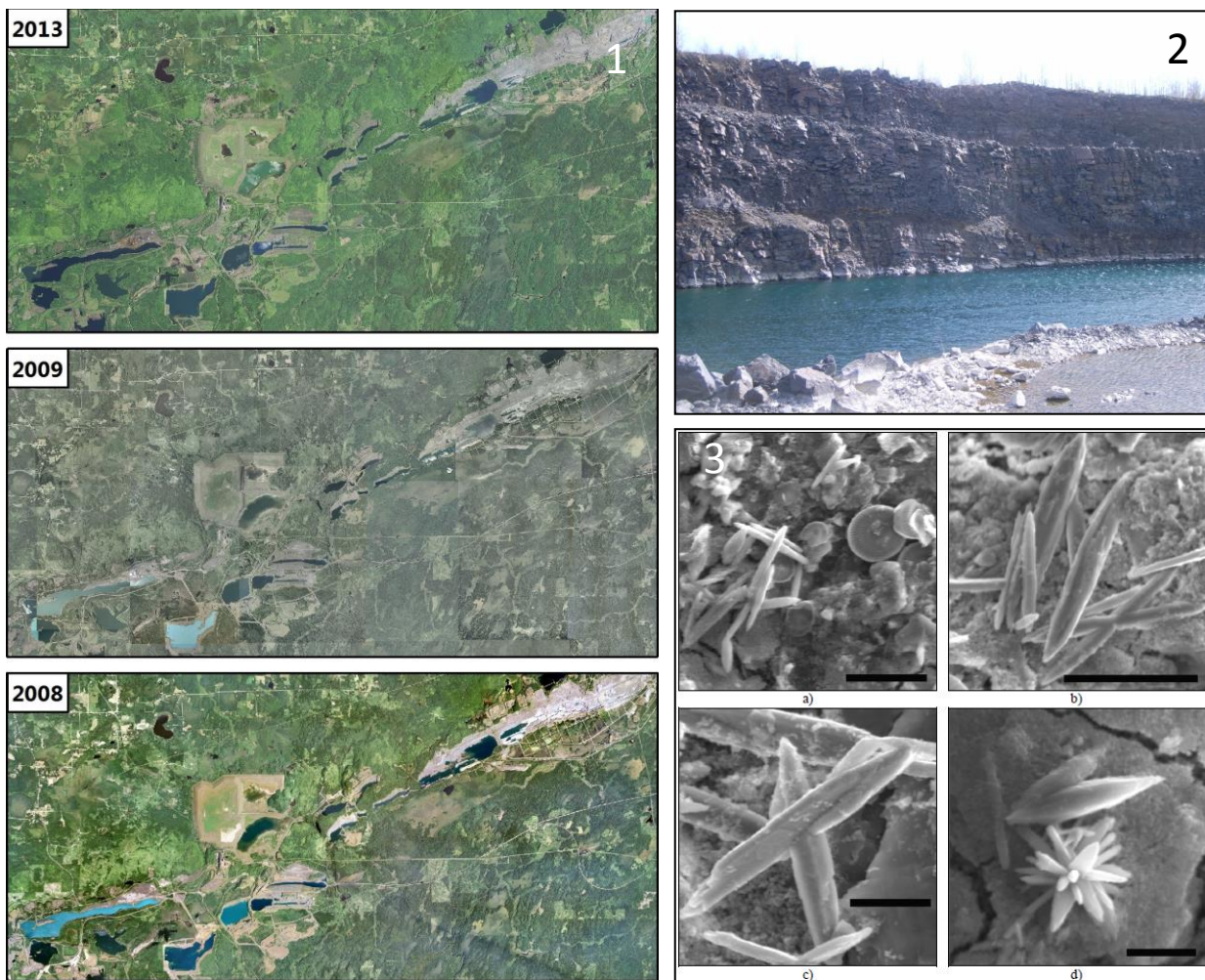
$$\Delta G = \Delta G^0 + RT \log (Q/ K_{\text{SP}}),$$

where  $R$  is the gas constant (8.314 J/mol K), and  $T$  is the temperature in Kelvin. The ion activity product,  $Q$ , is the product of the real concentrations of Ca and  $\text{CO}_3^{2-}$  in solution. When  $Q$  is greater than the  $K_{\text{sp}}$ , the solution is supersaturated, and precipitation of calcium carbonate is thermodynamically favorable. Several solution parameters can act to modify saturation state by increasing the carbonate concentration. For example, as pH increases, the carbonate equilibrium shifts to the right, meaning carbonate ( $\text{CO}_3^{2-}$ ) concentrations increase, as does saturation state of calcite. Similarly,  $\text{CO}_2$  influences saturation of calcite because of its control on pH. Finally, carbonates demonstrate retrograde solubility: as temperature increases, they are more likely to precipitate. Taking advantage of these relationships may facilitate passive chemical precipitation.

