

A NEW PROCESS FOR SULFATE REMOVAL FROM INDUSTRIAL WATERS¹

by

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Abstract: Many waters associated with mining and mineral processing contain high concentrations of sulfate. These concentrations typically exceed the drinking water guideline of 250 mg/L and may be subject to future discharge limits between 250 and 2000 mg/L. In the Cost-Effective Sulfate Removal (CESR) process used by Hydrometrics, Inc., a proprietary reagent is added after standard lime treatment to precipitate a compound called ettringite, which can be removed using a clarifier and filter press. Sulfate, heavy metals and other contaminants may be removed in the process, which generates no liquid waste. Sulfate concentrations lower than 100 mg/L are easily achievable using this process, with the final concentration dependent upon the reagent dosage and contact time. The CESR process is simpler and less expensive than other sulfate-removal technologies such as sodium aluminate addition, reverse osmosis or evaporation, and is more effective than standard lime precipitation. This process is a true reduction of total dissolved solids (TDS) in that all chemicals added for treatment are precipitated during the reactions. Operating costs for near-complete sulfate removal using the process, which has been used successfully in electroplating, battery recycling and agricultural applications, are estimated at \$3 to \$6 per 1000 gallons treated. The process has been demonstrated at the bench scale for waters associated with mining and mineral processing.

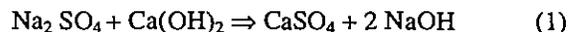
Additional Key Words: lime treatment, ettringite, total dissolved solids

Introduction

Environmental laws presently do not classify sulfate ions (SO_4^{2-}) as pollutants like metals or organic halogen compounds, although proposed EPA regulations may place a 400 to 500 mg/L limit on drinking water. However, sulfate concentrations as low as 250 mg/L can have a serious cathartic effect on humans. In addition, sulfate contributes to an increase in surface water salinity and inhibits some advanced wastewater treatment processes. Sulfates are also of concern because they are indirectly responsible for two other problems often associated with the handling and treatment of wastewater. These potential problems, odor and corrosion, both result from the reduction of sulfates to hydrogen sulfide under anaerobic conditions (Sayer et al., 1994).

The most common method for removing high concentrations of sulfate from water is through addition

of lime or calcium hydroxide ($\text{Ca}(\text{OH})_2$). This precipitates the sulfate as calcium sulfate (CaSO_4):



Calcium sulfate, which hydrates to become the common mineral gypsum, has a solubility of approximately 2000 mg/L as sulfate. Reuse of water with a sulfate concentration this high typically causes problems such as severe scaling in heat exchange systems, clogging of reverse osmosis or electrodialysis membranes, and precipitation in pipes. Discharge into surface water or to local sewage disposal systems may not be possible due to the water's high specific conductivity and total dissolved solids (TDS). Sulfate reduction below 2000 mg/L has been possible in the past only through expensive technologies such as reverse osmosis or ion exchange. Large volumes of liquid waste are generated with these technologies, which typically create additional treatment and disposal costs.

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Many waters associated with mining and mineral processing contain high concentrations of sulfate. The CESR process can reduce the sulfate concentration in these wastewaters to less than 100 mg/L through the use of a proprietary powdered reagent. The addition of this reagent to lime-pH-controlled water precipitates sulfate as a nearly insoluble calcium-alumina-sulfate compound known as ettringite. The formation of ettringite also can provide a polishing effect, allowing precipitation of difficult-to-remove metals such as chromium, arsenic, selenium and cadmium, often below their respective laboratory analytical detection limits. Boron, fluoride and up to 30 percent of the chloride and nitrate-nitrite concentrations in the water have also been removed. The metals and other constituents which the ettringite removes are typically not leachable, allowing disposal as a nonhazardous waste.

Since metals are common in wastewater containing high concentrations of sulfate, minimization of metal-bearing hazardous waste is essential to making a treatment process economical. The CESR process uses a sequential design to separate the sulfate precipitation, both as gypsum and ettringite, to ensure a concentrated hydroxide sludge. This design increases removal of metals and allows the process to effectively treat a broad range of water qualities. It also allows addition onto existing systems.

