- ORAL PRESENTATIONS -

REMOVAL OF TOXIC METALS AND SULPHATE FROM MINE WATER TECHNOLOGY COMPARISON ETTRINGITE PRECIPITATION VS. NANO-FILTRATION BY PILOT TRIALS

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Abstract

A pilot plant for the treatment of acid mine drainage was tested in the Apuseni Mountains on behalf of the Rosia Montana Gold Corporation. A containerised mobile unit was developed and built by a team of WISUTEC, G.E.O.S. and BAUER Water and operated for a period of 7 months. The plant allowed testing of two innovative treatment technologies, a two-stage precipitation process, and nano-filtration including optional solution pre-treatment and concentrate neutralisation, both of which proved their reliability in relation to durability and compliance to the stringent Romanian discharge limits (NTPA 001/2005). Valuable operating and cost data for future process design were obtained.

Keywords: SIMI 2013, acid rock drainage, sulphate removal, ettringite precipitation, nano-filtration, pilot plant, technology comparison, NTPA 001/2005.

1. Objectives

Sulphate is the most common anion in acid mine waters due to the oxidation of sulphide minerals. Even though sulphate is not a toxic substance, it can attack concrete structures and affect water quality downstream of mining areas. In many mining regions of the world, the removal of sulphate from mine waters is therefore becoming increasingly important, in addition to the removal of metals. While the removal of the metals with hydrated lime is a well-established process, the removal of sulphate is more difficult, particularly if concentrations below the solubility of gypsum must be achieved, as is the case in Romania where the discharge standard for sulphate is ≤ 600 mg/L.

Conscious of these requirements, WISUTEC Umwelttechnik GmbH and UIT GmbH developed two alternative technologies for metal and sulphate removal from mine waters, on a laboratory scale. The results were published by JANNECK et al.; (2012). Continuing the process development, pilot scale testing ensued to obtain valuable operating, design and cost data, while simultaneously verifying that these technologies can work reliably under real world conditions, meeting all required discharge parameters on a continuous basis.

In this context RMGC entrusted a consortium of WISUTEC and BAUER Water GmbH (BAUER) to design, construct, test and deliver a containerised pilot plant. Subsequently the water treatment technologies were tested directly on acid rock drainage (ARD) continuously emanating downstream from the historical underground mine workings and waste dumps located in the Rosia Montana region. The pilot plant was designed to meet the following objectives:

- Implementation of two alternative technologies (combined metal / ettringite precipitation, and nano-filtration with pre-and post-treatment) on multiple ARD sources, treated separately or as a blend, under field conditions;

- Verify that both technologies operate reliably, meeting all permissible discharge parameters, as per Romanian discharge standard NTPA 001/2005 [1] ;

- Derivation/elaboration of design parameters for a full-scale treatment plant design;

- Containerised plant concept for mobility, although also able to receive ARD from remote mine sites for treatment.

2. Description of the Technology

There are a number of ARD sources, and potential sources, located in the Cetate/Rosia valley in Rosia Montana. These include the discharge from the so-called Adit 714 (this adit at an altitude of 714 masl is the lowest access to the historical underground mine workings), as well as a number of other adits at higher levels, and the drainage from existing waste dumps (legacies of historical mining activities). The following flows contribute to the ARD that must be treated: (1) the relatively benign Rosia Valley Flows (RVF), and (2) the Adit 714 ARD comprising significant flowrate, low pH and high metal and sulphate concentrations. Typical characteristics of both flows are presented in Table 1.

Table 1: Adit 714 and Rosia Valley Flow Properties at Average Flowrate vs. NTPA Discharge Parameters

Parameter	*Unit*	*Adit 714 Mine Effluent*	*Rosia Valley Flow*	*Discharge Limits: (NTPA 001/2005)*
Flowrate	m^3/h	50 - 55	270 - 280	n/a
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

Two principally different treatment approaches were considered for the potential combination of high metal concentrations, low pH and high sulphate concentrations: a chemical approach comprising staged metal hydroxide and ettringite precipitation, and a nano-filtration approach (including feed solution pre-treatment and subsequent concentrate treatment).

