Sulf-IX™: Water Treatment Utilizing Fluidized Resin Beds

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Introduction

Ion Exchange (IX) columns are often operated as a packed bed for the removal of ions from a liquid stream, however utilizing a fluidized resin bed within an IX column comes with many advantages and challenges. The Sulfate Ion Exchange (Sulf-IX™) process capitalizes on these advantages to remove calcium associated sulfate from groundwater.

The Sulf-IX™ technology was originally developed by Chemeffco in South Africa and was known as Gypsum-Continuous Ion Exchange (Gyp-CIX). The process was re-engineered by BioteQ Environmental Technologies, Inc. and renamed the Sulfate-Ion Exchange (Sulf-IX™) process. Freeport-McMoRan Inc. (FMI) took an interest in Sulf-IX™ as part of an effort to develop an expertise in technologies for mine water treatment and constructed a 100gpm Sulf-IX™ demonstration plant. After three years of operation at the company's Water Treatment Test Facility, the plant underwent major modifications in 2014 to operate at 20% nominal flow in order to test critical design criteria. The test program was completed by the third quarter of 2014. Results from this program were the driving force behind the redesign of the fluidized bed columns by FMI and BioteQ team members. FMI is moving forward with the revised process by reconstructing the demonstration plant to operate at the modified design parameters.

Process Overview

The Sulf-IX™ technology is a continuous flow, two-step process for removing calcium associated sulfate from groundwater. Groundwater first passes through the cationic circuit where a strong acid cation (SAC) resin exchanges two hydrogen ions for a calcium ion, as shown in equation 1.

$$Ca_{2+} + 2RH \gg 2RCa + 2H_{+} \qquad (1)$$

The effluent from the cationic columns is then transferred to the anionic circuit. The cationic effluent, now the anionic feed, enters the anionic columns which contain a weak basic anion (WBA) resin for the removal of the H_2SO_4 molecule now present in the water, as shown in equation 2.

$$2H_{+} + SO_4{}^{2-} + R \gg RH_2SO_4 \qquad (2)$$

The anionic effluent is discharged from the plant with both calcium and sulfate levels greatly reduced. Once the cationic and anionic resin beds reach their respective working capacities the regeneration cycle begins. The cationic regeneration solution consists of a dilute sulfuric acid solution, which strips the SAC resin of calcium and replaces it with two hydrogen ions. The anionic regenerant solution is a lime solution which releases the H_2SO_4 from the WBA resin. Each spent regenerant solution is sent to its respective solids handling loop to relieve the gypsum super-saturation and replenish the regenerant solution prior to the next regeneration cycle. As part of the process the solution passing through the fluidized bed changes depending on the current cycle, however the resin remains in the same column for the entire process.

This is the advantage that the fluidized bed provides over the packed bed for the Sulf-IX™ process; the ability to pass a super-saturated gypsum solution through the resin bed without clogging or clumping. Fluidizing the resin allows complete removal of gypsum particles from the column without the need to remove the resin and separate the gypsum through a different process.

