

Ettringite Precipitation vs. Nano-Filtration for Efficient Sulphate Removal from Mine Water

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Abstract

Sulphate is the most common anion in mine waters due to the oxidation of sulphide minerals. Even though sulphate is not a toxic substance it can attack concrete structures, and it can affect water usage downstream of mining areas. Despite the European Water Framework Directive, EU Member States have very different approaches to dealing with sulphate containing mine waters. For example, in Germany the site-specific sulphate pollution situation and ecological parameters of surface waters, based on an environmental impact analysis, are used to determine the sulphate effluent limits. In Romania and some other countries, a relatively low fixed legal limit (600 mg/l) has to be complied with. In this context the consulting firms WISUTEC GmbH, EcoInd Bucharest and UIT Umwelt-und Ingenieurtechnik GmbH have developed two effective technologies to treat highly polluted mine water including sulphate removal. The first technology utilises heavy metal precipitation followed by the precipitation of ettringite for sulphate removal; whilst the second utilises nano-filtration (NF), after a chemical “pre-treatment” stage, to produce a high quality permeate. Reagents tested for NF pre-treatment included hydrated lime, sodium hydroxide and magnesium oxide. Similarly, a range of reactive aluminium sources (calcium aluminate, aluminium rich cements, aluminium hydroxide and others) were tested to optimise the precipitation of ettringite. Both flow sheets developed by laboratory test work are well-suited to treat acid rock drainage (ARD) at the Rosia Montana mine site in Romania.

Keywords: acid rock drainage, sulphate removal, ettringite precipitation, nano-filtration

Introduction

The Romanian mining operator Rosia Montana Gold Corporation (RMGC) is developing the Rosia Montana Gold Project, located in central Romania. The project development includes the collection and treatment of various water streams. Several acid rock drainage (ARD) sources exist, emanating from the

historical mining area, which includes approximately 140 km's of underground mine development, open pit development and waste rock stockpiles.

As part of the ARD water treatment process development work, RMGC initiated a comprehensive laboratory test work program comprising lime neutralization to precipitate metal species from solution, sulphate reduction techniques including ettringite precipitation, and membrane separation. The purpose is to determine the advantages and disadvantages of these techniques, and which approach to pursue in the full-scale operation.

Characterization of the mine effluents

Table 1 shows the composition of the ARD effluents at Adit 714 and in the Rosia Valley in comparison with the Romanian legal discharge standard NTPA 001/2005. Many parameters in the effluent from the Adit 714 significantly exceed their respective discharge limits.

Lime precipitation has been used worldwide for the treatment of ARD. The low pH and the relevant metals can be adequately treated by lime precipitation, raising the pH to the alkaline range (9.5 – 10.0) so that metal concentrations and pH are well within the permitted limits. In contrast to the removal of metals, the reduction of the sulphate concentration to values lower than what would result from the solubility of gypsum (ca. 1600 mg/l), and the reduction of the total dissolved solids (TDS), are challenging tasks. For sulphate removal, ettringite precipitation and nano-filtration were identified as the most prospective options. The tests presented in this paper focus solely on the reduction of sulphate and TDS using these two approaches.

Table 1 Composition of the ARD effluent at Adit 714 and Rosia Valley flow in comparison with the NTPA 001/2005¹⁾ limits

Parameter		Adit 714 mine effluent	Rosia Valley flow	Limits NTPA 001/2005
pH		2.5	5.9	6.5-8.5
TDS	mg/L	6400	280	2000
Ca	mg/L	280	49	300
Mg	mg/L	95	7.5	100
As	mg/L	1.47	0.0005	0.1
Cu	mg/L	2.18	< 0.003	0.1
Zn	mg/L	35	0.3	0.5
Cd	mg/L	0.21	0.01	0.2
Ni	mg/L	0.75	0.018	0.5
Mn	mg/L	254	3.1	1
Fe	mg/L	416	0.13	5
Al	mg/L	230	1.5	5
Sulphate	mg/L	3910	160	600

¹⁾NTPA 001/2005 - Romanian norms regarding discharge of wastewater into surface waters - Approved by Government Decision 188/2002, amended and updated by Government Decision 352/2005

State of the art for sulphate removal by ettringite precipitation and membrane separation

An excellent overview of sulphate removal from mine waters is given by INAP (2003). Sulphate can be removed by several processes from mine water using physical, chemical and microbiological methods. The Walhalla process for ettringite precipitation is a well-known process and can be described as a standard method for sulphate removal from industrial wastewater at relatively small flow (SCHUSTER et al., 1996). This precipitation process is well-understood, reliable and can be easily controlled. The SAVMIN process is similar to the Walhalla process. It consists of successive steps for metal, gypsum and ettringite precipitation. A specialty of the SAVMIN process is the recycling of aluminum hydroxide by decomposition of the precipitated ettringite using sulphuric acid (INAP 2003), which leads to cost savings for the aluminium source reagent.