The water quality at several northern Minnesota taconite mine pit lakes is supersaturated with respect to carbonates, but there may not be adequate “driving force” to overcome the barrier to nucleation (Teng et al, 2000). The barrier to precipitation may be removed when a nucleation seed is presented to solution, thereby promoting precipitation in systems with lower driving force. This type of “nucleation seeding” strategy may result in alkalinity and hardness reductions in systems supersaturated with respect to carbonates. A form of this strategy has been used successfully to remove metals and TDS and to regulate pH for more than a decade at a 20-acre mine pit lake in Duck Town, Tennessee (Chermak, 2004). The pit lake water has elevated acidity and dissolved metals and is treated by adding lime to water highly concentrated in metals and TDS, such that nano-particulate iron-oxides begin to form. This water is then introduced to the more dilute pit lake, and metals within the pit lake water precipitate on the iron-oxide particulates, which then settle out at the bottom of the pit lake as sludge.

Precipitation of metals was kinetically limited in the Duck Town mine pit lake by a barrier to nucleation. Once the pit lake water was seeded with crystals that provided surface area, metals precipitated out. The following suggests that similar treatment might work at several of the flooded taconite mine pits to remove alkalinity and hardness:

- Water with the highest TDS occurs at the bottom of stratified pit lakes.
- Preliminary geochemical modeling of the quality of water in the mine pit lakes indicates that the water is supersaturated with respect to carbonates, both calcite and aragonite.
- Aragonite ( $\text{CaCO}_3$ ) has been identified by X-ray diffraction (XRD) as an authigenic precipitate at the bottom of one of the mine pit lakes, and in the adjacent rock stockpiles.
- Occasional spontaneous formation of carbonates may be responsible for observed phenomenon within the pit lakes: the presence of a white “bathtub ring” surrounding several of the lakes, and periodic “whitings”, when pit lake water color, which is normally dark blue, changes to a bright turquoise color.



**Figures 1, 2, 3** 1) Aerial images of pit lakes during summer months (different years) capture color of individual lakes, normally dark blue, changing to turquoise during “whitings”. Width of images above are approximately 40 km. 2) Top right picture shows Pit Lake “A”, including the remnant highwall (approximately 37 meters high) and a white “bathtub ring” in foreground. 3) SEM Micrographs of aragonite crystals in a taconite mine pit lake sediment sample. a) and b) show single blades and clusters. c) a twinned crystal. d) single blades and a radiating cluster of aragonite crystals. SEM images- scale bar: a) 1,500X; 20  $\mu\text{m}$  scale b) 4,000X; 12.5  $\mu\text{m}$  scale c) 6,000X 5  $\mu\text{m}$  scale; d) 3,500X; 10  $\mu\text{m}$  scale.

We investigated, through modeling and bench-testing, whether it is possible to induce chemical precipitation of carbonates, thereby decreasing concentrations of hardness, alkalinity, and, by extension, TDS and specific conductivity from the pit lake water, with little mechanical input.

## METHODOLOGY

The investigation consisted of two phases: experimental modeling in the geochemical software Geochemist’s Workbench (Bethke, 2008) (GWB) and laboratory testing to explore a) if precipitation of  $\text{CaCO}_3^{2-}$  from very concentrated pit water can be promoted, and, if successful, b) whether

alkalinity and hardness removal from the more dilute pit water will occur through precipitation onto seed crystals.

Water from Pit Lake “A” was collected from two depths (1 and 20 meters) corresponding to the two stratified regions of the meromictic lake: the mixolimnion, the uppermost portion of the water column that behaves as a holomictic or normally mixing lake, and the monimolimnion, or lower isolated portion of the lake. The monimolimnion is generally colder, more anoxic and saltier than the upper water column. The location of the chemocline was determined in the field, based on the temperature and salinity gradient. Chemical analyses of these water samples were conducted and the data are presented in Table 1.

