# IMPROVED LIME NEUTRALIZATION PROCESS[1]

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**Abstract:** A two-step lime neutralization ("NTC") process was developed to produce denser and more stable sludges. In this process, pH of the influent is raised to 4-5 with recycled sludge in the first reactor and, in the second reactor, pH is set to 9-10 and aeration is provided. Three pilot studies at three different mine sites were conducted. In all cases, sludge density and settling rates were improved by 30-50% as opposed to sludges generated by the high density sludge (HDS) process.

**Key Words:** Acid mine drainage, treatment, lime neutralisation, precipitation, sludge, high density sludge, two-step NTC

## Introduction

Acid mine drainage (AMD) occurs naturally at mine sites as a result of oxidation of sulphitic mine tailings and waste rock, and it is characterized with high acidity, sulphate, and metal concentrations. Since it has a detrimental effect on the environment, it must be controlled and treated. Mining industries face the challenge of treating AMD in a cost-effective manner. The desired degree of treatment is usually obtained by neutralization of free sulphuric acid and insolubilization of metal ions such as Fe (2+/3+), Zn, Cu, Al, and Pb. Lime or hydrated lime, (CaO or $Ca(OH)_2$), is the most commonly used neutralizing agent for treating AMD because of their high reactivity, availability, and relatively low cost. The principal reaction in lime neutralization can be expressed as follows (Eq. 1).

$$Ca(OH)_2 + Me^{2+}/Me^{3+} + H_2SO_4 <--> Me(OH)_2/Me(OH)_3 + CaSO_4 + H_2O \quad (1)$$

In some cases, other alkaline chemical reagents such as $NH_3$, NaOH or $CaCO_3$ can be used. The mixture of metal hydroxide precipitates and gypsum ($CaSO_4$) is called "sludge" and is allowed to settle in ponds or in a solid/liquid (S/L) separation device (e.g. clarifier/thickener). The settled sludge is then disposed in specifically-designed storage ponds. Hydroxide sludges are usually voluminous due to their gelatinous texture and, as a consequence, solid/liquid separation is difficult. Formation of a voluminous sludge is an undesirable side effect of the process. Therefore, many recent studies in the field of AMD treatment have been directed toward generating denser sludges.

The current state-of-the-art lime neutralization process for treating AMD and other acidic waters is called "High Density Sludge (HDS)" process and is capable of producing a more compacted sludge as compared to other methods of liming (Herman, 1983; Herman et al, 1984). In the HDS process, more than one reactor are used to perform the neutralization (Figure 1). A mixture of sludge, recycled from the clarifier underflow, and lime is used as alkaline reagent in the first reactor. Both reactors are aerated to oxidize Fe(2+) and pH is continuously monitored. The neutralized AMD with metal precipitates is then flocculated with a polymer and a clarifier/thickener is used for S/L separation. The solid content in the resulting sludge is significantly higher (e.g. 10-30%) as opposed to the case not involving sludge recycle (Kuyucak and Sheremata, 1991). A 1991 survey (Bartlett and Payant, 1991) found 23 lime treatment plants operated by Noranda Minerals Inc. including the HDS process at several sites (Les Mines Gallen, Waite Amulet, Mattabi, Brunswick Mining and Smelting).