Both processes require chemically available aluminium to form the ettringite. The best known aluminum sources are Walhalla lime and aluminum hydroxide. The risk associated with the dependence on a single supplier and cost motivated the search for other aluminum containing substances suitable for ettringite precipitation. One of the objectives of this work was to investigate the applicability of a wide range of alternative aluminum containing products available on the market.

The INAP (2003) report concludes that membrane treatment is “not well suited for the treatment of mine waters” because of the scaling risk and the high costs. In recent years nano-filtration (NF) has become an interesting option for the removal of sulphate from different kinds of waters. The process is used on a large scale for drinking water processing, where sulphate removal is necessary (MELIN). In comparison to reverse osmosis, NF has the advantage that a relatively low pressure is needed for the separation process. NF membranes show a distinct selectivity between single- and multi-valent ions based on the different solution and transport behavior of hydrated ions. PREUß et al. investigated the sulphate removal from mine water after metal precipitation by lime. In this investigation, the sulphate retention was between 90 and 95%, the feed sulfate content was 1943 mg/L, the operating pressure was 10 bar, and the cross flow velocity was 0.25 m/s. Although NF process offers a low energy separation of sulphate, the risk of scaling has to be carefully investigated. Furthermore, brine treatment is needed to convert the dissolved sulphate into a solid residue.

Results of the ettringite precipitation

The water from Adit 714 (Table 1) was first treated with lime to pH = 10.0, the metal containing sludge was removed by filtration and the remaining filtrate with a sulphate content of 2910 mg/L was used for ettringite precipitation. It should be noted that for the ettringite precipitation, another lime dosage is required to elevate the pH to a range of 11.0 to 11.5 prior to the addition of an aluminium source to facilitate the formation of ettringite. The quality of the aluminium source influences the residual sulphate content in the treated water, and also the required reagent dosage. The substances listed in Table 2 were subjected to screening tests to determine their suitability for ettringite precipitation.

Table 2 High aluminum content reagents for ettringite precipitation

<i>Liquid products</i>				
Product	Producer / supplier	Active ingredient	Al content [g/L]	
Sachtoklar 39	Sachtleben Wasserchemie GmbH, Germany	Poly-aluminum chloride	89	
SULAN	Remondis Production GmbH, Germany	Sodium aluminate	155	
SP134 solution	Solution produced by dissolving Al(OH) ₃ in NaOH	Sodium aluminate	100	
<i>Solid products</i>				
Product	Producer / supplier	Active ingredient	Al ₂ O ₃ [%]	
SP134	SC Alum SA, Tulcea, Romania	Al(OH) ₃ , D ₅₀ =112 μm	64	
SH30	Specialty aluminas,	Al(OH) ₃ , D ₅₀ =4 μm	65.2	
SH500	Aluminium Pechiney, Gardanne, France	Al(OH) ₃ , D ₅₀ =50 μm	65.2	
Gorkal 80	GORKA cement, FAC Cluj Napoca, Romania	Calcium aluminate	79-82	
Istra 50	ISTRA cement Calucem Group, Pula, Croatia	Calcium aluminate	50-53	
CA S44	Walhalla Kalk GmbH, Regensburg, Germany	Calcium aluminate	53-56	

Table 3 Test results for the liquid products

Parameter	Unit	Sachtoklar 39	SULAN	SP134 solution*
Lime consumption in the ettringite precipitation stage	g/L	10.4	5.4	5.4
Aluminium source reagent dosage (solution)	g/L	10.4	6.5	9.6
Precipitation time	min	240	60	60
<i>Final values after ettringite precipitation</i>				
pH		12.4	12.7	12.7
Sulphate	mg/L	15	9	6
Na	mg/L	14	852	1610
Ca	mg/L	1920	306	162
Al	mg/L	0.24	0.98	1.6
Sludge dry mass	g/L	14.9	13.1	12.9