Process Description

The CESR process is a further development of wastewater treatment with lime in that it can meet more stringent requirements for sulfate removal. Lime is inexpensive, readily available and produces stable products which can be reused or disposed in landfills. Unlike treatment methods such as sodium aluminate addition, all of the chemicals added during the CESR process can be precipitated from the water. Water treated by the CESR process typically meets or exceeds recommended drinking water standards for sulfate, metals and other contaminants.

The ability to adjust the CESR process to achieve desired sulfate concentrations allows the process to be economically used by a wide variety of industries. Over 20 treatment plants in Europe and the United States now use the process, at flow rates up to 350 gpm. The CESR process essentially consists of four steps:

1. Initial precipitation of sulfate as gypsum
2. Precipitation of metals as hydroxides in a gypsum matrix

3. Additional sulfate removal via ettringite precipitation
4. pH reduction using recarbonation.

Step 1 -- Initial Sulfate Precipitation

For wastewater with a high metals content and a sulfate concentration greater than 8000 mg/L, hydrated lime is used initially to precipitate most of the sulfate as gypsum. This precipitation occurs at a pH below which the metals will precipitate. For example, if the water being treated contains ferric iron (Fe^{3+}), precipitation should be conducted at a pH below 2.5. In acidic wastewater, the pH may already be below 2, making it readily adaptable to initial precipitation of sulfate. Over 80 percent of the sulfate in many wastewaters can be precipitated prior to metal precipitation in order to minimize the volume of hazardous sludge. It is essential to determine the solubility characteristics of metals in the wastewater to prevent hydroxide precipitation in this step.

A mixing time of 40 to 60 minutes is adequate for initial sulfate precipitation. The sulfate content of the wastewater can be lowered to 4000 to 5000 mg/L, with the resulting gypsum easily dewatered in a filter or belt press. Approximately 1.8 pounds of gypsum are precipitated per pound of sulfate. Since this is pure gypsum, no special handling or disposal permits are required. Any sludge not reused can be placed in a Class III landfill or transported to a gypsum-consuming facility.

Step 2 -- Metal Hydroxide Precipitation

Wastewater with an initial sulfate concentration below 8000 mg/L, or which has already been treated using gypsum precipitation, is adjusted to a pH of 10.5 with hydrated lime. This removes metals as hydroxides and further precipitates gypsum, so approximately 2000 mg/L of sulfate remains in solution. Laboratory tests typically would be used to determine the optimum pH for hydroxide precipitation since some metals will begin to go back into solution at pH 10.5.

As with the initial sulfate precipitation step, a mixing time of 40 to 60 minutes is adequate. This sludge is dewatered separately in a filter press to prevent contamination of the pure gypsum or ettringite. In a typical metal-bearing wastewater, approximately 45 pounds of gypsum and metals sludge are produced per 1000 gallons of water treated. Depending on state regulations, this sludge may require disposal in a Class II or Class I landfill.

Step 3 -- Final Sulfate Precipitation

The next step of the process is removal of sulfate to the desired concentration. The wastewater pH is increased to approximately 11.5 with hydrated lime. At this stage a proprietary reagent is dosed at the rate of approximately 1.0 pound of reagent per pound of sulfate to be removed. The reagent combines with soluble sulfate to form an ettringite precipitate. As ettringite forms with the sulfate, contaminants such as nitrate, chloride, fluoride, boron and metals may be incorporated into its structure. Insoluble gypsum will interfere with this reaction if not removed in a previous step. Depending on the wastewater source, ettringite sludge can be disposed in a Class III landfill.

This sulfate removal takes 30 to 300 minutes, depending on the level of removal required, other contaminants in the water and the amount of reagent added. Ettringite sludge is easily dewatered, and may be reused in the process as seed sludge to reduce the quantity of coagulation aid required.

Step 4 -- pH Reduction/Recarbonation

Prior to discharge into a sewage disposal system or to surface water, it is often necessary to lower the pH of the effluent to meet discharge pH criteria. If treated water is to be reused in the plant or process as mixing or wash water, it is recommended to reduce the pH and stabilize the water to prevent deposition of hard carbonate scale on filters and distribution piping. Recarbonation is a process which would likely be used to adjust the pH.

Approximately 2 pounds of CO₂ are required per 1000 gallons of water for reduction to pH 8.5. This reduction yields approximately 4 pounds of calcium carbonate and aluminum hydroxide sludge per 1000 gallons of treated water.

