# Removal of Hardness and Sulfate from Flue Gas Desulfurization Effluent Using Ion Exchange

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ABSTRACT

Treatment of effluent from flue gas desulphurization (FGD) systems in the metallurgical and power industries represents a significant water treatment challenge. FGD effluents typically contain high levels of Total Dissolved Solids (TDS), including calcium and sulfate. Wet FGD scrubbers typically use lime or limestone slurries to capture sulfur oxides ($SO_x$) present in the flue gas. As a result the scrubber blow-down is saturated with respect to gypsum. Depending on the make-up water quality and the amount of HCl present in the flue gas, this translates into sulfate levels ranging from 1,400 to 5,000 ppm and calcium hardness of 1,000 to 3,000 ppm. As regulations for the discharge of sulfate and TDS into receiving waters become tighter, downstream processing of FGD effluent is required prior to final discharge. Removal of calcium hardness and sulfate is also required for the re-use of FGD effluent. Options for hardness and sulfate removal include softening followed by membranes, barium precipitation and ion exchange. A case study of a recent pilot test of an ion exchange process treating lime treated FGD effluent at an US metallurgical plant will be presented. Operating data from the pilot shows that the ion exchange process achieved the target hardness and sulfate levels to meet regulatory limits when treating lime plant effluent containing up to 1,700 mg/L $SO_4$. Operating and capital costs for a commercial scale implementation of an ion exchange process for hardness and sulfate removal will also be presented based on the results of the pilot testing.

## INTRODUCTION

Management of water resources has become a critical issue in many jurisdictions. Industrial operations are increasingly subject to rigorous legislation related to both water discharge quality and overall water consumption. As a result, industrial operations are forced to find new ways to reduce water consumption and to meet increasingly stringent discharge criteria.

The management of effluent from wet flue gas desulphurization (FGD) scrubbers represents a major water treatment challenge. Wet FGD scrubbers remove $SO_x$ emissions and other contaminants from gas through contact with lime-saturated water or lime slurry, neutralizing acid and forming gypsum. Gypsum can be thickened to produce high density gypsum sludge suitable for disposal. The clarified solution resulting from such thickening is gypsum saturated, containing 1,400-5,000 ppm sulfate and 1,000-3,000 ppm calcium hardness. Both of these constituents may be subject to regulatory discharge limits, depending on the jurisdiction, as illustrated in Table 1.

Table 1 - Sulfate Discharge Limits by Jurisdiction

| Jurisdiction | Sulfate level (mg/L) |
|---|---|
| US EPA Drinking Water | 250 |
| Canada Livestock | 1,000 |
| Australia ANZECC 2000 General Water Use | 1,000 |
| Chile DS90 - Surface Water | 1,000-2,000 |
| Chile DS46 - Ground Water | 250-500 |

Small amounts of hardness and sulfate can be removed from water using conventional membrane technology. However, membrane technology is not well suited for treatment of gypsum saturated waters because scaling becomes a major concern. Additionally, membrane technology results in a concentrated liquid brine product. This brine product not only represents an additional disposal challenge, but also limits overall recovery of water to 50–80%.

## SULFATE REMOVAL WITH SULF-IX™ TECHNOLOGY

An alternative to membrane technology is the removal of hardness and sulfate through an ion exchange process called Sulf-IX™. The Sulf-IX™ process uses two stages of ion exchange to remove sulfate from wastewater. In the first cationic ion exchange circuit, a strong acid cationic (SAC) resin is used to selectively remove calcium from the feed water. The SAC resin is regenerated with dilute sulfuric acid, eluting calcium from the resin. Eluted calcium subsequently precipitates as solid gypsum.

In the second stage, the calcium depleted feed water is fed to the anion exchange circuit where sulfate is removed with a weak base anion (WBA) resin. This resin is regenerated with lime solution in order to release sulfate from the resin. Released sulfate reacts with calcium to precipitate as solid gypsum.