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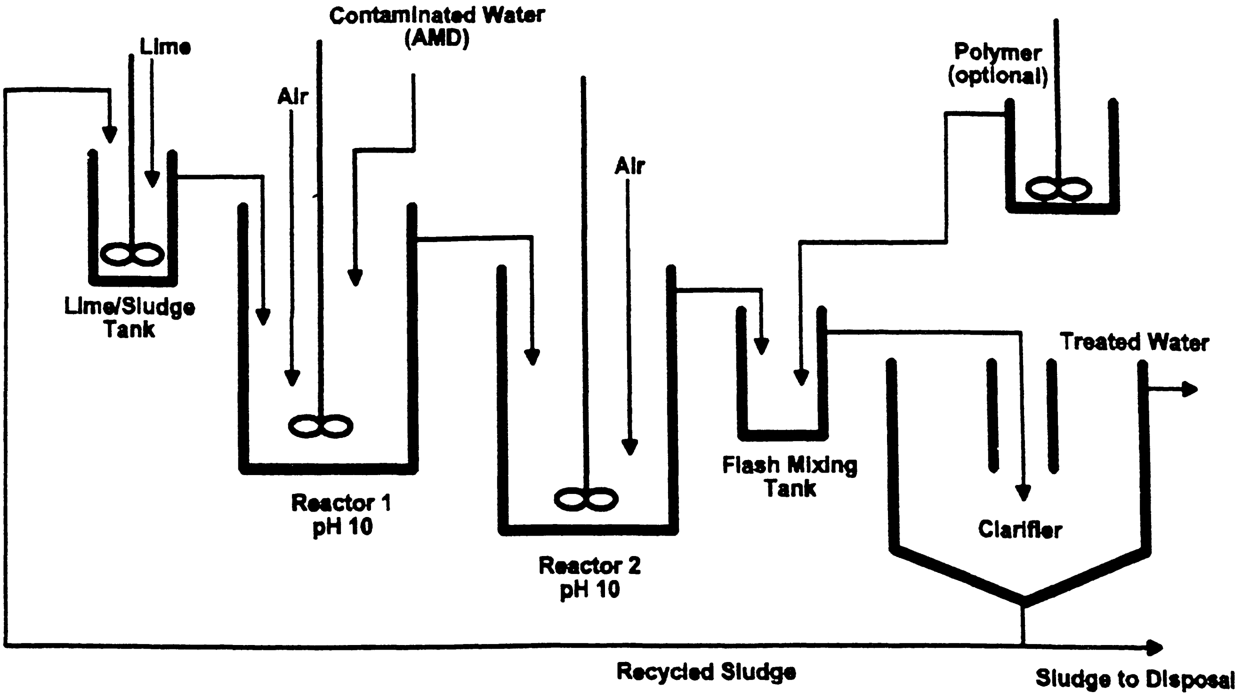

Figure 1 - High Density Sludge Process Flowsheet

A research program was initiated at NTC in 1990 to investigate the fundamentals of the lime neutralization process so as to gain an understanding that would enable production of denser and more stable sludges (Kuyucak and Sheremata, 1991; Kuyucak et al., 1991). As part of a joint research project between NTC and the CANMET Fuel Processing Laboratory, a correlation between crystal morphology of gypsum in lime sludge and sludge density was established (Payette et al, 1991). In conjunction with this, an intensive bench-scale experimental program was conducted where process variables, such as rate and method of sludge recycle, method of lime addition, mixing rate, and residence times were examined and correlated with sludge density, settling rate, and crystal morphology. From this work, the two-step NTC lime neutralization process (Patent Pending) was developed (Kuyucak and Sheremata, 1992). The process flowsheet is depicted in Figure 2.

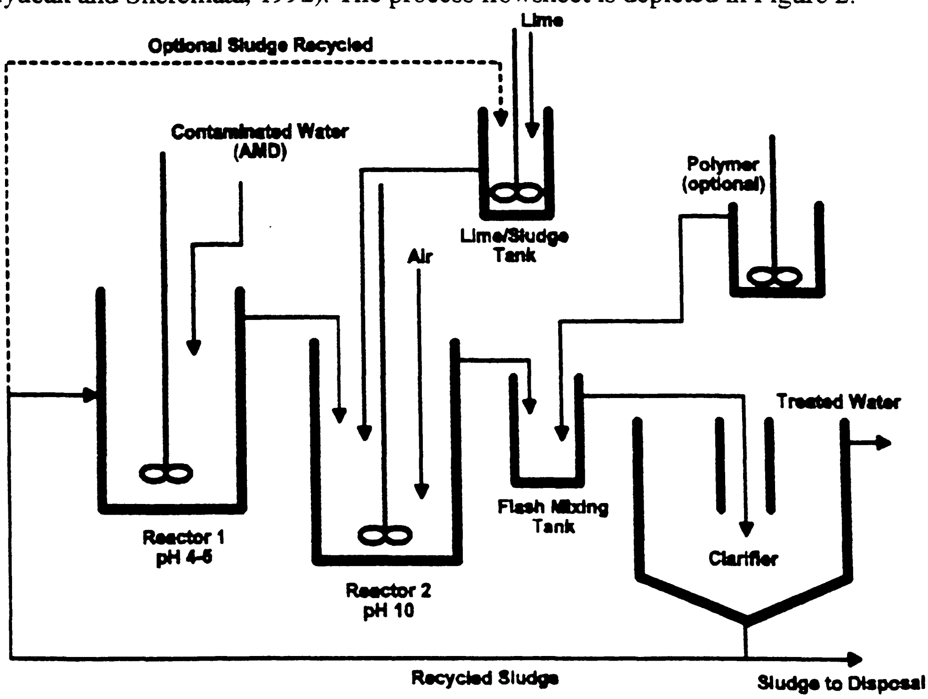

Figure 2 - Two-Step NTC Process Flowsheet

This paper summarizes pertinent experimental results that led to the patent application and the results of pilot testing at Waite Amulet (WA), Geco and Les Mines Gallen (MG).