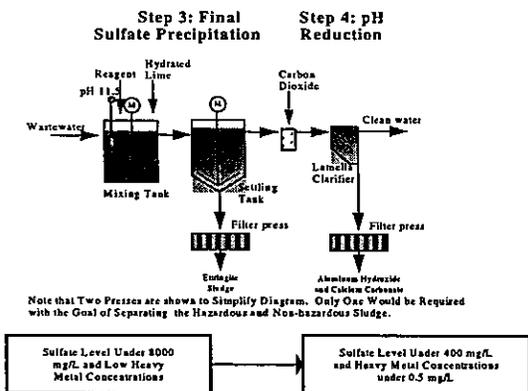


Figure 1. One-step CESR process with pH reduction

Figure 1 shows the simplest version of the process where only final sulfate removal is required. Only Steps 3 and 4 of the CESR process are shown. The CESR process can be added to an existing wastewater treatment plant, and designed as a fully automated continuous process or a manual batch system.

Results

In bench tests over the past several years, concentration targets for sulfate and metals were consistently met for 47 industrial wastewaters of varying compositions. Table 1 shows the quality of different wastewaters treated with the CESR process in these bench tests and several full-scale processes. The results achieved were typically well below applicable water quality limits; in some cases, drinking water standards were met.

Table 1. Results of the CESR process in Full-Scale and Bench-Scale Tests

Industry	Parameter	Influent Concentration (mg/L)	Effluent Concentration (mg/L)
Glass	SO ₄	60,000	< 400
	Pb	10	< 0.5
	F	14,000	< 30
	Sb	60	< 0.3
Battery Factory	SO ₄	3000 - 5000	< 50
	Pb	5 - 15	< 0.1
	Cu	0.3 - 0.4	< 0.05
	Sn	0.2 - 0.4	< 0.01
	Zn	0.3 - 0.5	< 0.01
Chemical Plant	SO ₄	2000 - 3000	< 50
Metal Galvanize	SO ₄	1000	< 400
	Cr	-	< 0.1
	Zn	-	< 0.3
Metal Polishing	SO ₄	6000 - 8000	< 400
	PO ₄	2000 - 3000	< 1
	Cu	70 - 100	< 0.1
	Ni	70 - 100	< 0.1
	Cr	200 - 300	< 0.5
Photo Processing	SO ₄	> 100,000	< 50
Mining Process Water	SO ₄	50,000	< 400
	Ni	1.64	< 0.02
	Cr	1.92	< 0.2
Incinerator Ash Runoff	SO ₄	54,000	< 400
Metal Surface Treatment	SO ₄	54,000	< 400
	Ni	604	< 0.2
	Cr	33.5 - 390	< 0.2
Wire Mfg.	SO ₄	4000 - 6000	< 400
	Cu	250 - 300	< 0.1
	Fe	400 - 600	< 0.1

Several sets of bench tests also have been conducted recently using mine waters. Acid rock drainage from the Berkeley Pit in Butte, Montana was tested to find an efficient method for sulfate removal.

Sulfate concentrations as low as 4 mg/L were obtained in treated water, with higher concentrations measured when using lower reagent dosages and/or shorter contact times (Table 2). Concentrations of metals analyzed were low and often below their respective analytical detection limits (Table 2).

Table 2. Berkeley Pit Bench Testing Results

Parameter	Concentration (mg/L)			
	Influent	Test 1	Test 2	Test 3
SO ₄	8730	4	15	56
Cd	2.16	< 0.001	< 0.001	< 0.001
Cu	193	0.05	0.02	0.01
Fe	972	0.31	< 0.03	0.09
Mn	231	0.02	< 0.01	< 0.01
Ni	1.2	< 0.01	< 0.01	< 0.01
Zn	603	< 0.01	< 0.01	0.04

Water from a closed gold mine in Montana was also tested in CESR-process bench tests. In reducing the sulfate concentration to approximately 30 mg/L, the total dissolved solids (TDS) concentration of this water was reduced from approximately 4400 mg/L to 1400 mg/L in the process (Table 3). Effluent concentrations of antimony and arsenic were below the analytical detection limits and concentrations of constituents such as selenium, thallium and nitrate were also significantly reduced (Table 3).

