

An Innovative Process to Reduce Sulfate in Membrane Concentrate Enhances Mine Water Recovery

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ABSTRACT

A treatment process was developed to reduce sulfate from nanofiltration (NF) concentrate to less than 100 mg/l. The treatment system is comprised of a two-stage chemical precipitation process. The impacts of sludge recirculation ratio, pH and chemical dosages were investigated. Calcium sulfate crystal growth kinetics was determined. Bench and two pilot-scale studies were conducted to evaluate the performance of the system. The studies also evaluated the performance of an NF system for removing sulfate from copper mine tailing pond water. Using the ion chromatography (IC) method, the concentration of sulfate in water was analyzed. Membrane performance was evaluated at various flux rates, water recovery rates and trans-membrane pressures. The process recovers more than 95% aluminum from the precipitated sludge for reuse. Based on the two pilot study results, a preliminary concept was developed. The innovative process increased overall water recovery significantly.

Keywords:

Sulfate; membrane concentrate; precipitation; calcium sulfoaluminate; water reuse

INTRODUCTION

The high solubility and stability of sulfate ions in aqueous solutions make processes for removal of this anion from water to low levels extremely complex. The application of nanofiltration (NF) for sulfate reduction is becoming popular with the promulgation of new regulations and increased interest in water reuse. However, handling of the NF concentrate with high sulfate is problematic. State-of-the-art sulfate treatment technology includes chemical precipitation, biological degradation, adsorption and/or ion-exchange, and membrane (nanofiltration and reverse osmosis) processes. Each of the processes is discussed in detail by Silva et al. (2010). Under favorable reaction conditions (water with low ionic strength), the desaturation process generates effluent containing about 1,800 mg/l of sulfate (as SO₄). The major drawback of the biological reduction of sulfate is the generation of sulfide gas, a long residence time, and the metabolic waste products, which are difficult to handle. Evaporation/crystallization is an energy-intensive process. Ion exchange produces regenerants containing extremely high concentrations of sulfate, which are also difficult to handle. Therefore, a sulfate removal technology that can reduce the sulfate concentration in the treated effluent of the desaturation process down to a low level (say <100 mg/L) is needed.

The primary objectives of this project were to determine and validate an appropriate membrane (NF) process to reduce the sulfate concentration in the water as well as to establish an innovative sulfate treatment technology for the membrane reject. The treated effluent then could be blended with the NF permeate to achieve a higher water recovery for reuse.

METHODOLOGY

Initially, a treatability study was conducted to validate the proposed sulfate treatment system and to generate data that were used as baseline information for the on-site pilot-scale experiment.

Wastewater Sampling and Characterization

Samples were collected from the tailings pond of a copper mine site. The analytical results of the “as-received” sample are presented in Table 1. All metals were analyzed using the Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS) method, and sulfate was analyzed using the Ion Chromatography (IC) method.

Table 1 Characteristics of Untreated Pond Water

Parameters	Concentrations
pH, S.U.	7.4
Total Alkalinity , mg/l CaCO ₃	28
TDS, mg/l	3070
Turbidity, NTU	1.41
TOC, mg/l	2.4
Chlorides, mg/l	66.8
Sulfate, mg/l	1,830

Calcium, mg/l	692
Iron, mg/l	0.01
Magnesium, mg/l	21.1
Manganese, mg/l	0.17
Molybdenum, mg/l	0.25
Potassium, mg/l	124
Sodium, mg/l	104

Laboratory-Scale Study

Using the actual pond water sample from the mine site, a laboratory study was conducted, including molybdenum removal, SDI reduction followed by NF for sulfate reduction, and treatment of the NF concentrate.

Molybdenum Removal and SDI Reduction

To ensure a molybdenum concentration below 0.05 mg/l, iron (as Fe³⁺) was added under slightly acidic condition (pH between 6.0 and 6.5), and SDI was reduced to <3 by adding a polymeric flocculent.