2. 1 Precipitation Process

Due to the combination of high heavy metal and sulphate concentrations, a conventional lime precipitation process is not sufficient to achieve the stringent limits shown in Table 1. This is because the solubility of gypsum ($CaSO_4$) formed exceeds the permissible sulphate discharge parameter by a factor of approximately 3.

Therefore, a two stage chemical precipitation process comprising the sequential precipitation of metal hydroxides, followed by the precipitation of ettringite (a sulphate mineral comprising calcium and aluminum), was implemented based on successful testing at laboratory scale (JANNECK et al.; 2012).

The process includes the following steps:

1. Precipitation of the heavy metals and gypsum by raising pH (lime treatment):

   $Me^{2+} + Ca(OH)_2 \rightarrow Me(OH)_2 + Ca^{2+}$ (Me = Ni, Cu, Zn, Cd)

   $SO_4^{2-} + Ca(OH)_2 \rightarrow CaSO_4 + 2\ OH^-$

   Oxidation of Fe(II) and Mn(II) with subsequent precipitation:

   $2\ Fe^{2+} + 0{,}5\ O_2 + 5\ H_2O \rightarrow 2\ Fe(OH)_3 + 4\ H^+$

   $Mn^{2+} + 0{,}5\ O_2 + 2\ OH^- \rightarrow MnO(OH)_2 \rightarrow MnO_2 + H_2O$

2. Sedimentation and removal of the precipitation products.

3. Sulphate removal by ettringite precipitation:

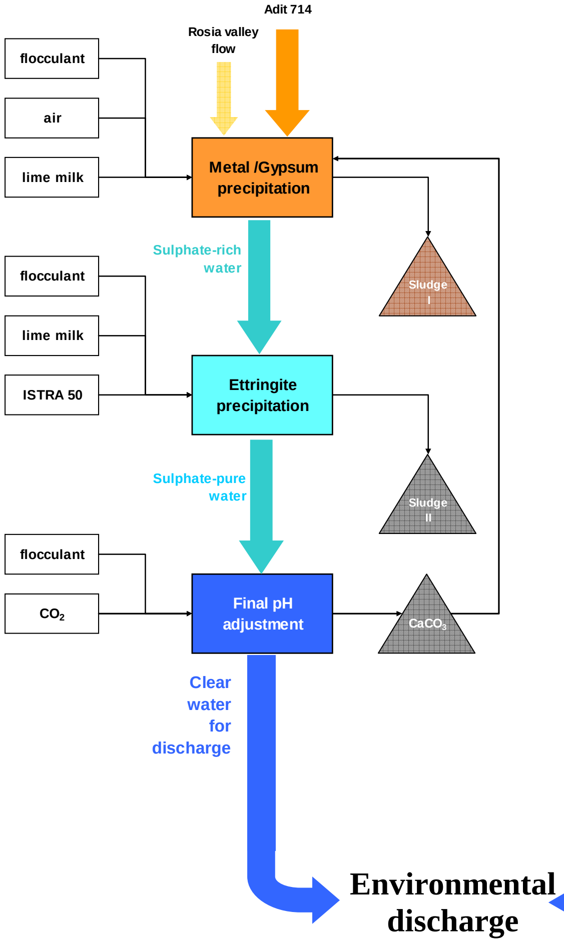
$$Ca_3[Al(OH)_6]_2\ 6\ H_2O + 3\ Ca^{2+} + 3\ SO_4^{2-} + 20\ H_2O \rightarrow Ca_6Al_2[(OH)_4(SO_4)]_3\ 26\ H_2O\ ^2$$

4. Sludge dewatering.
5. Adjusting pH value by contacting discharge with CO_2 gas:

$$OH^- + CO_2 \rightarrow HCO_3^-$$

The sludge resulting from the respective heavy metal and sulphate precipitation / thickening were combined and dewatered by a chamber filter press to produce a solid waste product for disposal.

A schematic flowsheet for the process is presented in Figure 4.