Both ion exchange stages take place in fluidized bed reactors where the rise rate is such that precipitated gypsum is rejected from the column without scaling on resin beads. After collection and filtration, the gypsum product can be shipped off site for disposal or for use in fertilizer or building

materials. As both regenerant circuits are decoupled from the wastewater flow, the gypsum precipitated through the process is pure and can be classified as non-hazardous waste according to toxicity

characteristic leaching procedure (TCLP) analysis techniques. A simplified schematic flowsheet of the Sulf-IX™ process is shown in Figure 1.
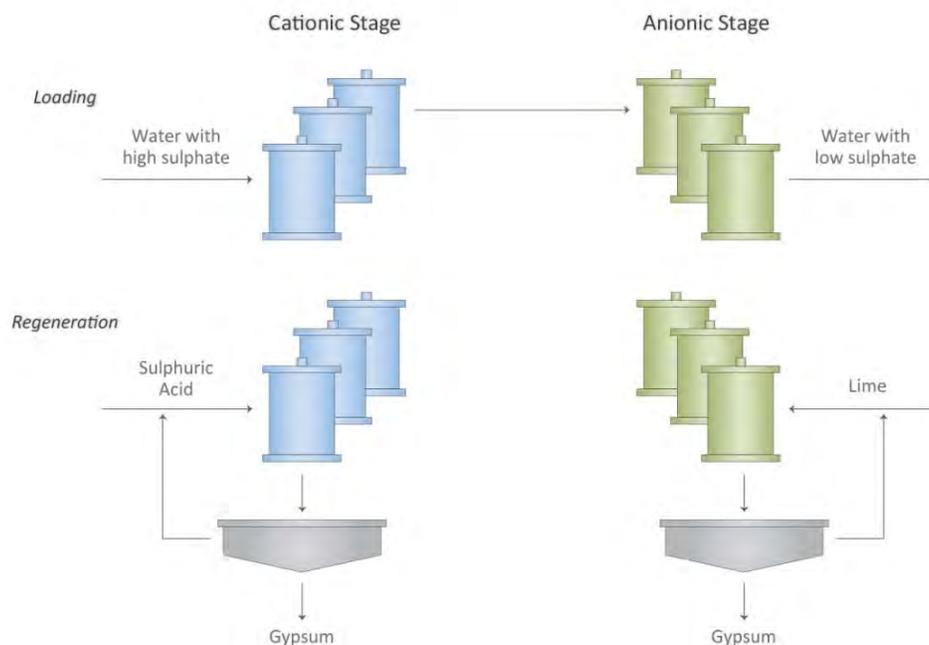


Figure 1 – Sulf-IX™ Process Schematic

Equation (1) shows the removal of calcium from feed water using ion exchange. R represents chemistry on the resin. The cationic resin used in the process is selective for calcium and as a result, the Sulf-IX™ process is highly effective at removing calcium water hardness.

$$Ca^{2+}_{(aq)} + 2(R\text{-}SO_3\text{-}H)_{(s)} \rightarrow \\ 2(R\text{-}SO_3)\text{-}Ca_{(s)} + 2H^+_{(aq)} \tag{1}$$
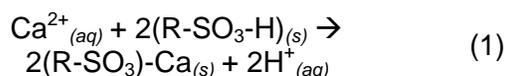
The cation resin is regenerated with a gypsum saturated solution of dilute sulfuric acid in equation (2):

$$2H^+_{(aq)} + SO_4^{2-}_{(aq)} + 2(R\text{-}SO_3)\text{-}Ca_{(s)} + \\ 2H_2O \rightarrow 2(R\text{-}SO_3\text{-}H)_{(s)} + \\ CaSO_4 \cdot 2H_2O_{(s)} \tag{2}$$
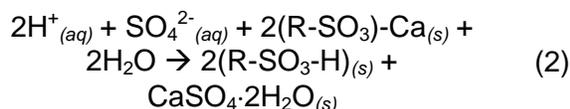
In equation (3), sulfate is removed during the anionic exchange stage:

$$2H^+_{(aq)} + SO_4^{2-}_{(aq)} + 2R\text{-}NH_{3(s)} \rightarrow 2(R\text{-} \\ NH_3) \cdot H_2SO_{4(s)} \tag{3}$$
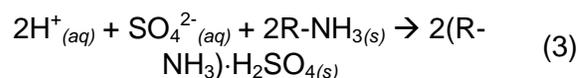
Regeneration of anionic resin occurs through contact with solution saturated with gypsum and lime in equation (4):

$$2(R\text{-}NH_3) \cdot H_2SO_{4(s)} + Ca^{2+}_{(aq)} + 2OH^-_{(aq)} \\ \rightarrow 2(R\text{-}NH_3)_{(s)} + CaSO_4 \cdot 2H_2O_{(s)} \tag{4}$$
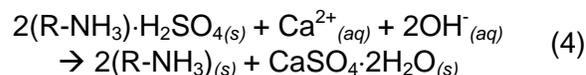
In the Sulf-IX™ process both anionic and cationic regenerant streams are completely recycled. As a result, make-up water is only necessary to balance the small amount of pore water deported with the

solid gypsum product and the waters of hydration associated with gypsum. This

allows overall water recovery in the range of 98-99% with the Sulf-IX™ process.



Figure 2 – Mobile Sulf-IX™ Pilot Plant

## SULF-IX™ PILOT PROJECT

A mobile Sulf-IX™ pilot unit for sulfate removal was constructed and deployed for on-site testing on FGD blowdown. The mobile unit is housed in a 53' self-contained insulated aluminum-sided trailer pictured in Figure 2 and has a capacity of 10 L/min of feed water. The pilot run consisted of a total of 24 days of operation in two campaigns.

PROJECT OVERVIEW. The site for the Sulf-IX™ pilot was an US metallurgical plant. The local regulatory agency required site-wide sulfate and hardness balances to be completed and that methods for mitigating an increase in the concentration of these constituents across the process as a whole are identified. The balances clearly showed wet FGD scrubbers that capture $SO_x$ gas represent the primary source of sulfate and hardness in the overall project flowsheet. The capture of $SO_x$ is accomplished with lime slurry which leads to an increase of sulfate and hardness in process water. While process water is

currently recycled with little or no off-site discharge, the hardness and sulfate levels produced by the scrubber circuit exceed the operating permit limits. The operator has identified Sulf-IX™ as a cost-effective strategy for removing sulfate and hardness from process water and bringing the overall scrubber circuit into compliance.

The existing scrubber system consists of a wet FGD system to remove $SO_x$ emissions followed by a high-density sludge (HDS) system to treat FGD blowdown with lime. The existing HDS system reduces the concentration of sulfate and calcium in the FGD blowdown through the production of gypsum, but this system is not capable of reaching compliance with the existing permit under current operating constraints.