Sulfate Removal with NF

After pretreatment, the pH of the NF feed water was adjusted to about 7.5. The membrane was operated at a 60% water recovery rate. An antiscalant was used to protect the membrane from scaling. Samples were collected from the permeate and the reject line, and the trans-membrane pressure (TMP) was noted. The treated samples were analyzed for sulfate, calcium, conductivity, total dissolved solids (TDS), and other pertinent cations and anions. The detailed laboratory study procedures are presented elsewhere (Banerjee et al., 2012).

NF Reject Treatment

Sulfate present in the NF reject at a high concentration was removed as a precipitate of calcium sulfate by the desaturation process. The study was conducted in a continuous system for two weeks using Veolia Water's proprietary Turbomix[®] reactor (a draft-tube, high-speed reactor). A detailed description of the Turbomix reactor is provided elsewhere (Banerjee et al., 2010). The reactor was equipped with a sludge recirculation system. NF reject was pumped into the reactor where calcium ion was added. Lime or a combination of lime and calcium chloride was used as the source of calcium ions. The precipitation reaction was performed in the presence of a seed material. After precipitation, solids were separated from the liquid in a clarifier. A portion of the sludge was recycled back to the reactor, and the other portion was dewatered. Samples of the clarified effluent were filtered through 0.45-μ paper and analyzed for calcium and sulfate.

The effluent from the above process was further treated with aluminum-based salt to precipitate sulfate as a highly insoluble calcium sulfoaluminate mineral. A high-speed Turbomix[®] reactor was also used in this case. At a specified sludge recirculation ratio, a sulfate removal kinetic study was conducted. Calcium sulfoaluminate mineral was separated from the clear water, and aluminum ion was regenerated from the sludge, after pH adjustment, and recycled back to the process.

Pilot-Scale Study

Based on the laboratory study results, a 1.3 l/s (4.5 m³/hour) pilot unit was designed and constructed. Pilot studies were conducted for about two months. The general process flow diagram of pilot study is included in Figure 1. The pretreatment included iron coagulation, gravity separation, and a Multimedia Filter (MMF). The NF system was comprised of three 200-mm-diameter elements (two DOW 90 – 400 elements and one DOW 270 – 400 element). The unit was run at three different flux rates ranging between 22 and 30 l/mh, and was operated continuously (24 hours/7 days a week) at 350 percent CaSO₄ saturation. Using lime and calcium chloride in the presence of a seed material, sulfate from the NF reject was desaturated in the first-stage high-speed Turbomix[®] reactor. Under the same process condition, about 80% of the samples were collected and analyzed three times to check the reproducibility of the results. Using a HACH kit, sulfate was analyzed at the site, and Ion chromatography method was used to determine sulfate concentration in the laboratory. Using water from a coal mine site, the 2nd set of pilot study was conducted. A similar sampling, analytical, and replication procedures were followed as described above.