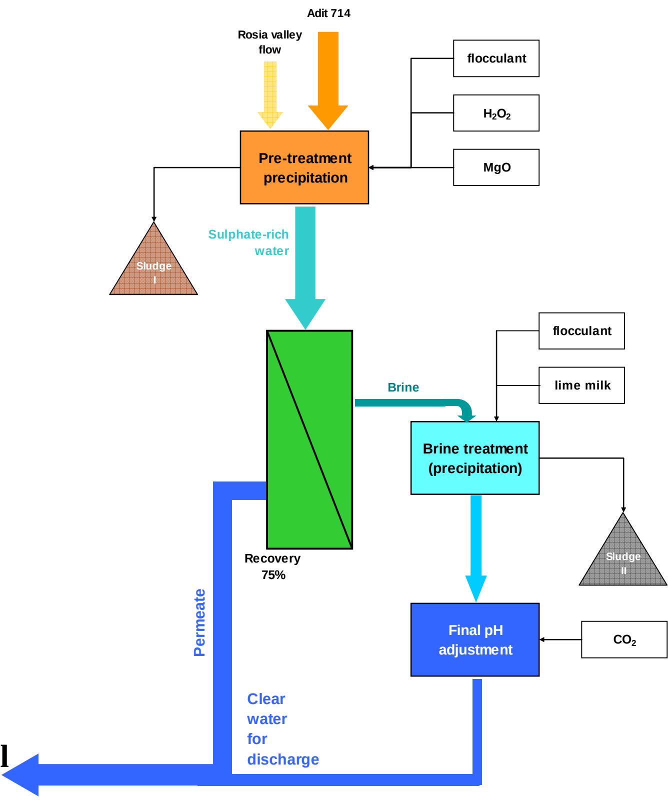


Figure 4: Two stage precipitation process: metals and gypsum precipitation (first stage), and ettringite precipitation (second stage).

Figure 5: Membrane separation process: pre-treatment, nano-filtration & concentrate treatment.

2.2 Nano-filtration

A schematic flowsheet for the membrane separation technology, which was also tested in the pilot plant is presented in Figure 5.

the feed solution(s), and provided a practical working (storage) volume for ARD solution transported from remote minesite locations by truck.

The pilot plant can be seen in Figure 6. The feed water tank is located to the right hand side of the dark blue pilot plant containers. Storage vessels and dosing equipment for hydrogen peroxide, magnesium oxide, hydrated lime and sodium hydroxide are also located to the right, on and in front of the pilot plant containers. The pilot plant was designed to treat 0.5 m³/h in the combined precipitation process configuration, or 1.0 m³/h in the nano-filtration process configuration, respectively.

Figure 6: Overview of the Pilot Plant

Following commissioning in January 2012, the pilot plant was operated until August 2012 by two operators per shift (4 panel shift roster) on a continuous basis, that is 24 hours per day, 7 days per week.

During this period the following volumes were treated at the pilot plant (Table 2).

Table 2: Volumes and Blends Treated for Two Flowsheets

Flowsheet	*Operation Time [d]*	*Treated Volume [m³]*	*Treated Mixtures Adit / RVF [% / %]*
Precipitation / Ettringite	*61*	*496*	*0/100, 20/80, 50/50, 100/0*
Nano-filtration	*130*	*2,722*	*20/80; 50/50*

Feed mixtures of Adit 714 and RVF were varied to establish whether either of the two technologies being tested was particularly vulnerable to variations in feed water quality by way of processing and/or variation in the treatment cost as a consequence.

In a separate review of the site wide water balance for the Rosia Montana Gold Project it was determined that concentrations of Adit 714 are not likely to exceed 20% during the life of the project. Therefore, following the testing of the chemical precipitation process for a large range of Adit 714 / RVF blends, nano-filtration testing was predominantly conducted on an 20% Adit 714 / 80% RVF feed blend.