For this pilot program the mobile pilot unit was used to treat overflow from the HDS clarifier. A schematic showing how the Sulf-IX™ pilot was integrated with the scrubber flow sheet is shown in **Error! Reference source not found.**Figure 3. A full scale Sulf-IX™ unit would be positioned in the overall flow sheet in a similar manner.
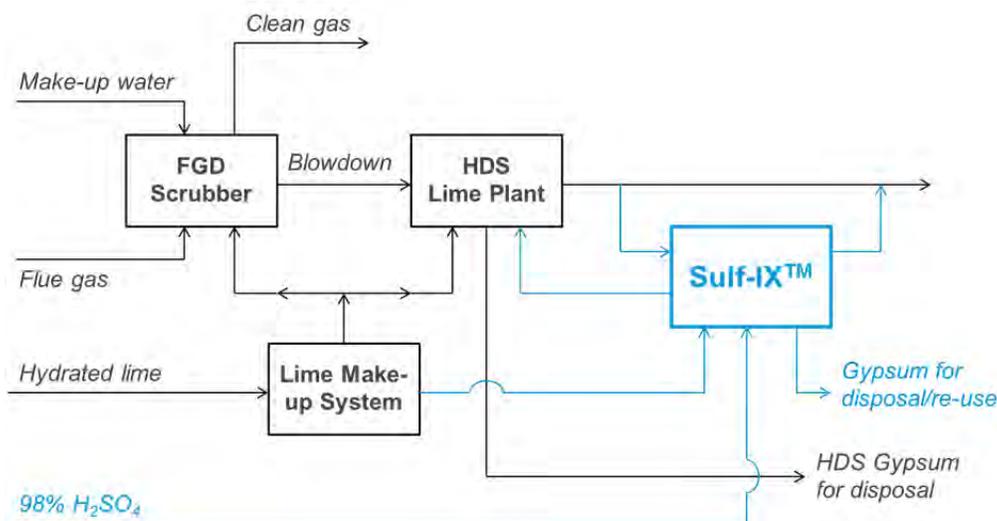
Figure 3 – Schematic Flow Sheet of Sulf-IX™ Integration with FGD Scrubber

DISCHARGE REQUIREMENTS. Plant personnel conduct regular sampling and water analysis of feed water and scrubber thickener overflow and use this data as the basis for environmental reporting of sulfate and hardness as required by the permit.

Table 2 summarizes the annual averages for hardness and sulfate in these streams in 2011 and 2012, and the mass of sulfate and hardness that must be removed on an annual basis in order to bring the scrubber line into regulatory compliance.

Table 2 – Sulfate and Hardness Balance Across Refinery Scrubber

| Yearly Average | Scrubber Make-Up | | | pH | Scrubber Thickener Overflow | | | Removal Needed | |
|---|---|---|---|---|---|---|---|---|---|
| | Hardness | Sulfate | Flow rate | | Hardness | Sulfate | Flow rate | Hardness | Sulfate |
| | mg/L as CaCO$_3$ | mg/L | gpm | | mg/L as CaCO$_3$ | mg/L | gpm | kg/day as CaCO$_3$ | kg/day |
| 2011 | 1,183 | 880 | 145 | 11.8 | 3,374 | 1,379 | 111 | 1,109 | 139 |
| 2012 | 1,136 | 847 | 138 | 10.8 | 2,591 | 1,612 | 96 | 503 | 207 |

The difference in operating strategy between 2011 and 2012 is notable. In 2011 the HDS thickener was operated at a higher pH set point than in 2012. During 2011 additional lime was added in order to decrease sulfate concentrations in the circulating process water. This strategy was successful in reducing the sulfate concentration by 233 mg/L, but also resulted in a 783 mg/L increase in water hardness. Additionally, this strategy led to an increase in lime consumption.

While both compositions of thickener overflow are appropriate feed water for Sulf-IX™, the 2012 operating strategy of a lower pH was more effective in terms of reducing hardness and sulfate while reducing reagent consumption.

# SULF-IX™ PILOT RESULTS

HARDNESS AND SULFATE REMOVAL. During piloting, the upstream lime HDS circuit generating feed water for the pilot was operated at a variety of pH set points. The pH of the feed water does not directly influence the performance of the Sulf-IX™ circuit, but changing the pH set point of the thickener changes the composition of the feed water by precipitating more or less magnesium.

Magnesium is present in the feed to the HDS circuit in concentrations of 300-400 mg/L. Consequently, magnesium accounts for approximately 40% of the water hardness in the feed to the HDS circuit. By changing the pH set point of the thickener, more or less magnesium can be precipitated, with 75% of the magnesium precipitated at pH 9.5 and 99% precipitated at pH 10.6. By increasing the pH of the thickener, magnesium hardness in the water is effectively exchanged for calcium hardness which improves the performance of the Sulf-IX™ process because the SAC resin used in the cationic Sulf-IX™ circuit is selective for calcium over magnesium.

