Designing a Mine Water Treatment Facility to Remove Sulfate

H. C. Liang, Joseph Tamburini and Frank Johns
Tetra Tech, USA

ABSTRACT

Due to the effects of weathering and oxidation of sulfide–containing ores, acid rock or acid mine drainage (ARD or AMD) from mining activities can generate sulfate–contaminated waters. Although sulfate has long been considered relatively harmless to human health and to the environment compared to other contaminants common in ARD or AMD, regulations for sulfate in mine water discharge have become more common, necessitating more advanced sulfate–removal processes at many mining operations. Where they apply, sulfate discharge standards in the United States typically range between 250 and 1,000 mg/L, with proposals in certain areas to apply sulfate discharge standards as low as 10 mg/L. The presentation highlights the design of a full–scale mine water treatment facility to remove sulfate in AMD–impacted waters at a mine in North America with a design flowrate of approximately 5 million gallons per day (MGD), where the average sulfate concentration is approximately 2,000 mg/L and would need to be treated to below 600 mg/L sulfate for discharge. The evaluation of chemical precipitation for sulfate removal such as gypsum and ettringite formation as well as the use of membrane filtration and the decision processes used to arrive at the final design are discussed.

Keywords: Sulfate, ettringite, gypsum, mine water

INTRODUCTION

Sulfate (SO_4^{2-}) is often produced in acid mine drainage (AMD) as a result of exposing pyritic rocks to air due to mining activities, which leads to a cascade of reactions forming both acidity and sulfate that can be summarized by Equation 1:

$$2FeS_2(s) + 7O_2(g) + 2H_2O(l) \rightarrow 2Fe^{2+}(aq) + 4SO_4^{2-}(aq) + 4H^+(aq) \tag{1}$$

Although acid mine drainage (AMD) is a major environmental concern (Liang & Thomson, 2010), and many AMD–impacted waters contain high levels of sulfate, most mine water treatment facilities have not been designed to remove the sulfate anion. Instead, when sulfate removal does occur at mine water treatment facilities, it usually occurs as an unintended consequence of using lime to raise the pH of the solution, which provides a source of calcium ions (Ca^{2+}) to precipitate and remove some of the dissolved sulfate ions as gypsum ($CaSO_4{\cdot}2H_2O$). One of the reasons why sulfate has been mostly ignored in mine water treatment is that it is traditionally considered a benign, non–toxic inorganic contaminant. For example, the U.S. Environmental Protection Agency (U.S. EPA) has not established an enforceable primary drinking water standard for sulfate and only has a non–enforceable secondary drinking water standard of 250 mg/L for sulfate. Because of the perception that sulfate is relatively harmless, mine water treatment has typically focused more on pH adjustment and the removal of more acutely toxic inorganic contaminants such as copper, cadmium, arsenic, antimony, selenium, and other inorganic contaminants that often occur as a result of AMD instead of on sulfate removal. Recently, however, research has shown that sulfate–reducing bacteria (SRB) can generate highly toxic and bioavailable methylmercury in the environment by methylating inorganic Hg^{2+} and converting inorganic mercuric compounds into methylmercury (Jeremiason et al, 2006). In addition, research has also shown that high sulfate levels in wetlands can induce the liberation of precipitated, bound phosphates in the sediment and lead indirectly to the eutrophication of wetland systems (Lamers, Tomassen & Roelofs 1998). Because of these issues, and because sulfate typically accounts for much of the total dissolved solids (TDS) in mining–impacted waters that need to be treated to acceptably low TDS levels to reduce the impact of mining waters on the salinity of the receiving waters, sulfate removal has become much more important in mining water treatment in recent years.

METHODOLOGY

The major criteria used to select the sulfate–removal treatment process were, in order of importance: 1) Capability to remove sulfate consistently to < 600 mg/L; 2) Treatment costs, which included examining the amounts of wastes generated by the treatment process; 3) Ease–of–operations. Any treatment process that in–and–of–itself cannot practically be expected to remove sulfate to < 600 mg/L on a consistent basis was not examined further.

As the stability diagram of sulfur in water shows (Figure 1), the sulfate anion is the predominant sulfur species under most conditions encountered in surface waters. Because of the high design flowrate (~5 MGD) and fluctuating water quantities and qualities for the mine water treatment facility, it was determined that it would not be practical to pursue biological sulfate reduction. Therefore, assessment of the treatment options focused on chemical precipitation or membrane filtration to remove the sulfate.