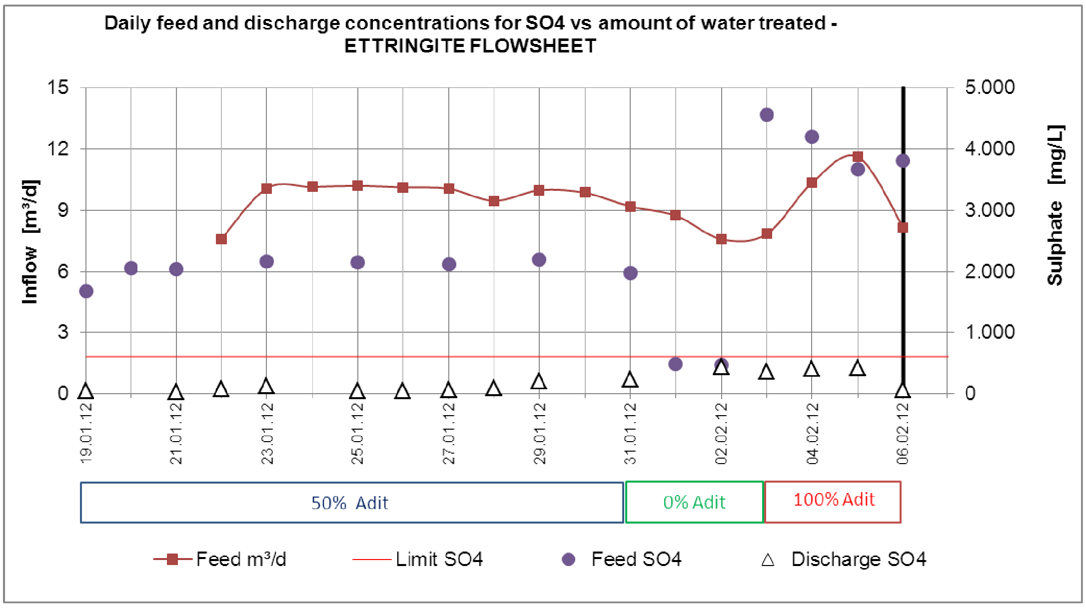
Nano-filtration of a representative feed blend over a longer time period was considered equally important in order to establish and/or confirm membrane life, and to identify any issues not becoming apparent during short term testing (e.g. gradual formation of scale in the process, and/or the partial blinding or fouling of the membranes over time).

3. Results

3.1 Precipitation Flowsheet

Initial testing of this flowsheet commenced in the winter months (Jan/Feb 2012) when ambient temperatures were regularly below zero degrees Celsius. Consequently solution feed temperatures were low. Despite the low ambient temperatures the two stage precipitation process was found to be a reliable and robust process which was easily controlled to accommodate variations in ambient conditions and feed solution properties. Subsequently the precipitation flowsheet was able to comply with all discharge parameters for a wide range of feed solution blends, as presented in Figure 7.

The first stage of the precipitation flowsheet, heavy metal and gypsum precipitation by the addition of hydrated lime in suspension (lime slurry) maintaining a pH of 9.5, is not discussed in detail herein given it is a well understood treatment method commonly applied to ARD solutions.