This result can be seen in Figure 4, which shows the relative amount of sulfate and hardness removed from feed water by Sulf-IX™ as a function of feed water pH. The values in Figure 4 were drawn from 8-24 hour composite samples of treated water from the pilot. The relative removal of hardness from the water is highest at approximately pH 10.6, when virtually all magnesium has been precipitated. When the thickener overflow pH was in excess of 11, the Sulf-IX™ circuit removed a similar absolute amount of hardness from the feed water as at lower pH, but the demand on the circuit was increased. In terms of Sulf-IX™ performance and overall hardness and

sulfate gain, the optimal pH for the thickener was found to be ~10.6. At this pH level the majority of magnesium is precipitated and water hardness is largely present as calcium.

The form of water hardness also affects the anionic circuit of the Sulf-IX™ process. Cation exchange introduces protons into solution and allows removal of sulfate by WBA resin in the anionic stage of the Sulf-IX™ process (equations 2 and 3). When the thickener was operated at a pH set point lower than 10, magnesium was left in solution and a significant portion of the total hardness simply passed through the cation stage without producing protons. The lack of protons in the cation stage discharge then limited the extent of sulfate removal in the anion stage. As a result, when water hardness is present as magnesium, both hardness and sulfate removal are hindered.

This can be clearly seen in Figure 4 and Figure 5, where the hardness and sulfate removal follow similar trends as a function of thickener pH. The main reason for the scatter in the pilot data presented in Figure 4 and 5 is the fact that the pH control in the HDS lime neutralization plant was subject to frequent upsets caused by lime supply interruptions, drifts in pH measurement due to scaling, and the large size of the lime plant clarifier which resulted in a major delay between changes in pH set point and the achievement of the desired water quality. The average amount of hardness and sulfate removal from feed at optimal pH is shown in Table 3.