## Experimental Protocol

### Reagents

Reagent grade hydrated lime ($Ca(OH)_2$) supplied by Anachemia was used for all tests. For flocculation, a nonionic polymer (Percol E-10, supplied by Allied Colloids) was used. Stock solutions (0.5 % strength) were prepared weekly. Working solutions (0.05 % strength) were prepared on a daily basis.

### AMD Characteristics

Three types of AMD (i.e. low, moderate and high strength) were evaluated. The classification was made according to total metal and sulphate content (i.e. ionic strength) of each water type. The chemical composition of the waters are given in Table I. In laboratory tests, MG water was mainly used.

Table I. Composition of actual WA, Geco and MG AMD

| Water Type | Concentration (mg/l) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Al | As | Cd | Cu | $Fe_T$ | $Fe^{2+}$ | Mn | Pb | $SO_4$ | Se | Zn | pH |
| WA* | 7.5 | <0.25 | <0.02 | 0.97 | 306 | 253 | 7.4 | <0.25 | 597 | <0.5 | 2.8 | 2.8 |
| Geco** | 45 | 0.60 | 0.15 | 2.5 | 1100 | 1000 | 13 | <0.05 | 4300 | 0.5 | 100 | 3.3 |
| MG*** | 200 | 2.3 | - | 10 | 1600 | 945 | - | <0.25 | 8000 | - | 800 | 2.3 |

*, ** and *** refer to relative ionic strength of AMD as low, moderate and high, respectively.

### Laboratory Tests

Neutralization of 1 L AMD was carried out in 2-L baffled reactors (height/diameter: 1/1). A mixer fitted with an axial type impeller was used for agitation. The primary purpose of the lab tests were: 1-) Establish a method for comparing the NTC and HDS processes on a laboratory scale. 2-) Determine optimal process parameters for each method.

The method for comparing the two processes consisted of batch neutralization, flocculation, and settling. A fraction of the sludge recovered after 1 h of settling was used for recycle in the subsequent batch test. After each batch neutralization, the volume of sludge produced was divided by the total volume of AMD that had been treated. This value was recorded as the compacted sludge volume, produced per volume of AMD treated. The compacted sludge volume decreased until it reached a steady value. Steady state was usually reached after 12 cycle. The test was then discontinued and the sludge set aside for percent solids determination.

### Simulation of HDS process

The HDS process was simulated by increasing the pH of 1 L of AMD to 10 with a lime/sludge slurry. The sludge used for recycle was taken from the previous batch and its volume was calculated as a percentage of the AMD treated in one batch. For example, 10 % recycle entailed 100 mL sludge recycled to 1 L AMD. The mixture was agitated at 350 rpm and aerated for 45 min. Mixing was continued for an additional 15 min at the same speed.

**Simulation of NTC process**

Optimum process parameters were determined with the simulation. Those parameters included the following: degree of agitation in each reactor, lime addition method in second reactor, optimum pH in the first reactor, rate of sludge recycle, residence time in each reactor. A 10-12% portion of the sludge produced was recycled to 1 L of AMD to increase the pH to 4. The mixture was agitated at 550 rpm for 30 min. The pH was further increased to 10 by adding lime. The mixture was agitated at 350 rpm and aerated for 30 min. The slurry was then flocculated and settled.

**Flocculation and settling**

To enhance settling, an optimal amount of Percol E-10, determined for each water type, was added as flocculant and the slurry was mixed for 2 min at 250 rpm. Settling was recorded as settled volume in a 2 L graduated cylinder at several intervals up to 60 min.