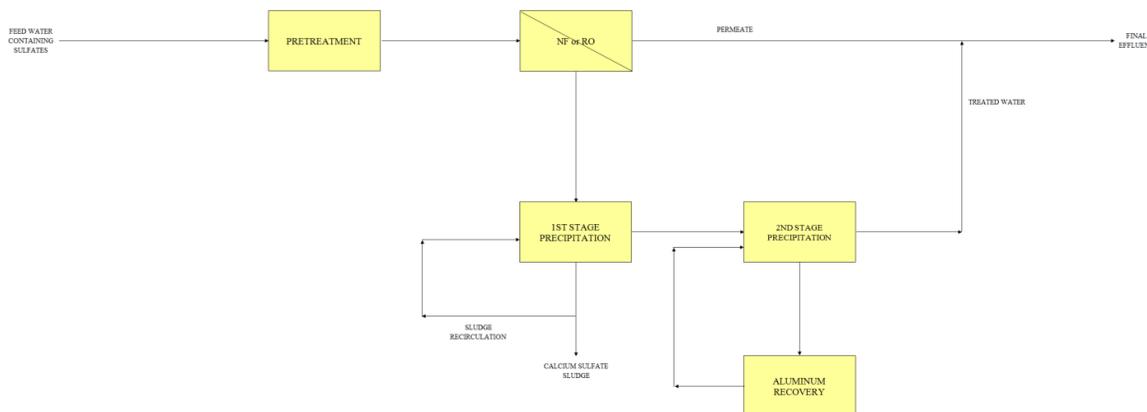


Figure 1 Pilot Flow Diagram

RESULTS AND DISCUSSION

Laboratory-Scale Study

The average calcium and sulfate concentrations in the NF feed water were 640 (as Ca²⁺) and 1,600 mg/l (as SO₄²⁻), respectively. More than 98% of the sulfate was rejected at the 60% water recovery rate. The average concentration of sulfate in the permeate was about 25 mg/l. Increasing the membrane flux rate did not affect the permeate quality significantly. The concentration of calcium in the NF reject at the 60% water recovery rate varied between 1535 and 1550 mg/l, and that of sulfate ranged between 3,500 and 4,100 mg/l. Results of the laboratory-scale membrane performance are shown elsewhere (Banerjee et al., 2012).

The results of calcium sulfate desaturation kinetics in the presence of seed material with sludge recirculation are shown in Table 2. As the table illustrates, sulfate in the treated water was reduced from 4,000 (average concentration) to 1,300 mg/l, which is less than the theoretical solubility limit of

1,800 mg/l as dissolved sulfate. The results also reveal that without the sludge recirculation, sulfate was reduced to about 2,000 mg/L. The seed material was added only once (during the process start-up). Detailed laboratory study results are presented elsewhere (Banerjee et al., 2012).

Table 2 Sulfate Removal after Calcium Sulfate Precipitation/Adsorption using Lime and Calcium Chloride, or Lime only, with Seed Material in a Sludge Recirculation System

Sludge Recirculation Ratio	20:1	15:1	10:1	15:1*	0*
pH	9.3	9.3	9.2	12.0*	12.0*
Dissolved Sulfate, mg/L	1,350	1,100	1,200	1,100*	2,000*

*This experiment was conducted only with lime.

The data show that sludge recirculation and seeding have a significant impact on the calcium sulfate desaturation process. The seed material used in this process has a highly reactive surface, which increases the reaction driving force and the available free energy of the system. It is anticipated that besides chemical precipitation, sulfate ions present in the NF reject are adsorbed onto the reactive surface of the seed material as well as onto the freshly precipitated calcium sulfate solids. Additionally, increased crystal growth of the precipitated solids takes place in the presence of the seed material.

Pilot-Scale Study

The sulfate concentration in the raw water ranged between 1,800 and 2,900 mg/l (average 2,300 mg/l). During the study, the sulfate concentration in the raw water increased by about 30%. The calcium concentration in the raw water did not change significantly, and the average turbidity in the water was about 25 NTU. After pretreatment, iron, manganese, molybdenum, and SDI were reduced to <0.3mg/l, <0.05mg/l, <0.05mg/l, and <3, respectively. Since the raw water contained a higher sulfate concentration, initially the NF was run at 50% water recovery to avoid scaling; after that, it was operated for two weeks at a 60% water recovery rate with an increased antiscalant dosage.

Sulfate and calcium rejection data are presented in Figures 2 and 3. As Figure 2 shows, about 98.5% of the sulfate was rejected, and sulfate in the NF permeate ranged between 25 and 55 mg/l. The average sulfate concentration in the permeate was 35 mg/l. The percent rejection of calcium ranged between 90 and 99% (see Figure 3). Calcium in the NF permeate ranged between 10 and 60 mg/l. Sulfate rejection showed a very stable line in the high 90's (Figure 1) in comparison to calcium rejection (Figure 2). Since the membrane surface is negatively charged, the membrane primarily rejects sulfate, and because of ion pairing, the sulfate holds back the positively charged calcium and magnesium ions from passing through the membrane.