Table 3 - Pilot Results on Optimal Feed

| Removal Targets | | Pilot Test Results | |
|---|---|---|---|
| Hardness | Sulfate | Hardness | Sulfate |
| kg/day as CaCO₃ | kg/day | kg/day as CaCO₃ | kg/day |
| 503 | 207 | 773 | 299 |
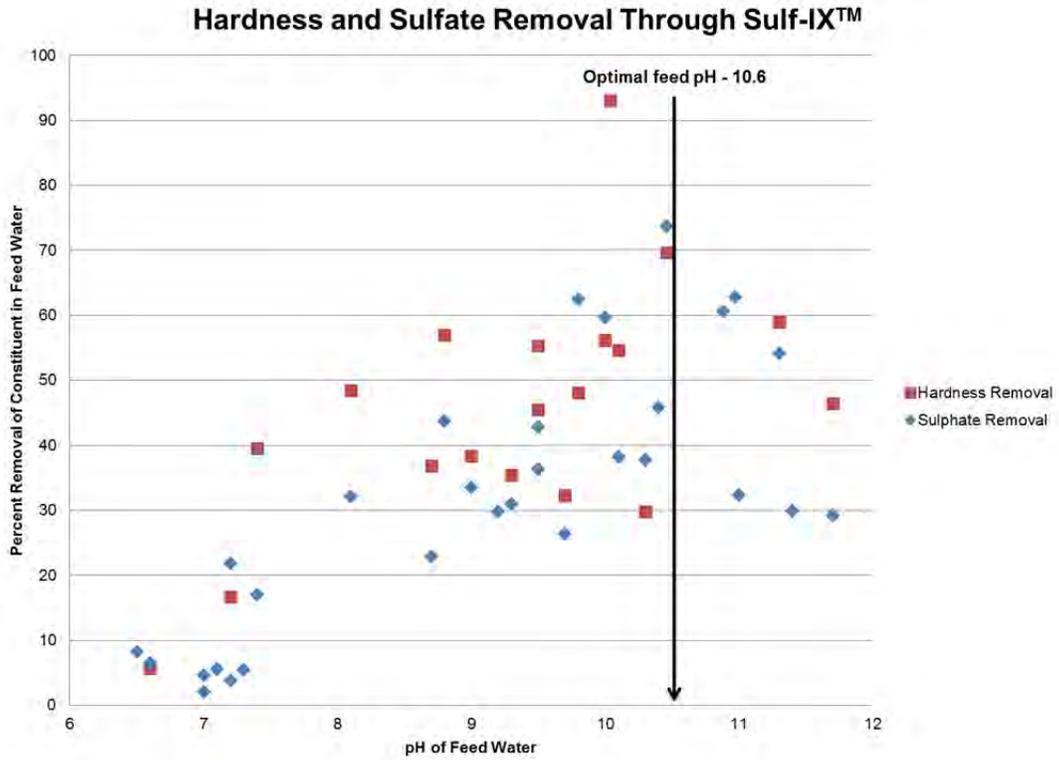
Figure 4 – Hardness and Sulfate Removal Through Sulf-IX™ Relative to Feed Water Composition
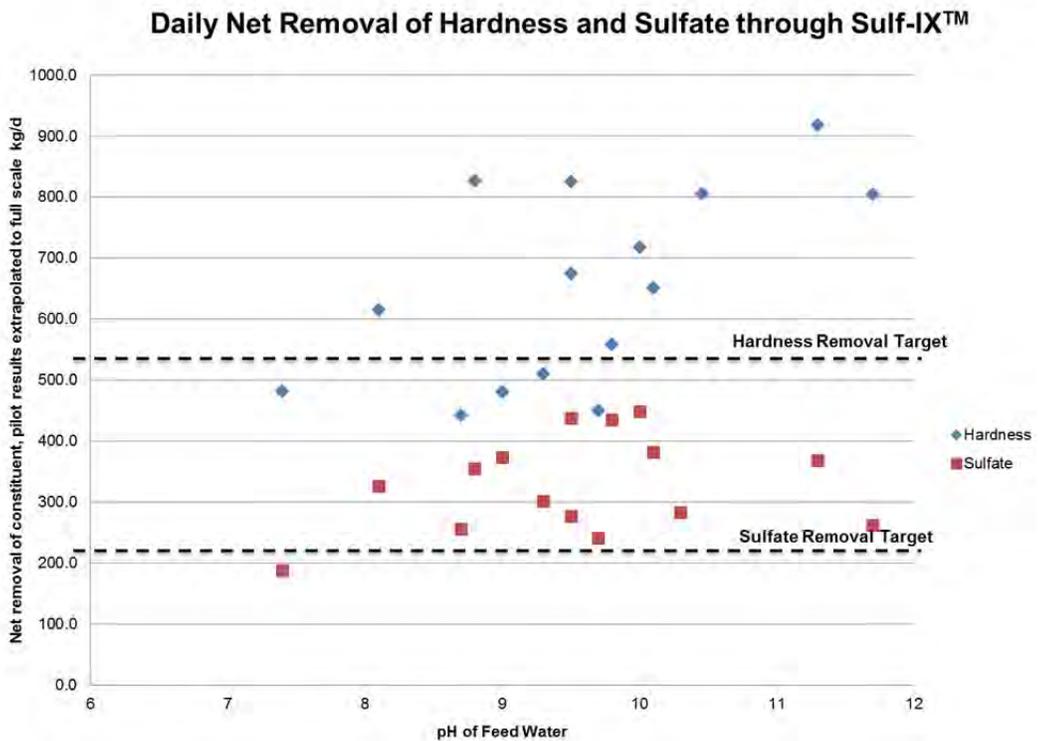


Figure 5 – Net Removal of Hardness and Sulf-IX™ Results Extrapolated to Full Scale Implementation