Assessment of treatment options

Chemical precipitation to remove sulfate

Adding hydrated lime to neutralize acidic mine waters and for chemical precipitation of gypsum to remove sulfate is one of the more common practices encountered in mine water treatment. The hydrated lime ($Ca(OH)_2$) is added to supply Ca^{2+} ions for removing sulfate as gypsum, as represented by Equation 2:

$$Ca(OH)_2(s) + SO_4^{2-}(aq) + 2H_2O(l) \longrightarrow CaSO_4{\cdot}2H_2O(s) + 2OH^-(aq) \qquad (2)$$

Because gypsum is slightly soluble in water ($K_{sp} = 3.14 \times 10^{-5}$), both theoretical calculations and field results show approximately 1,500 mg/L or higher of calcium would remain dissolved in solution after gypsum precipitation treatment. Therefore, gypsum precipitation by itself would not be sufficient to meet the 600 mg/L sulfate discharge limit at this mine.

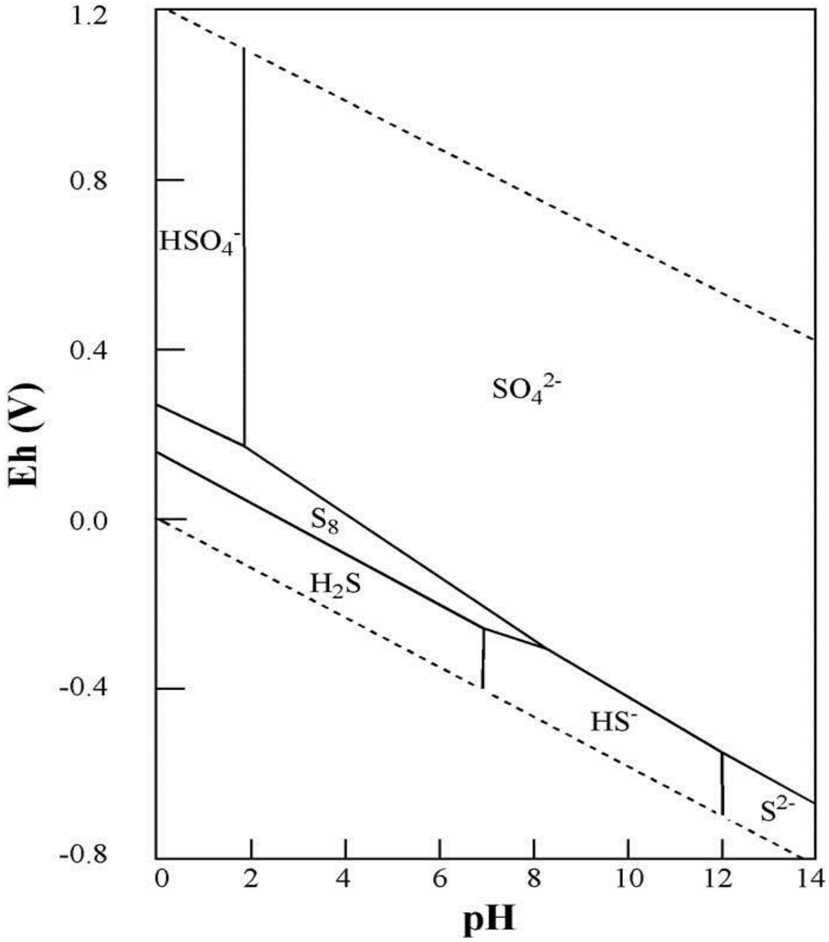

Figure 1 Stability diagram of sulfur showing the predominance of the sulfate anion in water. The dashed lines are the stability limits of water (Pourbaix, 1966)