Sulfate treatment results for NF concentrate by the desaturation process are presented in Figure 4. In this process, sulfate was removed through gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) precipitation using a combination of lime and calcium chloride under a controlled pH at a specified sludge recirculation ratio within 30 minutes of reaction in the presence of seed material, which was added one time during the study. During the desaturation process, utilizing a Turbomix™ reactor and MULTIFLO™ technology, sulfate was reduced to less than 1,500 mg/l.

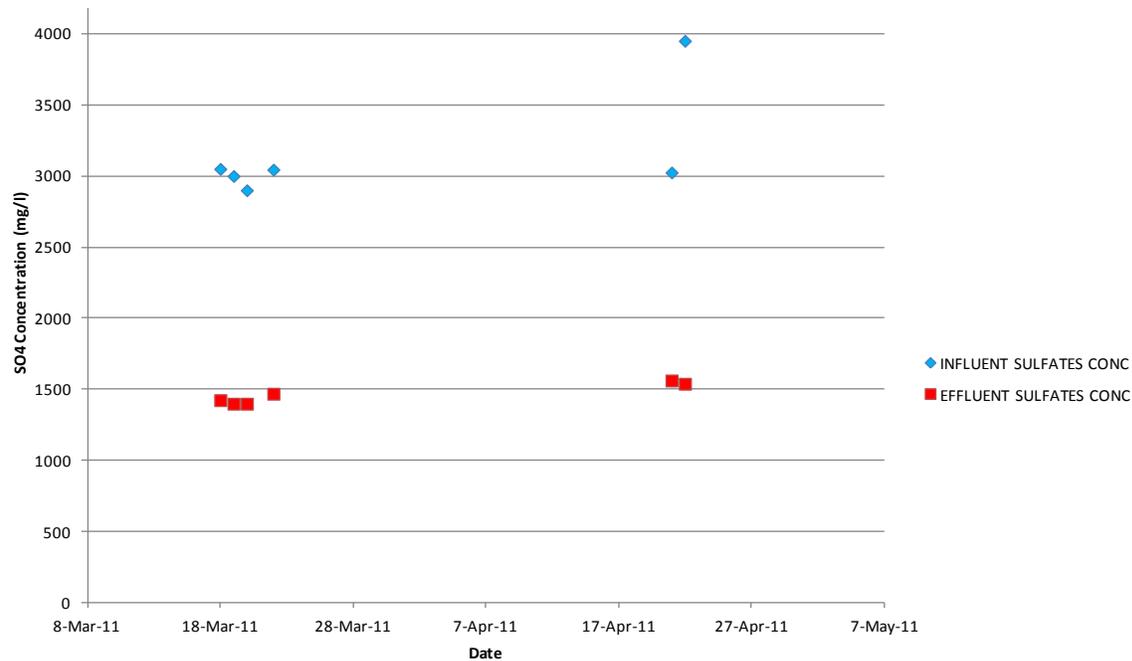


Figure 4 CaSO_4 Desaturation with Sludge Recirculation and with Seed Material

Further Reduction of Sulfate by Calcium Sulfate Complexation

Dissolved sulfate from the desaturated calcium sulfate effluent was further reduced by forming an insoluble complex known as calcium sulfoaluminate mineral. The associated chemical dosages and sludge recirculation ratios were determined from the preliminary laboratory study results. Sulfate reduction kinetics results for the most efficient recirculation ratio are shown in Figure 5.