Figure 5 shows the equivalent daily net removal of hardness and sulfate as a function of feed water pH. Figure 5 also shows the amount of hardness and sulfate removal needed in order to meet the hardness and sulfate discharge requirement set by the plant's operating permit. It can be seen that for the majority of the pilot run the necessary removal of hardness and sulfate was achieved. The ability of the Sulf-IX™ circuit to achieve the necessary removal was related to the pH of the feed water – when the pH set point of the thickener overflow was lower than 9.5 a significant amount of water hardness was due to magnesium that was not precipitated in the lime HDS circuit. The presence of magnesium limited the removal of both hardness and sulfate. However, when feed water was in the range of 10-11, the circuit reached and exceeded the amount of hardness and sulfate removal necessary. Both Figure 4 and Figure 5 clearly show the importance of integrating the lime HDS circuit and the Sulf-IX™ process in order to meet discharge requirements.

GYPSUM QUALITY. A sample of the gypsum product produced during Sulf-IX™ pilot operations at the plant was subjected to a TCLP test by a third party analytical laboratory. The results of this analysis are provided in Table 4.

Table 4 – TCLP Results of Sulf-IX™ Gypsum Product

| Metal Species | TCLP Result | TCLP Limit |
|---|---|---|
| | µg/L | µg/L |
| Arsenic | <10 | 5,000 |
| Barium | 53 | 100,000 |
| Cadmium | <2 | 1,000 |
| Chromium | <50 | 5,000 |
| Lead | 88.2 | 5,000 |
| Selenium | <20 | 1,000 |
| Silver | <2 | 5,000 |
| Mercury | <0.2 | 200 |

The TCLP showed the solids to be non-toxic and non-hazardous. As a result, the gypsum product is appropriate for disposal as non-hazardous solid waste or for re-use as building product in-fill or as feed for fertilizer production.

SAFETY. Over the course of the pilot program there were no MSHA reportable incidents. This amounted to 2,604 man-hours worked without any lost time incidents.

## SCALE UP

SIZING CONSIDERATIONS. Based on the results of pilot testing, Sulf-IX™ was shown to meet and exceed the hardness and sulfate removal requirements for the plant scrubber. The maximum flow rate of the FGD scrubber blow-down for the full scale application of Sulf-IX™ is 110 USGPM. In order to implement a Sulf-IX™ circuit in the most cost effective way possible two factors must be considered: integration of Sulf-IX™ with the lime HDS circuit, and proper sizing of the cationic and anionic circuits.

From Figure 4 and Figure 5 it is clear that the performance of the Sulf-IX™ circuit is strongly influenced by the behavior of the upstream lime HDS system, largely through the behavior of magnesium. The other important factor in sizing a Sulf-IX™ circuit is the ratio of hardness to sulfate removal necessary to achieve compliance with the plant operating permit. At a hardness to sulfate ratio of 1, both the anionic and cationic circuits are the same size. From the 2012 operating data shown in Table 2, at pH 10.8 the ratio of hardness to sulfate

removal is 2.3:1. At higher pH set points the ratio becomes greater than 2.3:1 and at lower pH set points the ratio is less than 2.3:1, but always remains greater than 1. Due to the fact that hardness removal requirements will always be greater than sulfate removal requirements, it stands to reason that the most cost effective full scale Sulf-IX™ circuit for the plant would have an anionic circuit that is smaller than the cationic circuit.

It can be seen in Figure 5 that with feed water above pH 10, the Sulf-IX™ pilot plant consistently exceeded the amount of removal needed for hardness and sulfate across the scrubber. As compliance with the permit is determined on an annual basis, the plant has significant flexibility in how to implement a Sulf-IX™ circuit. A Sulf-IX™ system that exceeds the minimum removal targets may only need to operate for several months per year and/or treat only a slip stream of the total scrubber thickener overflow. Both of these options would reduce the overall treatment expense to the plant.