**Table 1** Initial Water Chemistry

Parameter	Units	Pit A Deep- 20 m	Pit A Shallow- 1 m
Calcium	mg/L	165	60.5
Iron		0.196	ND
Magnesium		293	171
Manganese		14.1	0.0211
Alkalinity, bicarb		474	205
TDS		2360	1230
Sulfate		1370	732
Temperature		°C	6.6
Conductivity	μS/cm	1870	1420
pH		7.52	8.7
Calcite Saturation	Log Q/K <sub>sp</sub>	0.4198	1.0889
Aragonite Saturation	Log Q/K <sub>sp</sub>	0.2844	0.9443

*Phase 1: Reaction modeling in GWB*

GWB was used to model reactions aimed at increasing saturation state with respect to calcium carbonate phases, based on the Pit Lake chemistry data (Table 1). The thermodynamic constraints



for mineral reactions were based on the Lawrence Livermore National Laboratory database provided within the GWB platform. Calculations of saturation were based on equilibrium state. The system was assumed open to atmosphere and the CO<sub>2</sub> endpoint was modeled at atmosphere (log P<sub>CO<sub>2</sub></sub> = 10<sup>-3.4</sup>).

*Phase 2: a. Promoting formation of calcium carbonate*

In the laboratory, several clean jars (rinsed once with dilute acid, then 3 times with tap water, then 3 times with DI water) were filled with 500 mL of deep pit water (Pit A Deep – 20 m) and left open to atmosphere (some evaporation occurred). Carbonate precipitation was encouraged from concentrated pit water by 1) evaporation over three days and heating to room temperature (20 °C) (control), or 2) heating to 45 C. In the heated trials, jars were placed atop a hot plate. For the control, they were placed simply on the bench top. Neither trial was stirred. All of the tests were repeated 5 times, with concurring results.

*b. Measuring removal of hardness and alkalinity through continued precipitation*

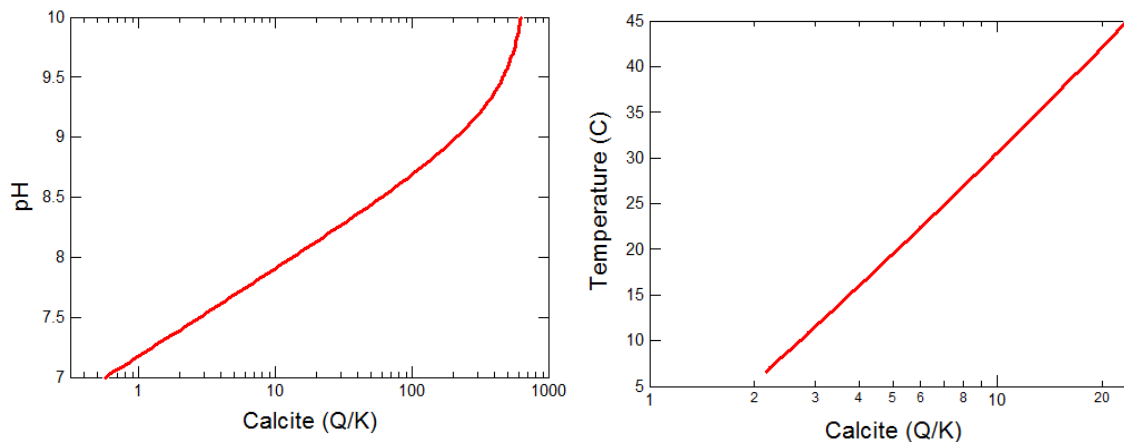
When seed crystal formation was observed from the deep pit water trials, the precipitate was harvested using a screen sieve. Two quantities of this material was then introduced into 500 mL (each) of the more dilute shallow pit water: 1) 0.01 mol, and 2) 0.02 mol seed crystal (determined by dry mass) harvested from the deep pit water experiments. In comparable trials, small quantities of other materials that had the potential to either increase saturation state, or to act as seed crystals, were added to 500 mL (each) of shallow pit water: 1) 0.01 mol ground lime, and 2) 0.03 mol of commercially available fine-grained aragonite. These four trials were compared to a control trial which was subjected to evaporation and heating to room temperature (20 C).

During each trial, a multi-parameter water quality meter (YSI 556 Multi-Probe Meter) was used to measure specific conductivity, pH, dissolved oxygen, and oxidation-reduction potential. Alkalinity was measured using an alkalinity titration kit. At the conclusion of the experiments, six samples were selected for chemical analysis of hardness (Mg and Ca) and alkalinity. In the lime trial, where sludge formed at the bottom, the supernatant water was decanted off the top of the solid and sent for analysis. In trials where calcite crystals formed at the top, water for analysis was collected from below the floating crystals.