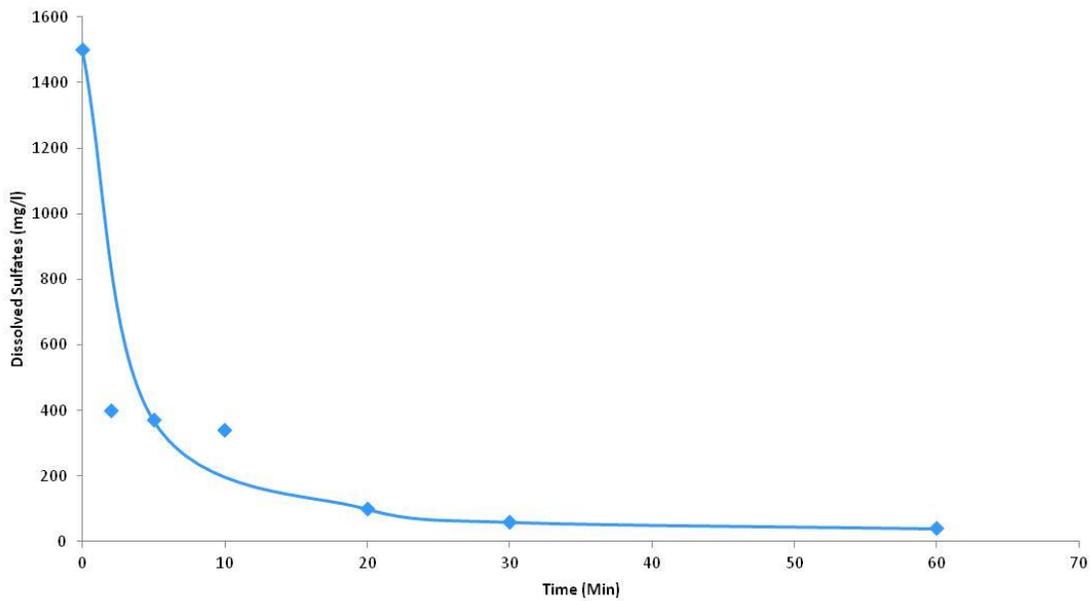


Figure 5 Sulfate Precipitations Kinetics as Calcium Sulfoaluminate Mineral

As the figure illustrates, increasing the reaction time decreased the sulfate concentration, and the reaction was completed within 20 minutes. During that period, dissolved sulfate was reduced to <100 mg/l.

As indicated earlier, using the water from a coal mine site, the 2nd set of pilot study was conducted. The primary objective was to recover aluminum from calcium sulfoaluminate (Ettringite) sludge, and reuse that in the process. The study was conducted for a period of 16 weeks. Freshly prepared tri hydroxide of aluminum (Gibbsite) was used for the first two weeks of the study to precipitate sulfate as the Ettringite mineral. Once the system reached to the steady state condition, regenerated tri hydroxide of aluminum was used for Ettringite precipitation.