<u>Pilot Tests</u>

**Portable Equipment**

A mobile pilot unit was designed and constructed at NTC by downsizing the actual WA treatment plant by a factor of 4000. The unit consisted of three 30 L, one 5 L, and two 2.5 L reactors with appropriately sized overhead mixers. There were also three clarifiers sized to handle low, medium, and high strength AMD and equipped with a rake rotating at 1 rpm. The flow of AMD was regulated at 1 L/min with a constant head tank (9.5 L) that fed the process through a flowmeter. The AMD was then treated in a cascade of two 30 L reactors and one 5 L flash mixing tank. The reactors were constructed with baffles in order to provide good mixing. Air was introduced under the impeller through a stainless steel pipe (0.95 cm I.D.). A 6-L tank was used for the lime slurry stock solution and a 2.5-L tank was used for mixing the lime slurry to the recycled sludge. Finally, a 2.5 L tank was used to stock the polymer solution. The reagents were added with peristaltic pumps. The process was controlled with two Yokogawa industrial pH meters/controllers. The pH meter/controllers were connected to peristaltic pumps which fed one or two reactors with a lime or lime/sludge mixture.

The equipment effectively simulated the HDS process, in terms of sludge and treated water qualities, that was in operation at WA and MG sites during the course of tests.

**Pilot Test Conditions**

The process parameters and optimal test conditions used in three pilot tests were summarized in Table II. Unfiltered samples of AMD, filtered and unfiltered samples of clarifier overflow, and sludge from the clarifier underflow were taken every 6 h over the 6 day test period.

<u>Analytical Methods</u>

**Analysis of Water and Sludge Samples**

Inductively coupled plasma (ICP) was used for metal ion analysis of the aqueous solutions. The <u>percent solids</u> of sludge samples (dry wt./wet wt.) were determined by weight difference before and after drying to a constant weight in a convection oven at 60 °C. For analysis of <u>sludge composition</u>, dry samples were ground and 1 g was combined with 10 mL concentrated HCl. After boiling for 5 min, the solution was allowed to cool and was then diluted to 100 mL with distilled/de-ionized water. Aqueous metals were determined by ICP in order to calculate the wt. % of individual metal species present. Air dried samples were used to examine the <u>sludge morphology</u> with a scanning electron microscope (SEM). <u>Viscosity</u> measurements were carried out using Brookfield Digital Viscometer (model DV-11).

Sludge stability (metal leachability) was evaluated using the NTC leaching test, as described below, as opposed to a regulatory test (Kuyucak and Sheremata, 1991). A sufficient amount of vacuum filtered sludge was combined with distilled-deionized water to make-up a liquid to dry solid ratio of 200:1, followed by mixing until the pH had stabilized. The pH was adjusted to 4 with 1 N $H_2SO_4$, and the slurry was agitated for 16 h with end over end agitation. The metals were measured by ICP, flowing filtration through a 0.45$\mu$m filter paper, and were expressed as $\mu$g leachable metal per g dry solid ($\mu$g/g). The advantages of the NTC test were that results were more comparable, since the pH and amount of dry solid was the same for each test, and the sulphate-based leaching medium was more characteristic of actual leaching conditions.

## Results and Discussions

### Laboratory Test Results

With low strength WA AMD, it was difficult to accumulate a sufficient amount of sludge in the bench scale tests. Therefore, only agitation rates in each reactor for WA AMD were optimized; they were 550 and 450 rpm in the first and the second reactors, respectively. With MG AMD, residence time, rate and method of sludge recycle, and the intermediate pH in the first reactor were optimized. Under optimized conditions, the compacted sludge volume and percent solids for the HDS and NTC processes were assessed. For the MG AMD, the pH in the first reactor was 4 and the residence times were 30 min in both reactors. The rate of agitation was 550 rpm in the first reactor. The rate of sludge recycle was 12% into first reactor which was enough to raise the pH to 4. The pH in the second reactor was raised to 10 with lime. A recycle ratio of 12% was optimum for reducing the sludge volume (13.1% solids) to minimum level. The optimum sludge recycle rate for HDS process was 6%, giving 10% solids. The residence times of 30 min in each reactor were ample to generate the sludge with optimal settling rate and sludge volume. Under the optimized conditions, sludge produced from MG AMD was significantly denser by the NTC process than as HDS. On the other hand, the sludge produced from WA AMD was under 2% in solids for both processes and lab results for WA AMD were inconclusive.