Results

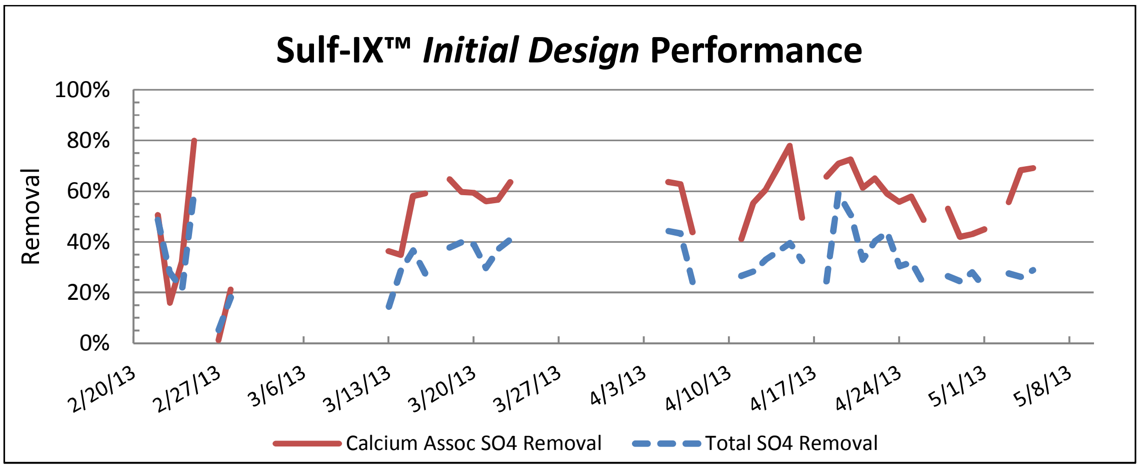

Figure 1. Data from Sulf-IX™ "Initial Design" from Feb. 2013 – May 2013

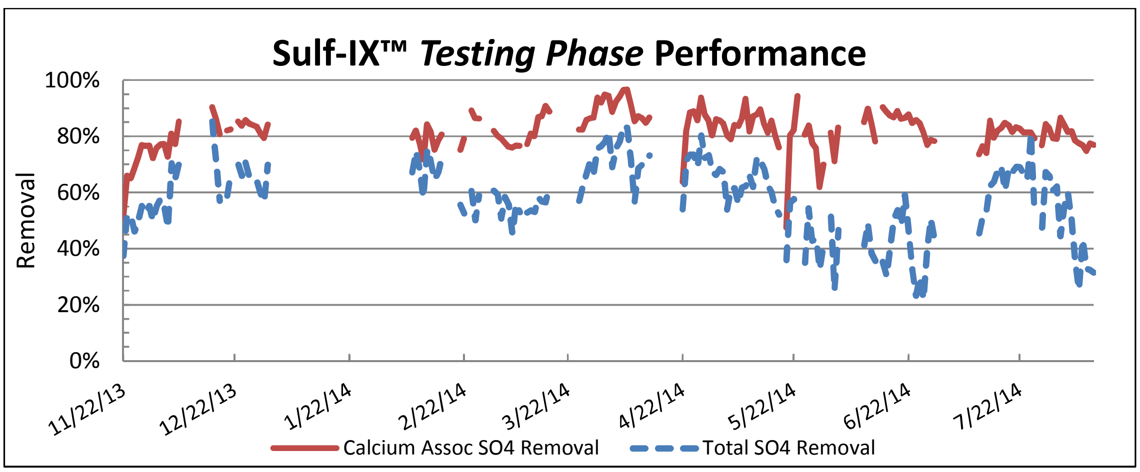

Figure 2. Data from Sulf-IX™ "Testing Phase" from Nov. 2013 – Aug. 2014

The above graphs represent data from daily 24 hour composite samples, the gaps in data correlate to down time for configuration changes, process modifications, maintenance and repairs. The “% removal” indicates the percentage of sulfate removed from the groundwater by the time water is discharged from the plant. Average groundwater feed to the plant was approximately 1500 mg/L SO_4, 450 mg/L Ca, and 95 mg/L Mg.

Discussion

The Sulf-IX™ technology has the ability to consistently remove calcium associated sulfate. However, a significant amount of other cations in the solution, such as magnesium or sodium, will reduce the overall efficiency of the process by competing with calcium on the SAC resin. The effect of magnesium can be minimized through a pre-treatment step.

The results from the testing phase (20% nominal flow) produced critical data on how to optimize solids removal from the columns and maximize efficiency in both the cationic and anionic phases. Key improvements in the cationic phase led to a 50% decrease in cationic reagent consumption which improved overall plant efficiency by decreasing the sulfate bleed to the anionic phase.

The key to any process is to produce results at a low cost. Using historical operating data from the Sulf-IX™ plant, FMI conducted a comparison of the lifecycle cost between Sulf-IX™ and Reverse Osmosis (RO) with solar evaporation. The comparison showed that potentially Sulf-IX™ could be more economical than RO because of the elimination of costly sludge and brine disposal. Further details of the cost analysis will be included in the presentation.

Conclusions

It has been demonstrated through the operation and testing of the reduced column size that the Sulf-IX™ technology can be successful. Next the process must maintain the high efficiency at a demonstration plant flow of 90gpm. The Sulf-IX™ technology is potentially applicable at various sites across the country where there is a gypsum saturated water concern. This process would transform contaminants from a liability to a resource rather than generating further hazardous wastes, as is the case were these waters to be treated with RO and evaporation ponds. The Sulf-IX™ process would remove calcium associated sulfate below 500ppm while producing a non-hazardous material that could be landfilled or marketed as a by-product gypsum. Sulf-IX™ could provide a new option for treatment of sulfate impacted water that would decrease the risk and liabilities associated with the contaminants while reducing costs compared to what is currently available.