## RESULTS AND DISCUSSION

The deep water (Pit A Deep – 20m) contained higher alkalinity, more dissolved constituents, and had a higher conductivity and TDS than the shallow pit water (Pit A Shallow – 1m), as shown on Table 1. Despite containing more than twice the concentration of alkalinity and approximately 2.5 times as much calcium as the shallow water, the geochemical equilibrium model predicted that the saturation state of calcite was lower in the deep pit water than it was in the shallow pit water. The solubility of CO<sub>2</sub> increased with decreasing temperatures; more CO<sub>2</sub> was

dissolved and the pH was lower in the deep pit water relative to the shallow pit water. Both temperature and pH exerted a strong influence on calcite saturation state (Figure 4).



**Figure 4** Predicted saturation state of Pit A Deep – 20 m water, as a function of A) pH, and B) temperature (°C).

The results of field and lab measurements from the laboratory experiments are presented in Table 2. Spontaneous precipitation of carbonate occurred with every test of Pit A Deep water (Figure 5). In the control experiment, as water equilibrated with atmospheric CO<sub>2</sub> and room temperature (~20 C), saturation state increased with increasing temperature and pH until precipitation of carbonate occurred after three days. Precipitation occurred more rapidly when Pit A Deep water was heated further: after four hours heating to 45 C. The increase in conductivity in the Pit A Deep water also reflected this temperature increase; conductivity of water increases by about 2-3% with every degree C. The precipitate formed at the water surface, coalesced into larger clumps with time (or application of heat), and settled to the bottom of water column with time (~2-3 days after formation in the control).

Little change in water quality was observed when carbonate seed crystals, precipitated from the Pit A Deep water, were introduced to the Pit A Shallow water. For example, conductivity remained fairly constant across almost all tests. Significant reductions in hardness, alkalinity, and specific conductivity were observed only in the lime addition test, which also experienced coincident increase in pH increase and saturation state. The formation of sludge at the bottom of the glass is also consistent with carbonate precipitation after the addition of lime.



**Figure 5** A) Precipitate that formed from the deep pit water control over a period of 3 days. B) Groups of precipitated crystals that occurred at the surface during heating of the deep pit water.

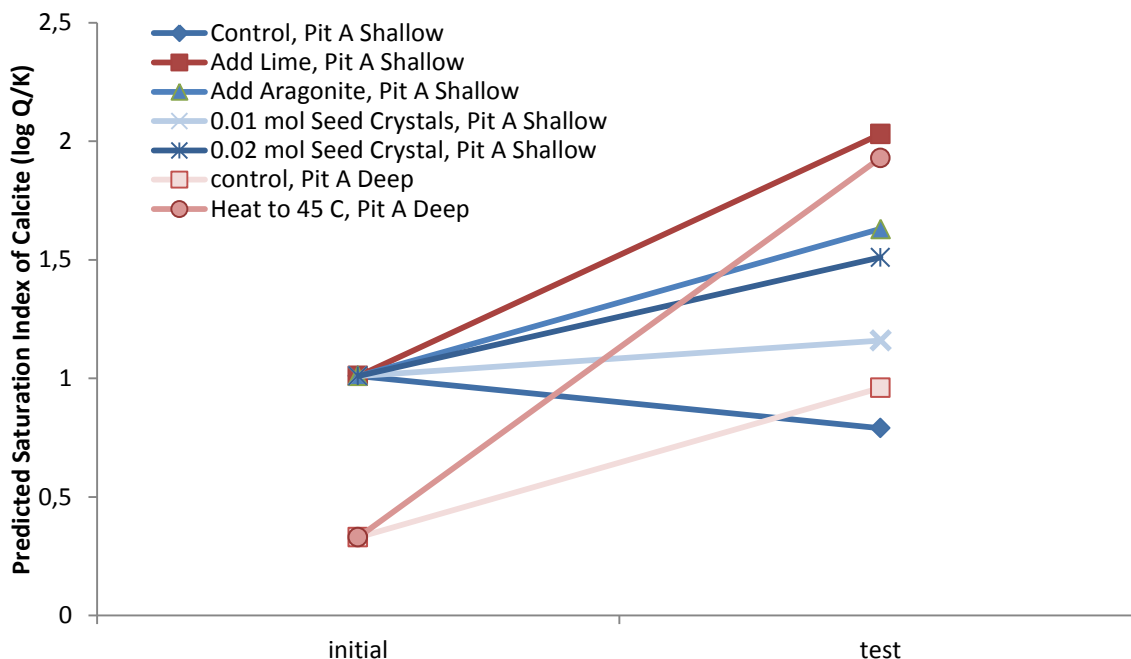
**Table 2** Experimental Results: Laboratory and Field Measurements, and Model Predictions