Table II. Process Parameters and optimal Conditions used in pilot tests

| Parameters/Conditions | Process | | | |
|---|---|---|---|---|
| | NTC | | HDS | |
| Reactor | Reactor # 1 | Reactor # 2 | Reactor # 1 | Reactor # 2 |
| pH | | | | |
| WA | 4.9 | 10 | 10 | 10 |
| Geco | 5.5 | 9.6 | 9.6 | 9.6 |
| MG | 4 | 10 | 10 | 10 |
| Retention time, min | | | | |
| WA | 30 | 30 | 30 | 30 |
| Geco | 30 | 30 | 30 | 30 |
| MG | 30 | 30 | 30 | 30 |
| Rate of agitation, rpm | | | | |
| WA | 550 | 450 | 400 | 400 |
| Geco | 550 | 450 | 400 | 400 |
| MG | 550 | 450 | 400 | 400 |
| Aeration | | | | |
| WA | no | yes | yes | yes |
| Geco | no | yes | yes | yes |
| MG | no | yes | yes | yes |
| Sludge recycle rate (%) | | | | |
| WA | 3.5 | | 14 | |
| Geco | 12 | | 12 | |
| MG | 12 | | 20 | |
| AMD flow, L/min | | | | |
| WA | 1 | | 1 | |
| Geco | 1 | | 1 | |
| MG | 1 | | 1 | |
| Lime conc., % slurry | | | | |
| WA | 5 | | 5 | |
| Geco | 10 | | 10 | |
| MG | 10 | | 10 | |
| Vol. AMD treated, L | | | | |
| WA | 8640 | | 8640 | |
| Geco | 3860 | | 3220 | |
| MG | 6180 | | 6360 | |
| Lime consumption, g/L | | | | |
| WA | 0.21 | | 0.24 | |
| Geco | 2.7 | | 2.4 | |
| MG | 4.5 | | 4.8 | |
| Conc. Percol E-10, mg/L | | | | |
| WA | 2.5 | | 2.5 | |
| Geco | 10 | | 5 | |
| MG | 14 | | 14 | |

## Pilot Test Results for Comparing NTC & HDS Processes (WA, Geco, MG)

The HDS and NTC processes were evaluated using the pilot unit. The tests were conducted at the WA, Geco and MG treatment plants. For each set of tests, percent solids, settling rates, metal leachability, elemental composition, particle morphology, viscosity) and treated water quality were compared.

### Sludge Recycling and Test Conditions

At WA, 3.5% sludge was recycled during the NTC and 14% for the HDS demonstrations (Table II). At MG, sludge recycle was 12% and 20% in NTC and HDS tests, respectively. The intermediate pH for the NTC process varied between 4-5.5 depending on the water type; the optimum pH was 5, 4 and 5.5 for WA, MG and Geco, respectively. The flow rate was 1 L/min for every test and the residence times were 30 min in each reactor.

The improved sludge density at optimal recycling rates implied the fact that there existed an optimum $Fe^{2+}/Fe^{3+}$ ratio for the system, as found by other investigators (Kostenbader and Haines, 1970; Bosman, 1974). Presumably, the optimum $Fe^{2+}/Fe^{3+}$ ratio was dependent on the available $Fe^{2+}$ ions in AMD that were adsorbed onto $Fe(OH)_3$ precipitates present in the recycled sludge. At the optimum ratio, $Fe^{2+}$ adsorption resulted in double layer compression and minimized adsorption of water molecules. As a result, denser and compacted metal hydroxide precipitates were formed.

### Water Quality

The total and dissolved metal concentrations in the effluent from NTC and HDS treatments were similar for both processes at the three test sites.

### Sludge Characteristics

The solids content in the WA sludge generated by the NTC and HDS processes over a period of 6 days were respectively 11% and 5.3%. The NTC process was operated with 3.5% sludge recycle whereas the HDS process was operated with 14% sludge recyle. The NTC process, therefore, produced a 50% denser sludge. The sludge of the pilot HDS process compared well with the 4.8% solids of the full-scale plant sludge. These results clearly indicated that results from the pilot plant were representative of what could actually be obtained in the plant. In the Geco sludge, 20.5% and 15% solids were generated with the NTC and HDS processes, respectively. With MG AMD, the NTC process also yielded a sludge with higher solids content than the HDS process. After 48 h, the % solids were 15.5% for the HDS and 20.5% for the NTC process at 20% and 12% sludge recycling, respectively. The results summarizing percent solids and settling rates found in each test are given in Table III.