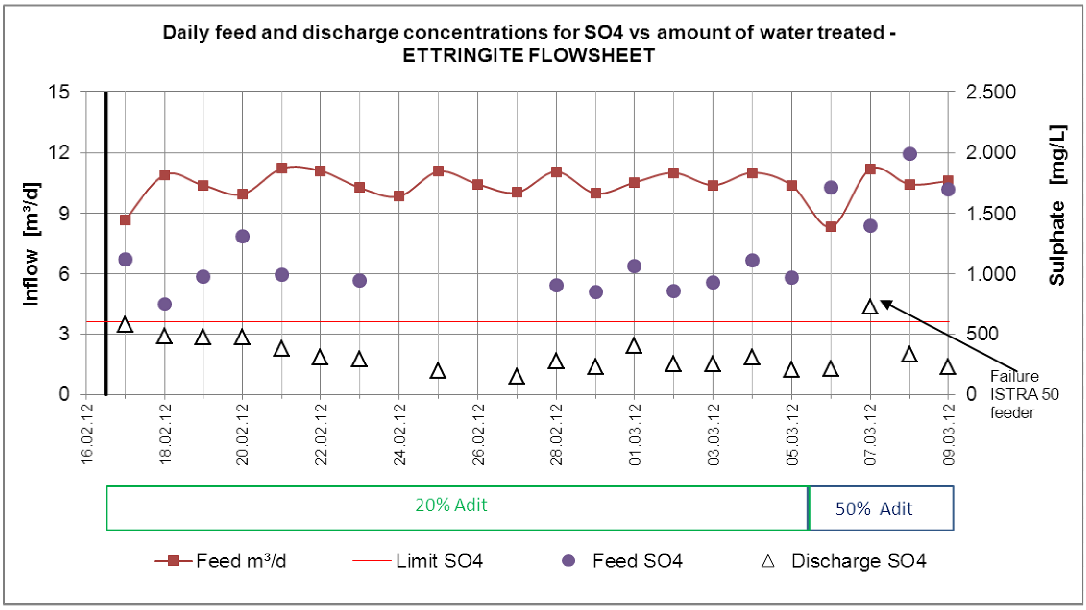


Figure 7: Precipitation Process Sulphate Feed and Discharge Concentrations for Various Feed Blends

The second stage of precipitation involves the addition of an aluminium source reagent to the clarified solution produced in the first stage of precipitation, at elevated pH (approx. 11.5), to promote the precipitation of ettringite. In addition to the aluminium source, lime slurry is added to establish and maintain the solution alkalinity as calcium is consumed to form the ettringite mineral.

The aluminium source used in the pilot plant testing of the precipitation flowsheet was a calcium alumina cement known by the trade name ISTRA 50. This reagent was selected following an extensive evaluation of commercially available aluminium source reagents during the laboratory testing phase (JANNECK et al.; 2012).

The residual sulphate in solution could be effectively controlled by regulating the addition of the calcium alumina cement. It was therefore possible to optimise the addition of the aluminium source reagent relative to the sulphate concentration.

Table 3 presents the average feed and discharge sulphate concentrations for various blends of Adit 714 and RVF tested, the net sulphate reduction achieved, and the mass of ISTRA 50 calcium alumina cement added for each blend tested. It was not necessary to test the 100% RVF flow as its sulphate concentration was already lower than the permissible discharge concentration of ≤ 600 mg/L sulphate.

Table 3: ISTRA 50 Consumption for Various ARD Feed Solution Blends

Percentage Adit 714	*ø Sulphate-concentration (influent)*	*ø Sulphate-concentration (effluent)*	*Sulphate Reduction*	*ISTRA 50 Demand*	*Ratio ISTRA50:Sulphate*
[%]	*[g/m³]*	*[g/m³]*	*[g/m³]*	*[kg/m³]*	*[g/g]*
0	200	200	0	Not tested	-
20	950	300	650	1.1	1.69
50	1,950	450	1,500	2.3	1.53
100	3,800	550	3,300	4.1	1.24

Significant optimisation of the ISTRA 50 reagent addition was achieved for increasingly higher concentrations of sulphate in the feed solution. For the highest sulphate concentration tested (100% Adit 714 solution), the ISTRA 50 consumption was 1.24 grams per 1.00 gram of sulphate, and therefore approaching the minimum stoichiometric demand.

The two stage chemical precipitation process complied with all Romanian surface water discharge parameters, as stipulated by NTPA 001/2005, for all blends tested. Furthermore the process was easily controlled with predictable outcomes supporting reagent consumption optimisation based on feed water composition.

3.2 Nano-filtration Flowsheet

Prior to nano-filtration, metals were precipitated by the addition of magnesium oxide (MgO). The reasons for using MgO as a pre-treatment reagent instead of more conventional reagents such as lime slurry were established during the laboratory testwork phase (JANNECK et al. 2012). The MgO was dosed as a powder directly into an agitated vessel rather than being premixed into a solution first, as is usual for the addition of hydrated lime, so that higher pH values might be reached during the pre-treatment stage (typically pH 8.5). A small volume of hydrogen peroxide (H_2O_2) was also dosed into the same agitated vessel to promote the rapid and complete oxidation of the manganese in solution. The pre-treatment of the feed solution with MgO / H_2O_2 was effective in precipitating the heavy metals in solution, including the slow reacting manganese.

Following the chemical precipitation and precipitate removal by thickening, the clarifier overflow was passed through two stages of pre-filtration (sand and ultra-filtration) prior to membrane separation (nano-filtration).