* Sodium aluminate solution obtained from SP134 and NaOH

Table 4 Test results for the solid products (precipitation time 240 min for all reagents)

Parameter	Unit	SP134	SH30	SH500	Gorkal 80	Istra50	CA S44
Lime consumption in the ettringite precipitation stage	g/L	0.3	5.4	0.15	1.47	2.02	2.27
Aluminium source reagent dosage (solid)	g/L	3.4	3.3	4.1	5.1	9.0	12.0
<i>Final values after ettringite precipitation</i>							
pH		11.5	12.5	11.3	11.4	11.5	11.5
Sulphate	mg/L	2670	2480	3685	47	10	12
Na	mg/L	12.6	7.8	10.8	16.5	14.0	12.4
Ca	mg/L	1440	2240	1245	104	618	215
Al	mg/L	< 0.1	0.1	0.1		770	227
Sludge dry mass	g/L	19.4	8.5			19.4	22.9

In the screening tests, aluminium in dissolved form was added in a stoichiometric excess of 20%. Based on solid aluminum sources, the stoichiometric excess dosage was 100%. As shown in Table 3, all liquid reagents led to very low sulphate concentrations in the supernatant. It was surprising that Sachtoklar 39, a poly-aluminium-hydroxy-chloride normally used as a flocculant in water treatment, showed good results as well. However the disadvantages of this reagent include high chloride content in the treated water, and a doubling of lime consumption in the ettringite precipitation stage, in comparison to the other two liquid reagents. Table 4 contains the test results for the solid reagents. It is surprising to find that products based on crystalline aluminium hydroxide (Hydrargillite), even at relatively high doses, are not appropriate for ettringite precipitation. The obvious reason is that crystalline aluminum hydroxide is chemically less "active" than freshly precipitated material. Freshly precipitated aluminum hydroxide is available as a gel and has an amorphous structure. It is noted that in the SAVMIN process discussed above, freshly precipitated aluminum hydroxide produced by decomposition of ettringite with sulfuric acid was also used, but other applications with aluminum hydroxide are not known to us.

With the solid products containing calcium aluminate, the ettringite precipitation was successful. In a next step, the dosage and the reaction time were optimized for the most suitable products, CA S44 and Istra 50. Despite acceptable precipitation results, Gorkal 80 was excluded from further investigations because of its comparatively high price.

For the optimisation of reagent dosage, the stoichiometric excess was reduced from 100% in the screening tests to 25% and 50%. As shown in Figure 1, only a slight excess of calcium aluminate is needed for sufficient sulphate removal, but a reaction time of at least 120 minutes is necessary for sufficient utilization of the precipitating agent.

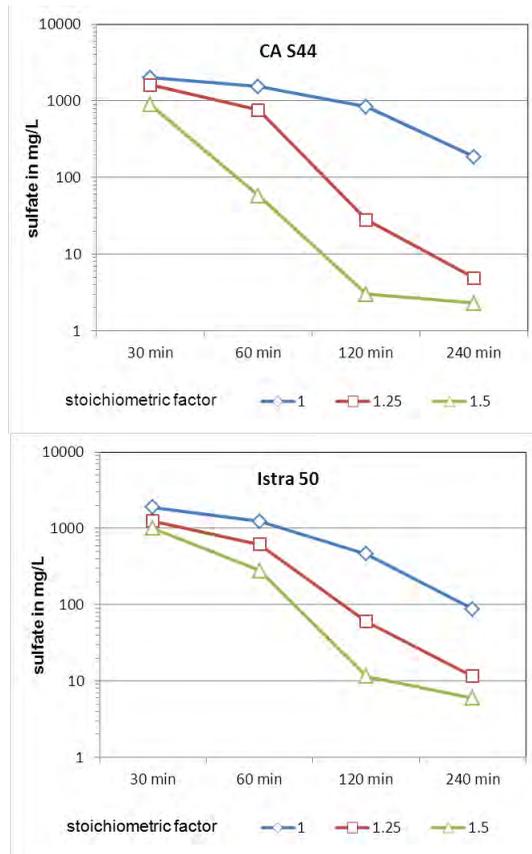


Figure 1 Residual sulphate concentration in the supernatant in dependence of reaction time and stoichiometric excess for ettringite precipitation using Wahalla lime (CA S44) and Istra 50

Results of the membrane lab scale test work

From the outset of the membrane test work, it was clear that operating the NF process without pre-treatment would lead to rapid membrane fouling by some feed constituents such as heavy metals. As a consequence, several pre-treatment methods were tested to remove the fouling components, including obvious candidates such as hydrated lime and sodium hydroxide. However, these pre-treatment methods were not pursued further as they had significant disadvantages. For example, lime pre-treatment would have required the addition of an anti-scalant to prevent gypsum scaling, but the anti-scalant would have negatively impacted concentrate treatment. Sodium hydroxide (NaOH) pre-treatment would have significantly increased the feed TDS and consequently led to a higher operating pressure across the NF module. Furthermore, the TDS limit of NTPA 001/2005 would have been exceeded.