OVERALL LIME UTILIZATION. In order to calculate the overall operating cost of a full scale Sulf-IX™ system applied to the plant scrubber, one must consider the lime HDS and ion exchange (IX) processes together. According to operating data from the plant, lime consumption by the thickener in 2011 was 2,600 kg/day in order to reach an overflow pH of 11.8. In 2012, when the pH of the overflow was 10.8, the average lime consumption was 1,400 kg/day. Almost twice the lime was required to reach pH 11.8 compared to 10.8. This figure has important implications when an integrated thickener-Sulf-IX™ circuit is considered.

In this pilot campaign it was found that the most efficient removal of sulfate

occurred when the feed from the thickener overflow was at pH ~10.6. Given the feed and flow rate of the scrubber, a full scale Sulf-IX™ plant would consume approximately 340 kg/d lime. When the overall system is considered, the use of a Sulf-IX™ circuit to treat thickener overflow at a lower pH set point can significantly reduce the overall consumption of lime while meeting more stringent sulfate discharge requirements (

).

ECONOMICS. Based on the pilot plant data, the cost of consumables including reagents and power is expected to be approximately USD 0.45/m$^3$. This figure also includes credit for reduction in lime consumption relative to the 2011 high pH operating strategy of the refinery, which offsets costs by approximately USD 0.26/m$^3$. The break-down of the operating costs is shown in Table 6. BioteQ is currently in discussions with the customer in regards to the business model for the implementation of the full scale Sulf-IX™ plant at site including a possible supply of a transportable plant with trained operators to run the treatment plant seasonally, or the design and supply of a customized plant that would be permanently integrated into the FGD scrubbing circuit.

Table 5 – Lime Consumption of Integrated System

|  | Over flow pH | Lime Consumption kg/d | | | Net ΔSO$_4$ kg/d |
|---|---|---|---|---|---|
|  |  | HDS | IX | Total |  |
| HDS | 11.8 | 2,600 | - | 2,600 | 139 |
| HDS + IX | 10.6 | 1,400 | 340 | 1,740 | -299 |
| Potential Lime Savings (kg/day) | | | | 860 | |

Table 6 – Estimated Reagent and Power Cost of Full Scale Sulf-IX™ Circuit

| Consumables | Unit | Unit Cost (USD) | Units per day | Cost per day (USD) | Annual Cost (USD) |
|---|---|---|---|---|---|
| Sulfuric Acid | Kg | 0.33 | 613 | 202 | 73,800 |
| Lime | kg | 0.18 | 340 | 61 | 22,300 |
| Power | kWh | 0.10 | 1800 | 180 | 65,700 |
| **Total** | | | | 439 | 161,800 |
| **OPEX USD/m$^3$** | | | | 0.45 | |

CONCLUSIONS

Sulf-IX™ process technology for the removal of hardness and sulfate from FGD effluent was piloted on-site at an US metallurgical plant. The objective of the pilot was to remove sufficient hardness and sulfate from FGD effluent to meet site specific permitting requirements across the scrubber circuit.

Results from the two pilot campaigns demonstrated that the Sulf-IX™ process could improve hardness and sulfate removal to meet the permit requirements for these constituents. An oversized transportable Sulf-IX™ plant would give the site owner the flexibility to operate for several months of the year and/or treat a slipstream of the FGD effluent. Each option provides the owner the ability to reduce overall treatment costs.

The pH set point of the upstream lime HDS circuit was an important factor in the operation of the Sulf-IX™ pilot, with the most cost effective removal of hardness and sulfate occurring with a pH set point of approximately 10.6. The results of the pilot indicate that an overall reduction in lime consumption can be achieved through integration of the HDS and Sulf-IX™ circuit while at the same time reaching compliance targets.

Piloting findings indicate the flexibility of Sulf-IX™ to be integrated with upstream processes and for the ability of the technology to be tailored to fit specific permitting requirements.