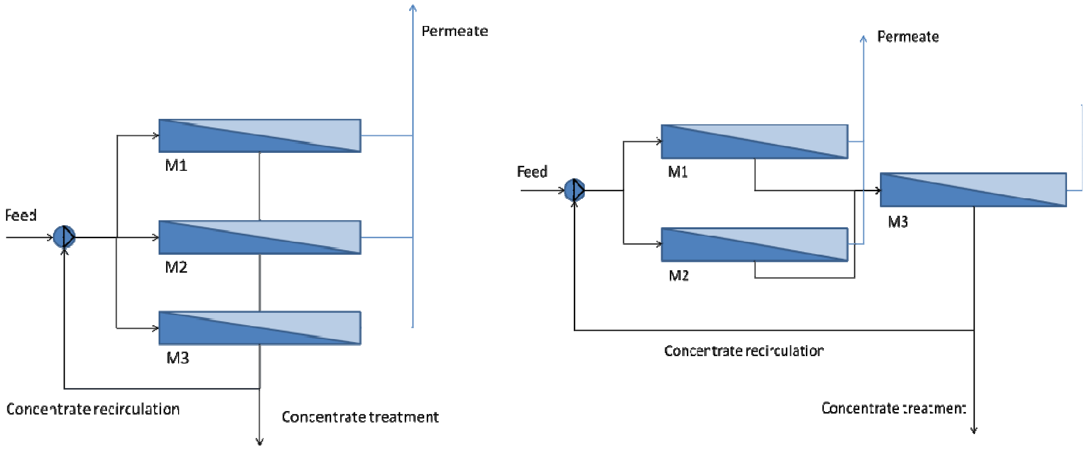


Figure 8: Membrane Module Test Configurations (left: 3-0, right: 2-1).

The nano-filtration pressure vessels were trialled in two different configurations (3-0 and 2-1) as shown in Figure 8. Each pressure vessel contained two commercial modules NE4040-70 (manufactured by CSM) connected in series.

The sulphate rich feed solution had a pH of approximately 8.0 following the chemical pre-treatment. At this pH, any carbonates present could precipitate on to the membrane surface increasing system pressures, and ultimately decreasing the permeate discharge flowrate. While the carbonate precipitate was acid soluble, and hence easily removed by acid washing with a dilute acid solution, controlling the system pH by continuously injecting acid into the feed solution was found to be effective in reducing the frequency of dedicated acid washing campaigns. The pH of the feed solution was controlled in the range of 3.5 to 4.5, while the selection of the acid(s) used for this process was the result of extensive testing.

Nano-filtration provided a stable operating platform for some 500 hours (uninterrupted) during which time the permeate recovery was consistently maintained in excess of 80%. Figure 9 graphically presents key operating data recorded during this 500 hour period.