Another chemical precipitation process, the formation of the insoluble mineral ettringite ($3CaO{\cdot}3CaSO_4{\cdot}Al_2O_3{\cdot}31H_2O$), was also explored (GARD Guide, 2014). Because ettringite is much more insoluble in water ($K_{sp} = 2.8 \times 10^{-45}$) compared to gypsum, removal of sulfate by precipitating ettringite could consistently reduce the sulfate levels to below 600 mg/L (Equation 3):

$$6Ca^{2+}(aq) + 3SO_4^{2-}(aq) + 2Al(OH)_3(s) + 37H_2O(l) \rightarrow$$

$$3CaO{\cdot}3CaSO_4{\cdot}Al_2O_3{\cdot}31H_2O(s) + 6H_3O^+(aq) \qquad (3)$$

One of the ettringite precipitation treatment processes that has been developed for sulfate removal is called the CESR process (Reinsel, 1999). In the CESR process, lime is first added to raise the pH and also to precipitate gypsum if the sulfate concentration is high enough and also to supply a calcium source to form the mineral ettringite. More lime and an aluminum reagent are then added in the next step, which results in the formation of the highly insoluble ettringite and the removal of most of the sulfate from solution (Figure 2).

Although bench scale testing showed that the CESR process can consistently remove sulfate down to < 200 mg/L, well below the 600 mg/L sulfate target (Reinsel, 1999), it was determined that CESR or similar ettringite–forming processes would not be suitable for several reasons. For example, careful examination of the stoichiometry of the ettringite formation reaction (Equation 3) shows that an exorbitant amount of sludge would be generated by the process, where more than four times the mass of sludge would be generated for every mass unit of sulfate removed. This compares to a mass ratio of less than two to one for the amount of gypsum sludge generated per mass unit of sulfate removed by the gypsum precipitation process (Equation 2).

Another reason for not considering further the CESR or related ettringite–formation processes for the full–scale mine water treatment plant to remove sulfate was because of the slow kinetics of the reaction to form ettringite using calcium aluminate as the reagent. Bench scale testing showed that it required long reaction times, up to 5 hours for completion (Liang et al., 2012). At a design flowrate of 5 MGD, a residence time of 5 hours would require more than one million gallons of capacity, which would be impractical for the full–scale water treatment system.

It should be pointed out that an ettringite–formation process using sodium aluminate as the aluminum source and hydrated lime as the calcium source to form ettringite has been developed and is reported to have much faster kinetics of ettringite formation (Outotec, 2014). Because of the large amounts of sludge generated by ettringite processes, the undesirable side effect of increasing sodium concentration in the treated water from using sodium aluminate, and the fact that the treated water sulfate concentration required at this site is not low enough to require ettringite formation, however, the ettringite process using sodium aluminate reagent was not considered either.