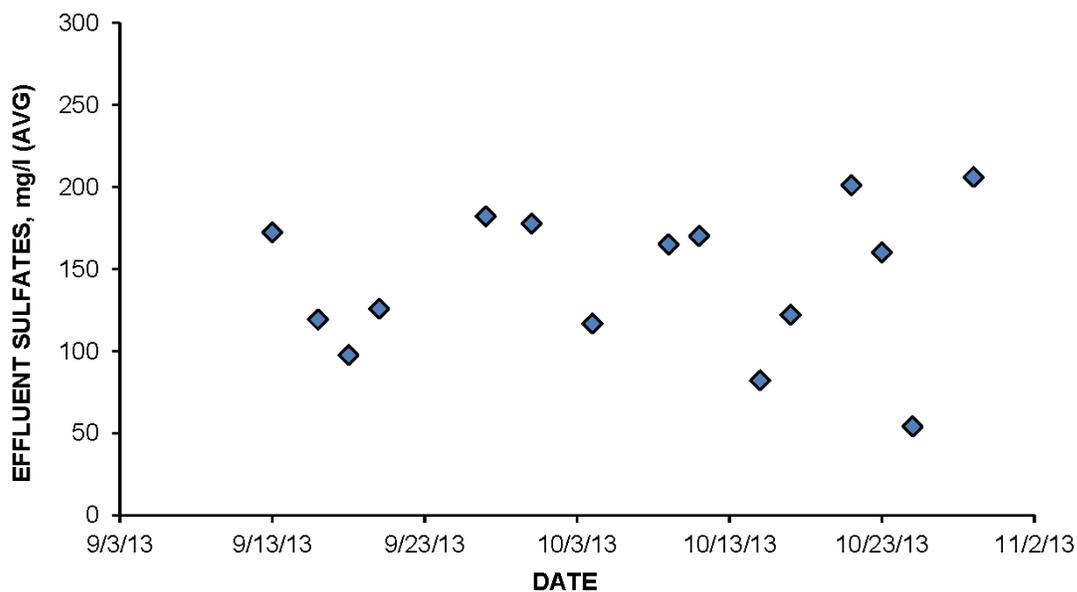


Figure 6 Effluent Sulfate with Regenerated Gibbsite

As indicated in Figure 6, after solid/liquid separation, sulfate was reduced to <100 mg/L. The particle size distribution results (not shown in the paper; will be included in the presentation) revealed that the average particle diameter of the Ettringite solids is 20 μ , and more than 1% of the particles have the diameter less than 1 μ . Consequently, carry-over of the fine colloids of Ettringite has contributed to elevate the sulfate results. It is anticipated that with adequate sludge recirculation, the solids carry-over problem would be under control. Dissolved aluminum in the treated effluent ranged between 0.1 and 0.35 mg/L (see Figure 7).

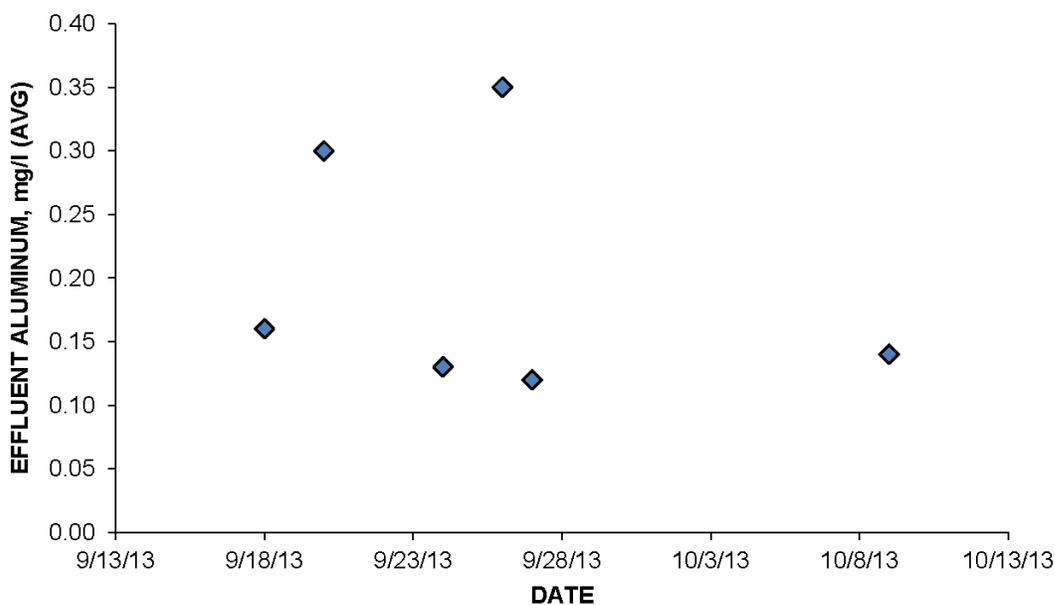


Figure 7 Aluminum in the Treated Effluent

Aluminum from the calcium sulfoaluminate precipitate was recovered by dissolving this mineral in acid. After solid/liquid separation, more than 95% of the aluminum-based salt was recovered and reused to precipitate calcium sulfoaluminate for sulfate reduction.