Magnesia (MgO) was tested as an alternative pre-treatment reagent to avoid the aforementioned problems and hydrogen peroxide (H₂O₂) was added to improve manganese oxidation. After MgO pre-treatment the NF process was tested at lab scale under stable conditions over a period of 12 hours with the membrane type NF90-2540. As no (or negligible amounts of) anti-scalant are needed, the NF brine can be treated using lime precipitation.

The following equations describe the chemical reactions:

<u>Pre-treatment:</u>	$\text{Al}^{3+} + 3 \text{OH}^- \rightarrow \text{Al}(\text{OH})_3 \text{ (solid)}$
$3 \text{MgO} + \text{H}_2\text{O} \rightarrow 3 \text{Mg}^{2+} + 6 \text{OH}^-$	$\text{Mn}^{4+} + \text{O}_2^- \rightarrow \text{MnO}_2 \text{ (solid)}$
$\text{Fe}^{3+} + 3 \text{OH}^- \rightarrow \text{Fe}(\text{OH})_3 \text{ (solid)}$	$3 \text{SO}_4 + 3 \text{Mg}^{2+} \rightarrow 3 \text{MgSO}_4 \text{ (aqu.)}$
<u>Concentrate (brine) treatment (if required):</u>	$\text{MgSO}_4 \text{ (aqu.)} + \text{Ca}(\text{OH})_2 \rightarrow \text{Mg}(\text{OH})_2 \text{ (solid)} + \text{CaSO}_4 \text{ (solid)}$

It is noted that under some circumstances it may not be possible to dispose of the brine separately into a tailings storage facility, and only a single NTPA 001/2005 compliant discharge is permitted. Therefore brine treatment and re-constitution of permeate and treated brine was also tested, as shown in Figure 2. Based on preliminary pre-treatment tests and membrane runs in order to tune in basic parameters, an optimised flow sheet was developed and tested in detail over sufficiently long test runs. Figure 2 shows, as an example, the flow sheet with flow balances for a specific blend of Adit 714 ARD and the less polluted Rosia Valley flow (RVF). The achievable recovery of the NF stage in this particular case is 68%.

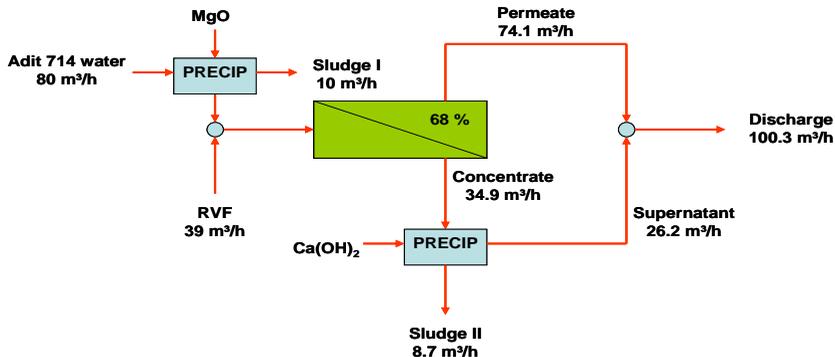


Figure 2 Flow sheet of membrane test work for a specific blending ratio of ARD and Rosia Valley flow

For the test work in Figure 2, the analysis of the NF feed (after pre-treatment of a blending ratio of Adit 714 : RVF = 2 : 1), the NF permeate, and the untreated and treated concentrates are shown in Table 5. This table also shows the composition of the discharge, which consists of re-constituted permeate and treated brine. All concentrations meet the NTPA 001/2005 discharge standards.