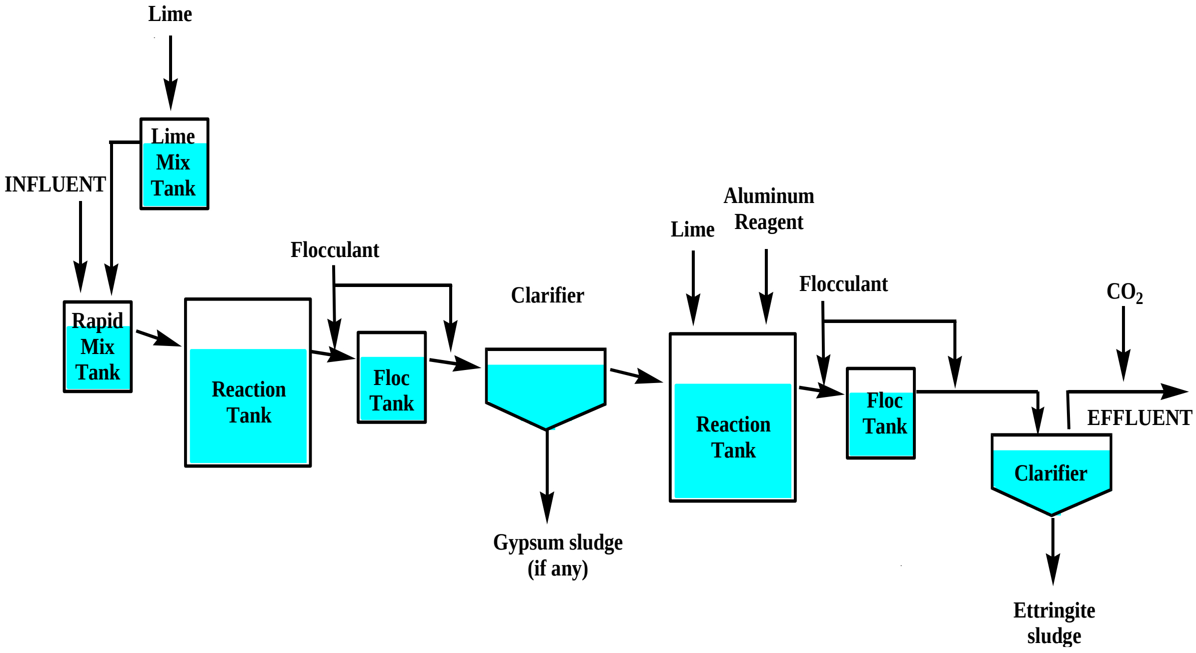

Figure 2 Schematic of CESR sulfate removal process

Membrane process for removing sulfate

Nanofiltration (NF) is also a potential option for sulfate removal for mine water treatment. NF can reject > 99% sulfate and would be able to consistently generate treated water with < 50 mg/L sulfate, much lower than the required 600 mg/L sulfate discharge target. Because of potential scaling issues on the NF membranes, especially for waters with high sulfate concentrations, pre–treatment for NF would need to be carefully considered. Another potential issue with using NF is that it would generate a lot of waste brine that would be expensive to manage. For example, at a 5 MGD flowrate and 70% recovery of the NF treatment process, 1.5 MGD of NF concentrate/brine waste would need to be managed and disposed (Figure 3).

Considering the issues of brine management and the fact that treating the water to < 50 mg/L sulfate would be an overkill at this mine site, it was determined that NF treatment in and of itself was not a viable option.

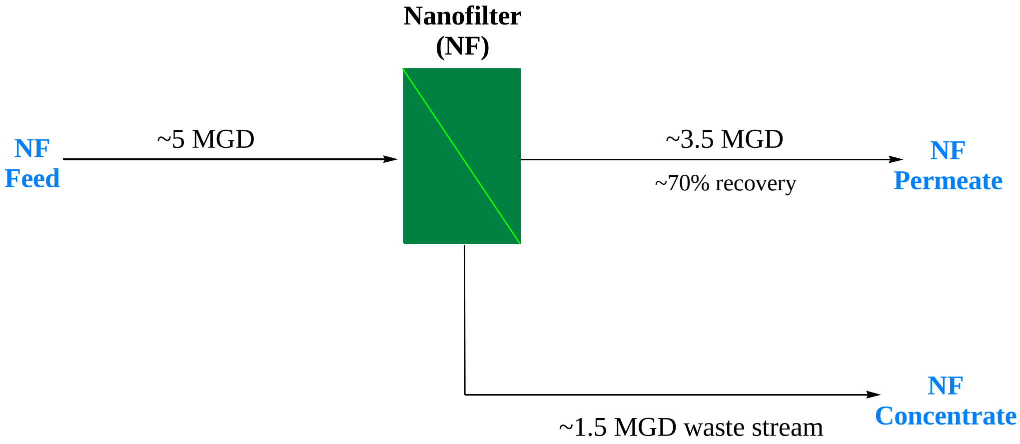

Figure 3 Schematic of NF treatment process showing need to manage large NF waste stream

RESULTS AND DISCUSSION

Hybrid membrane chemical precipitation sulfate removal process

Based on the issues with gypsum or ettringite precipitation and with NF membrane treatment discussed in the previous sections, preliminary evaluation of sulfate removal options for the mine water concluded that none of the options by themselves would be practical at the site.

Using the geochemical modeling software Phreeqc (USGS, 2014) to conduct chemical modeling suggested that a hybrid treatment process combining NF treatment with gypsum precipitation may be viable and meet the major criteria of consistently treating the water to < 600 mg/L sulfate and not generating as much waste sludge as the ettringite precipitation process. The concept was to use the NF to concentrate the stream so that more sulfate can be removed by gypsum precipitation in the NF concentrate stream compared to the more dilute full stream flow. And then the chemically treated NF concentrate stream can then be re–blended with the NF permeate stream so that no NF brine/concentrate stream will need to be managed or disposed separately; the re–blended stream will consistently meet the < 600 mg/L sulfate discharge limit due to the higher sulfate–removal capacity of gypsum precipitation of the brine stream compared to gypsum precipitation of the full flow stream because of the higher concentration of sulfate in the NF brine stream. There would also be a recycle stream for the gypsum removal clarifier overflow that can be adjusted to fine–tune the blended discharge water quality.