Based on the pilot-scale results, a flow and mass balance calculation was performed, and a conceptual process was proposed (see Figure 8). The process includes pretreatment for iron, manganese, molybdenum, total suspended solids (TSS), and other pertinent contaminants followed by NF for sulfate removal and sulfate reduction from NF reject by a two-stage chemical precipitation process. The flow and mass balance calculation for this specific site revealed that after blending the treated NF reject with the permeate, the overall water recovery increased from 60 to 90%.

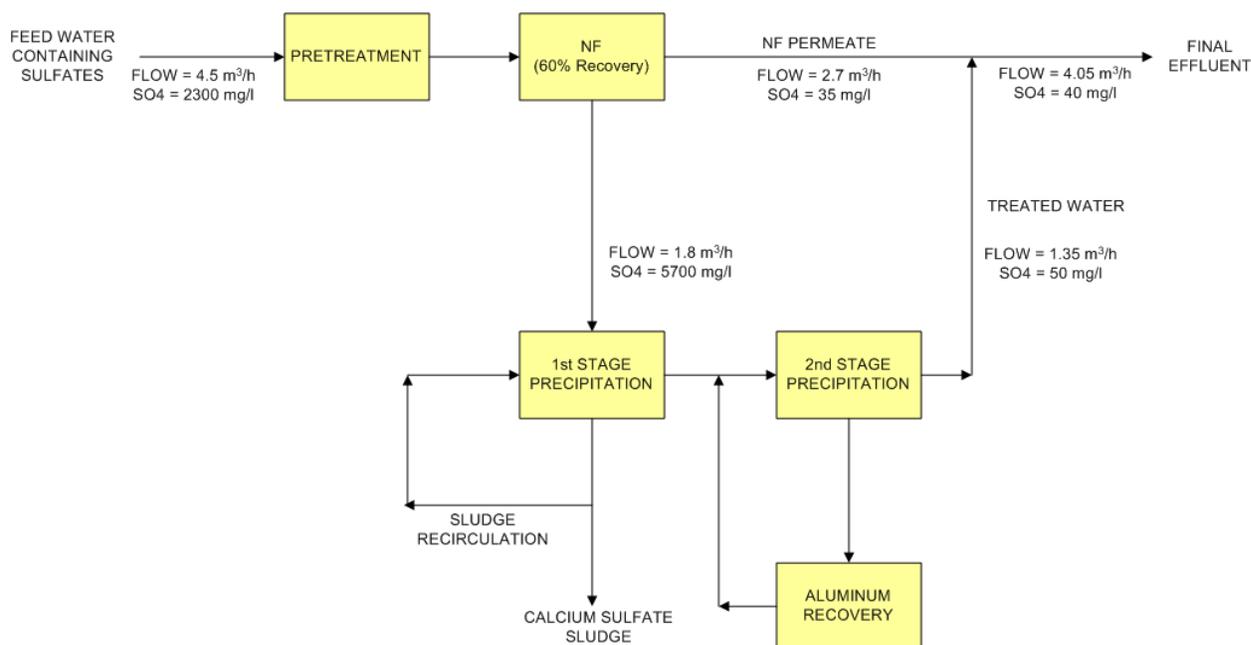


Figure 8 Process Flow Diagram

CONCLUSION

Sulfate from the NF reject can be reduced to less than 1,500 mg/l by a chemical precipitation and/or adsorption process in the presence of a seed material with sludge recirculation. Calcium sulfate crystal growth can be accomplished in a continuous system with a specified reaction time and sludge recirculation ratio. The sulfate concentration can be further reduced to less than 100 mg/l by a calcium sulfoaluminate precipitation process. The crystal growth and precipitation reaction kinetics of this process are fast and can be accomplished within 20 minutes of reaction. More than 95% of the aluminum was recovered and reused. This innovative concept increased overall water recovery significantly.

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