Table 3. Gold Mine Bench Testing Results

Parameter	Concentration (mg/L)			
	Influent	Test 1	Test 2	Test 3
SO ₄	2270	33	29	24
TDS	4390	1400	1450	1510
Sb	0.024	< 0.005	< 0.005	< 0.005
As	0.234	< 0.005	< 0.005	< 0.005
Se	0.155	0.071	0.066	0.063
Tl	0.834	0.262	0.254	0.276
NO ₃	125	91	96	100

Design Considerations

Wastewater treatment using the CESR process can be carried out continuously or in batch form depending upon the flow rate. At flow rates above 45 gpm, it is difficult to treat water on a batch basis due to long refilling times. Batch processing is preferred for lower flows because it is considerably easier to monitor the contaminant reduction and it has a low capital investment.

Final sulfate reduction requires a mixing time of 30 to 300 minutes as determined by bench testing. During the required reaction time, the pH should be maintained between 11.0 and 11.8.

The reagent can be added with a dry weigh feeder or as a 10 percent suspension using a progressive cavity pump. However, use of the reagent as a slurry is not generally recommended since it begins reacting immediately upon contact with water. This could result in decreased reaction efficiency or clogging of pipes and pumps.

For a treatment process requiring Step 1 or Step 2 of the CESR process, periodic analysis can be done using a portable sulfate analyzer rather than investing in an on-line system, since there is typically 2000 ± 300 mg/L sulfate content in the wastewater. If the sulfate concentration of the influent is expected to vary widely, use of an on-line sulfate analyzing system may be warranted to avoid unnecessary overdosing of reagent.

Sludges must be removed between treatment steps because the reagent reacts not only with free sulfate ions, but also with previously formed gypsum. Failure to remove the sludge would unnecessarily increase the amount of reagent needed and potentially overload the mixing and sedimentation tank. Sludge can be dewatered with a plate-and-frame or belt filter press.

Treatment Costs

Capital costs for installing the CESR process will normally be lower than alternative technologies such as reverse osmosis or ion exchange, especially if a lime treatment plant is already in place. Process equipment required for a continuous-flow operation may be as simple as a tank with a mixer, a reagent addition system and a filter press. Capital and operating costs will depend upon the:

- Flow rate
- Sulfate concentration to be removed
- Final sulfate concentration to be achieved, and
- Other water quality parameters (e.g., sodium and chloride concentrations).

Operating costs would probably be \$3 to \$6 per 1000 gallons treated for removal of sulfate to low levels, with a large portion of this due to reagent consumption. For example, the reagent cost would be approximately \$2.50 per 1000 gallons for removal of 1500 mg/L of sulfate. This portion of the operating cost is directly related to the sulfate concentration to be

removed. If less sulfate needs to be removed, operating costs will be lower.

The total operating cost is less than the cost of competitive technologies such as reverse osmosis (RO) and ion exchange (IX), primarily because the CESR process does not generate a liquid waste stream. RO and IX processes for wastewaters containing a high sulfate concentration incur high capital and operating costs because a relatively large percentage of the flow becomes a liquid waste stream, which typically must be evaporated. For streams which require sulfate removal, the CESR process is a cost-effective alternative, especially at low flow rates.

Summary

The CESR process has been developed as a technology to meet stringent wastewater discharge limits for sulfate and metals while minimizing the generation of hazardous waste. The process is a true TDS reduction in that all reagents added to treat the

water are precipitated. Sulfate concentrations may be reduced to below 100 mg/L while concentrations of most metals can be lowered to less than their respective analytical detection limits. The CESR process can be utilized for a wide range of water qualities and flows. It has been successfully used for several years in numerous European plants in various industries, and its application is being expanded to the United States and Canada, South America and other markets. Capital costs can be minimized if the process is added to an existing water treatment plant, especially a lime treatment plant, and operating costs are lower than those for competitive technologies. The CESR process is a potentially efficient and cost-effective method for achieving compliance with discharge limits for many waters associated with mining and mineral processing.

Literature Cited

Sayer, C.N., McCarty, P.L. and Parkin, G.F. *Chemistry for Environmental Engineering*. McGraw-Hill, New York, 1994.