Table III. Percent solids and settling rates for each sludge sample generated by pilot tests

| **Water Type** | **WA** | | **Geco** | | **MG** | |
|---|---|---|---|---|---|---|
| Process | NTC | HDS | NTC | HDS | NTC | HDS |
| Solid content (%) | 11 | 5.3 | 20.5 | 15 | 20.5 | 15.5 |
| Settling rate (m/h) | 20 | 6.3 | 8.5 | 5.7 | 9.1 | 5.6 |

Settling rate: Settling was much faster for the NTC produced sludge, particularly for Geco AMD. The sludges generated by the NTC process had a sand-like appearance as opposed to a paste-like texture of the other sludges.

Sludge Composition: Higher metal levels were found in the NTC-produced sludges as compared with the HDS-produced sludge and the full-scale plant sludges. Sludges produced by the NTC process contained lower proportions of Ca and $SO_4^{2-}$ than those produced by the HDS process. This could be due to the use of excess lime, as the case in the WA test, or presence of more gypsum in the HDS sludge.

Morphology: The electron micrographs indicate that the NTC sludge was composed of finer particles than the HDS sludges. It was likely that improved crystallization also played a role in improving the sludge compaction. The three necessary conditions for crystallization (i.e. supersaturation, nucleation, and crystal growth (Kirk-Othmer, 1979)) were incorporated in the NTC process. In addition to adsorption/co-precipitation of metals by $Fe(OH)_3$, there was supersaturation with respect to certain metals because metals in the recycled sludge could dissolve at pH 4-5 in the first reactor. In the second reactor, undissolved gypsum and iron hydroxide particles act as nucleation sites for hydroxide precipitation. Crystal growth was enhanced in the second reactor by slow agitation (350-450 rpm) and 30 min of mixing. Evidence of improved crystallization was sought by SEM examination. The micrographs indicated that gypsum crystals were more developed in the sludge produced by the NTC process.

Viscosity: Actual and pilot plant HDS sludge from WA AMD, of which percent solids were 4.8 and 5.3, had similar viscosities of 27 and 21.5 cp, respectively. The NTC pilot sludge had a measured viscosity of 125 cp, but the solids of this sludge was 11% for WA AMD. However, they were all considered very low.

With MG AMD, for the HDS process, small increases in percent solids were accompanied by large increases in viscosity. At 15% solids, the NTC process produced a sludge with lower viscosity (81 cp) than the HDS process (456 cp). At that point, the clarifier rake was not able to move in the HDS-produced sludge. The NTC process, therefore, exhibited additional advantages over the HDS process in terms of generating a higher density but lower viscosity sludge which was easier to handle.

**Sludge Stability**

Stability of the three sludges produced from full-scale and pilot tests showed that there were slightly higher levels of leachable Zn, Mn, and Cu in the NTC-produced sludge compared to the other HDS-produced sludges, particularly for WA case. However, the leachability of the HDS sludge at the MG and Geco sites was similar to the NTC sludge, except that the Zn was slightly more leachable (e.g. 0.3 vs 0.1 mg/L). The increased leachability of the divalent metals is likely due to the fact that they are adsorbed and co-precipitated onto $Fe(OH)_3$ precipitates at pH 4. Co-adsorption/precipitation of metals at low pH is a common approach in water treatment design (Patterson, 1985). Once the metals are associated with $Fe(OH)_3$, they will not precipitate as hydroxides at pH 10. Metal hydroxides retain water by hydrolysis reactions when they are formed (Benefield et al, 1982). Therefore, by favouring co-precipitation of divalent metals in the first reactor over hydroxide precipitation, a higher density sludge was formed.

**Scaling**

The influent sulphate levels in WA AMD were too low (ave. 624 mg/L during the test period) for gypsum precipitation to occur. Therefore, it was not necessary or relevant to assess scaling. At the MG site, it was evident that there was less scale formation in the NTC process, as measured from the accumulation of gypsum on metal coupons. Another indicator of reduced scaling was that the average sulphate concentration in the final effluent from the NTC test was 3,250 mg/L compared with 2,810 mg/L in the HDS test at the MG site. However, it was almost the same for the Geco site.

## Conclusion

Results of laboratory and pilot tests indicated that the two-step NTC lime neutralization process resulted in a denser, but less viscose sludge compared to the state-of-the-art HDS process. Settling rate was faster and scaling was less. Metal and suspended solid levels in the clarifier overflow were similar for both processes. Pilot test results also showed that sludges produced with pilot tests were denser than those found with lab tests. Therefore, field testing on a pilot scale is preferable to laboratory testing to demonstrate treatment processes.

Future work will focus on sludge management issues (e.g., the benefits of freeze-thaw on de-watering and sludge fixation/stabilization).

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