Test	Units	Pit A Deep - 20 m			Pit A Shallow - 1 m					
		Start	Control	Heat to 45 C	Start	Control	0.01 mol lime	.03 mol Arag	.01 mol Seeds	.02 mol Seeds
Calcium	mg/L	165	113	--	60.5	60.8	26.2	60	63.3	64.2
Magnesium	mg/L	293	321	--	171	164	166	170	171	172
Hardness, dissolved	mg/L as CaCO <sub>3</sub>	1610	1600		852	824	746	847	859	866
Temperature	°C	6.6	20.35	45	19.3	19.51	19.53	19.42	19.51	19.73
Conductivity	uS/cm	1870	3111	3343	1420	1720	1467	1727	1716	1746
pH		7.52	8.43	8.02	8.7	8.53	9.08	8.4	8.39	8.4
Field alkalinity	mg/L as CaCO <sub>3</sub>	860	780	640	540	520	280	400	400	480
Precipitate Evident		none	yes, see fig 3A	yes, fig 3B	no	no	sludge	few at surface	no	no
Calcite Saturation	Log Q/K	0.33	0.96	1.93	1.01	0.79	2.03	1.63	1.16	1.51
Aragonite Saturation	Log Q/K	0.19	0.82	1.79	0.87	0.65	1.89	1.48	1.30	1.37

Experimental results were modeled in GWB, and predicted saturation state post-reaction is plotted in Figure 6. The results indicate that precipitation of calcium carbonate occurred only during those tests during which the predicted saturation index increased by a factor of two or more (colored red in the figure. Tests in which no precipitate formed are colored blue). Though predicted saturation state is lower in the Pit A Deep control than it is in three of the Pit A Shallow tests, the relative change from the initial saturation state was greater in the Pit A Deep tests, and this change correlates with observed precipitation. All tests and controls were supersaturated with respect to calcite; only tests where the change in driving force was greater than 2 led to precipitation.



An additional factor that may explain the continued resistance to precipitation in the shallow pit water is inhibition due to high concentrations of Mg and sulfate in solution (Berner, 1975). Kinetic inhibition due to Mg can sometimes be overcome by a larger driving force ( $\Delta G$ ), such that precipitation can proceed. Generally, reactions with larger Gibbs free energies are more likely to proceed spontaneously than are those with smaller free energies (Langmuir, 1997). In either case, driving up saturation state to  $>2$  via the addition of lime was the only test that successfully led to precipitation of calcite from the shallow pit lake water.



**Figure 6** Predicted saturation with respect to calcite for Pit A Deep and Pit A Shallow, in initial waters and in each test. Precipitation of calcium carbonate was observed in tests shown in pink and red; precipitation did not occur in any of the tests colored blue. Precipitation occurred in both tests from the Pit A Deep water, during the control experiment and when the water was heated to 45 °C, and it occurred more rapidly and to a larger extent in the heated test. Lime addition was the only test that resulted in the precipitation of carbonate from the Pit A Shallow water.

**CONCLUSION**

Calcite precipitation occurred from the deep pit water in the control when it was removed from cold storage: changing temperature of deep pit water and allowing CO<sub>2</sub> to exolve increased saturation to the point of precipitation. This suggests that one potential treatment strategy to remove alkalinity and hardness is to pump the deep water to the surface and allow it to equilibrate with atmospheric conditions. The “whiting” events that have been observed at surrounding pit lakes demonstrate this process on a much larger scale, possibly due to turnover of the mixolimnion, which brings deeper, more saturated water to the surface. As saturated water equilibrates with atmospheric conditions, calcium carbonate precipitates, temporarily coloring the pit lakes a bright turquoise-blue. Test results predict that about 25% of the hardness and alkalinity

in the Pit A Deep water may be removed by pumping to the surface. The effect of pumping on pit lake hydrodynamics and stratification has not been investigated at this time.

Precipitation of hardness and alkalinity from shallow pit water was not achieved with the addition of nucleation seed crystals. It is possible that the quantity of seed crystals introduced to the dilute surface water didn't present enough surface area for additional precipitation to occur. Furthermore, adding a larger quantity of seed crystals could act to increase saturation state enough relative to the initial state to overcome the barrier to precipitation. Reductions in hardness and alkalinity in the shallow pit water was achieved by addition of a small amount of lime, a conventional wastewater treatment approach used to decrease water hardness.

#### ACKNOWLEDGEMENTS

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