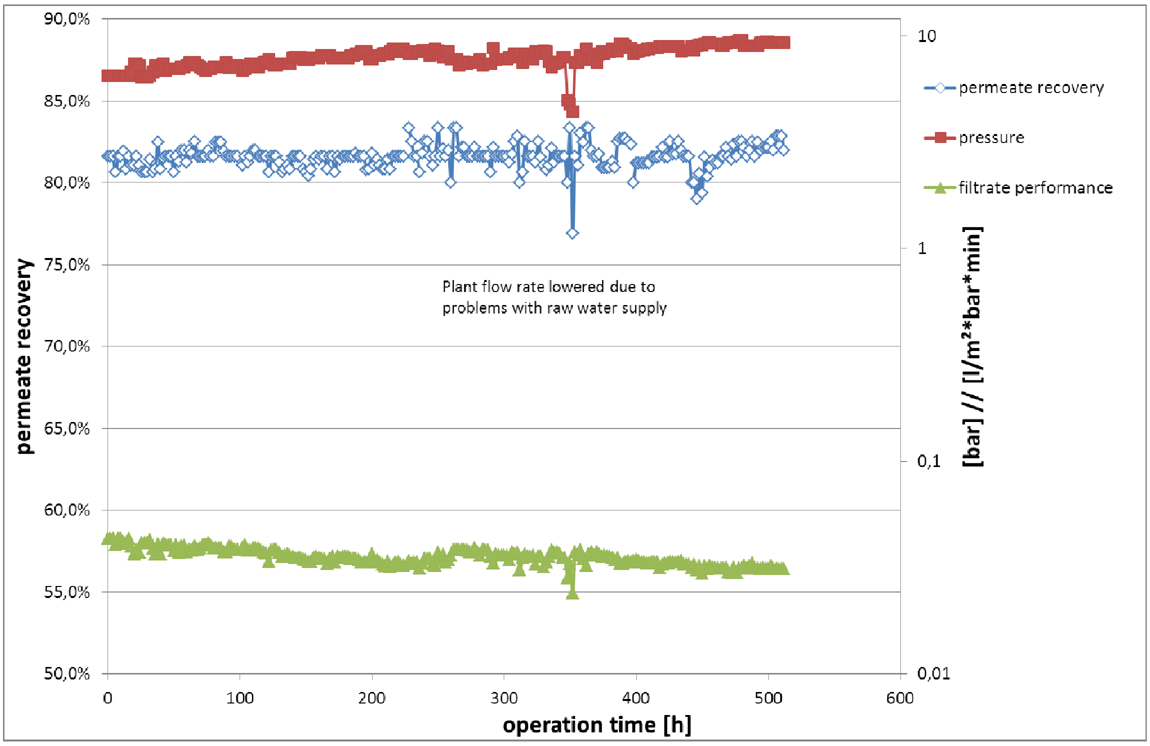


Figure 9: Continuous Operation of "2-1" Membrane Configuration for 500 Hours (20 % Adit 714)

Despite pre-treatment of the feed solution with MgO / H_2O_2, 2 stages of pre-filtration (sand / UF) and continuous acid injection into the nano-filtration feed solution, scaling in the membrane system was still apparent. This observation was supported by the increasing system pressure (red line) which was necessary to maintain steady permeate recovery, and decreasing membrane permeance, or filtrate performance (green line), which occurred over the 500 hour testing period.

Consequently, while the scaling potential of this 20% Adit 714 feed solution was reduced, it was not entirely eliminated. This infers that the routine acid washing of the entire membrane system would be required periodically in addition to the continuous pre-treatments and pH control within the membrane system. The risk of scale formation within the membrane system, and on the membrane surface itself, is therefore always present.

As system pressures were increased to maintain steady permeate recovery and discharge flowrates, a periodic 1 hour acid wash was generally all that was required to bring the membrane system back into normal operating parameters.

Operation and acid washing cycle times varied subject to the varying feed blends, pre-treatment reagents and membrane pressure vessel configurations being trialed, as graphically presented in Figure 10.