The main components of the hybrid sulfate removal process are: 1) Pre–treatment using hydrated lime to decrease sulfate concentration to the gypsum saturation point. The pre–treatment process also precipitates and removes metals and silica to protect the nanofilter downstream in the process and increase the NF recovery; 2) Filtration upstream of the NF; 3) Nanofiltration process, which serves to concentrate the stream; 4) Hydrated lime treatment of NF concentrate stream to further remove sulfate as gypsum; 5) Re–blending of the chemically–treated NF concentrate stream with the NF permeate stream. The hybrid sulfate removal process is summarized and depicted in Figure 4.

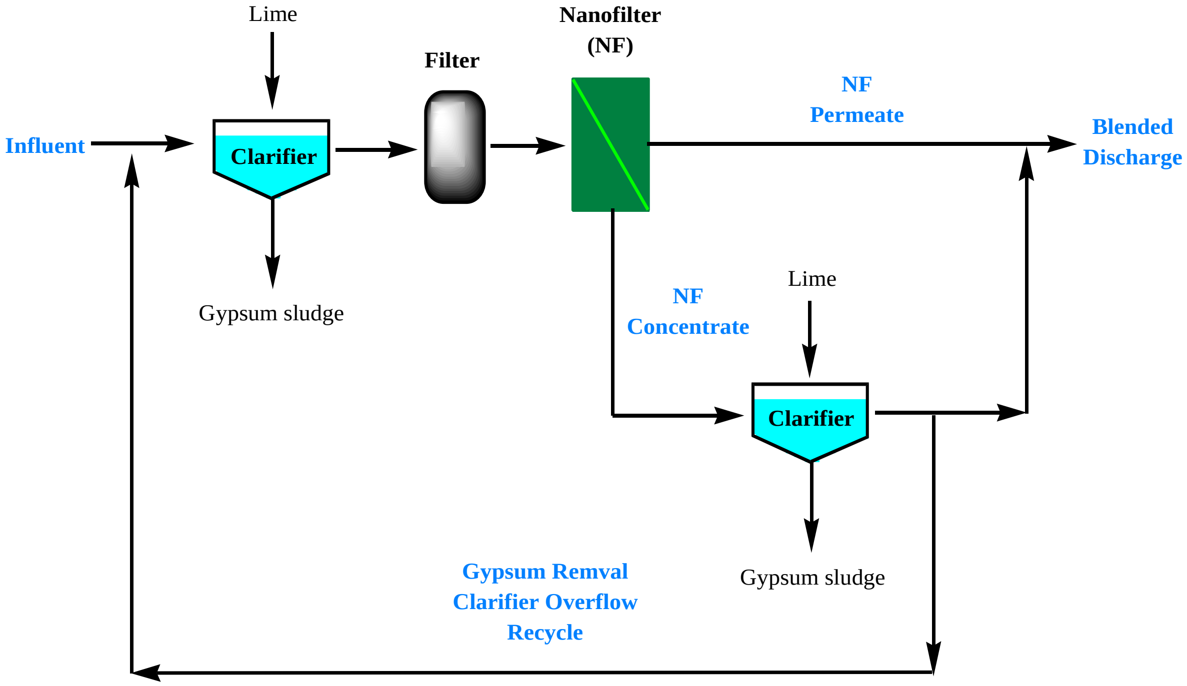

Figure 4 Schematic of hybrid gypsum precipitation and NF treatment processes

Pilot testing data

The hybrid treatment process depicted in Figure 4 and described above has been examined in a pilot test. The pilot testing was run for seven months at an average overall flowrate of approximately 20 gallons per minute (gpm), and the average NF recovery was approximately 70% with the use of a polyacrylate scale inhibitor and after iron, aluminum, and manganese were removed in the hydrated lime pre–treatment process. Data on the removal of these potentially scaling components in the lime pre–treatment process are shown in Table 1. It is of interest to note that aluminum was removed to low concentrations even at the pH of approximately 10. Data from major components of the pilot test are summarized in Table 2, which show data of the mass balance of sulfate removal across the hybrid treatment processes as determined from the pilot testing.