Table 5 Analytical data of relevant media according to the flow sheet shown in Figure 2

Parameter	Unit	NF Feed	NF Permeate	Untreated Concentrate	Treated Concentrate	Discharge
TDS	mg/L	3,200	34	7,900	4,100	910
Sulphate	mg/L	2,050	10	4,370	2,020	507
Phosphor	mg/L	< 0.05	< 0.05	0.06	< 0.05	0.11
Aluminum	mg/L	< 0.05	< 0.05	0.09	< 0.05	< 0.05
Arsenic	mg/L	< 0.005	< 0.005	0.005	< 0.005	< 0.005
Cadmium	mg/L	0.007	< 0.001	0.015	< 0.001	< 0.001
Calcium	mg/L	184	1	568	1,140	256
Copper	mg/L	< 0.005	< 0.005	0.010	< 0.005	< 0.005
Magnesium	mg/L	493	2.14	1,300	0.08	1.42
Manganese	mg/L	64	0.29	170	0.006	0.077
Nickel	mg/L	0.041	< 0.005	0.13	< 0.005	< 0.005
Zinc	mg/L	0.16	< 0.01	0.47	< 0.01	< 0.01

Comparison of the ettringite and membrane based processes

Table 6 summarises the advantages and disadvantages of the two processes.

Table 6 Comparison of the ettringite and membrane based processes

Comparison criteria	Ettringite process	Membrane process (nanofiltration)
Achievable residual sulphate concentration	< 100 mg/L	< 100 mg/L
Advantages	Reliable and proven technology, robust with respect to variations in water quality High quality of the treated water with low concentration of sulphate and calcium Two step precipitation process	Innovative separation technology that has recently attracted new attention due to improved membrane modules with potential cost advantages Very high quality of the permeate with low concentration of sulphate and hardness Multi-stage process with pre-treatment, membrane separation. Brine treatment may be needed unless untreated brine can be managed elsewhere.
Disadvantages	High CAPEX due to large reaction/ settlement tanks and thickeners (slow kinetics of ettringite precipitation)	Scaling and fouling risk strongly depending on the water quality, requires sophisticated process control and experienced plant operator personnel
Waste characterisation	<u>Sludge from metal precipitation:</u> Al(OH) ₃ , Fe(OH) ₃ , MnO ₂ , CaSO ₄ , Mg(OH) ₂ <u>Ettringite precipitation stage:</u> Al(OH) ₃ , 3CaO·Al ₂ O ₃ ·3CaSO ₄ ·32H ₂ O	<u>Pre-treatment stage:</u> Al(OH) ₃ , Fe(OH) ₃ , MnO ₂ <u>Brine treatment, if applicable:</u> CaSO ₄ , Mg(OH) ₂ , Zn(OH) ₂
Relative operating costs	Base case	Less sludge production if brine can be disposed of without treatment Comparable or slightly higher than ettringite process if ARD from Adit 714 is undiluted Lower if Adit 714 ARD and Rosia Valley flow can be blended. Significantly lower if no brine treatment is required
Relative capital costs	Base case	Comparable if brine treatment is required Lower if now brine treatment is required

Summary and conclusions

From the laboratory test work, two different flow sheets were developed that are well-suited to treat ARD at the Rosia Montana mine site. The ettringite precipitation and membrane based flow sheets are both capable of achieving the Romanian NTPA 001/2005 discharge standards for all water constituents.

The lime neutralisation/ettringite precipitation technique is well understood, and the test work presented here has mainly focused on research to identify the most

suitable aluminium source reagents available on the market, to mitigate the supply and cost risks to a mining operation that will need a reliable ARD treatment solution for more than two decades. The results are encouraging in that a variety of suitable reagents has been identified and tested, with one cement product (Istra 50) being very reactive at reasonable market price, while other products with acceptable reactivity and price are available as well. Realistic ettringite precipitation reaction times are in the order of 120 minutes, which is an important parameter for future plant design.

The advantages and risks of the nano-filtration-based flowsheet including a pre-treatment stage is also better understood as a result of the testwork carried out. The critical parameters of the membrane-based techniques include the choice of the pre-treatment reagent (MgO or NaOH source), and the operation parameters of the membrane modules, such as operating pressure and cross flow.

The testwork is currently continuing at pilot plant scale at Rosia Montana. The pilot plant includes both the ettringite and membrane flow sheets. The objective of the pilot plant operation is to further optimise the operational parameters and to obtain valuable information on the stability of the processes, and to firm up design parameters needed for the full scale water treatment plant at the planned Rosia Montana gold mine. The operation of the pilot plant will be the subject of a forthcoming paper.

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