Table 1 Data from lime pre–treatment process to remove metals and increase NF recovery

	Al (Total, mg/L)	**Fe (Total, mg/L)**	**Mn (Total, mg/L)**
Raw Water	18	2.5	19
Lime Pre–Treated Water	0.15	0.02	0.01

Table 2 Data from pilot testing of hybrid gypsum precipitation and NF treatment processes (average values reported using two significant figures)

	pH	**Sulfate (mg/L)**	**Total Dissolved Solids (TDS) (mg/L)**
Raw Water	6.3	1,900	2,600
Lime Pre–Treated Water	10	1,400	2,200
NF Permeate	10	2.3	42
NF Concentrate	10	4,600	7,100
Lime–Treated NF Concentrate	11	1,800	2,400
Blended Discharge	7.5*	540	750
Treatment Goals	6.5–9	600	1,000

**After pH adjustment using* CO_2

As can be seen from the data presented in Table 2, the pilot study confirmed that it would be possible to use a hybrid treatment process to achieve the goal of treating sulfate down to 600 mg/L or less. Final design of the full-scale mine water treatment facility has been completed, and the mine water treatment plant is currently being constructed.

CONCLUSION

A full–scale mine water treatment facility has been designed and is currently under construction for treating up to approximately 5 MGD of water to remove sulfate to < 600 mg/L on a consistent basis. Assessment of chemical precipitation options showed that gypsum precipitation alone would not meet the 600 mg/L sulfate discharge target. So gypsum precipitation by itself was ruled out as a viable option. Although treating the water using ettringite precipitation would generate water that would meet the 600 mg/L sulfate discharge standard, it would also generate large amounts of waste sludge that would be difficult and expensive to manage. Additionally, bench scale testing showed that ettringite precipitation using calcium aluminate reagents were exceedingly slow and would require unrealistically large reaction tanks at a flowrate of 5 MGD, while using sodium aluminate, which is a potentially viable from a kinetics standpoint, would add too much sodium to the water as well as still generate exorbitant amounts of sludge. Therefore, chemical precipitation by itself, either using gypsum or ettringite precipitation, was ruled out as a practical option at the mine site. Evaluation of NF treatment also showed that while it would generate treated water that could easily meet the 600 mg/L sulfate discharge limit, the high flows of NF brine waste would be expensive to manage. Based on further evaluation of treatment options, a hybrid treatment process combining NF treatment and gypsum precipitation was developed first based on chemical modeling and then confirmed by pilot testing. The pilot testing confirmed that 600 mg/L sulfate in the treated water is achievable on a consistent basis.

REFERENCES

GARD Guide, Chapter 7, http://www.gardguide.com/index.php?title=Chapter_7, accessed October, 2014.

Jeremiason, J. D.; Engstrom, D. R.; Swain, E. B.; Nater, E. A.; Johnson, B. M.; Almendinger, J. E.; Monson, B. A.; Kolka, R. K. (2006) Sulfate addition increases methylmercury production in an experimental wetland. *Environ. Sci. Technol.* **40**: 3800–3806.

Lamers, L. P. M.; Tomassen, H. B. M.; Roelofs, J. G. M. (1998) Sulfate–induced eutrophication and phytotoxicity in freshwater wetlands. *Environ. Sci. Technol.* **32**: 199–205

Liang, H. C.; Thomson, B. M. (2010) Minerals and mine drainage. *Water Env. Res.* **82**: 1485–1533.

Liang, H. C.; Zinchenko, D.; Billin, S.; Barta, J.; Jones, R.; Willis, W. B.; Tamburini, S. (2012) Membrane vs. chemical treatment to remove mine water contaminants – Determining which process works best for mine water treatment needs. Proceedings of the SME Conference, Seattle, Washington, 600–603.

Outotec, http://www.eurominexpo.com/wp/wp–content/uploads/2014/06/12–thursday–13.30–outotec.pdf, accessed December, 2014.

Reinsel, M. A. (1999) A new process for sulfate removal from industrial waters. Proceedings of the Annual National Meeting – American Society for Surface Mining and Reclamation 16.

Pourbaix, M. 1966. *Atlas of electrochemical equilibria in aqueous solutions*, Pergamon Press, Oxford, New York.

USGS, http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/, accessed April, 2014.