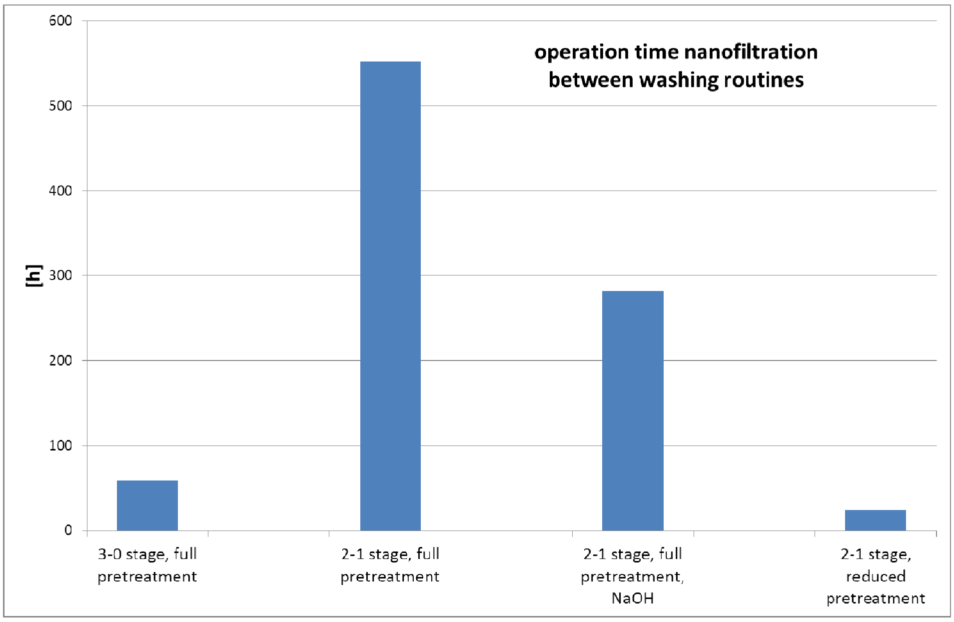


Figure 10: Operation Time Between Washing Routines

It was apparent that the efficient precipitation of heavy metals high prior to nano-filtration and precise control of the membrane system are indispensable for successful long term operation. Overall the “2-1” membrane module configuration appeared to be more stable, and perhaps less susceptible to scale formation compared to the “3-0” system despite the higher overall operating pressures which were required.

Figure 11 graphically illustrates sulphate concentrations for the feed, permeate, concentrate and a combined discharge solution produced while testing the “2-1” membrane module configuration over several months. During the test period the feed solution contained 20% Adit 714 and 80% RVF, and was pre-treated using the reagents MgO and H_2O_2.

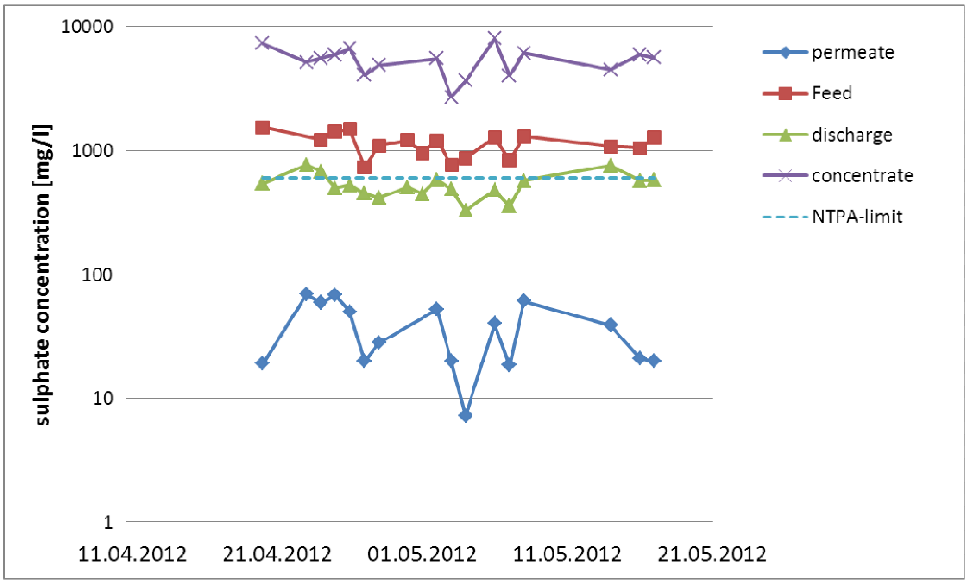


Figure 11: Nano-filtration Sulphate Concentration for 20% Adit 714 Feed Solution (2-1 configuration)

Nano-filtration feed sulphate concentrations were typically in excess of 1,000 mg/L. Permeate quality was generally high with measured sulphate concentrations ranging between 80 and 90 mg/L. With permeate recovery being maintained at around 80% (by volume); high concentrate enrichment could be achieved in the absence of serious scaling issues around the membrane system.

With concentrate, or brine, sulphate concentrations in excess of 5,000 mg/L, it was possible to precipitate out a significant proportion of the sulphate as gypsum by the addition of lime slurry. Treated concentrate solution with sulphate concentrations in the order of 2,000 mg/l could then be mixed back with permeate for discharge while still maintaining the sulphate discharge limit of ≤ 600 mg/L.

For the majority of the trial duration, the NTPA 001/2005 effluent discharge concentrations could be easily maintained. As the permeate sulphate concentration rarely exceeded 100 mg/L, small overruns of the permissible discharge concentration for sulphate (≤ 600 mg/L) were the result of blending too much treated concentrate solution back into the combined discharge with permeate (green line in Figure 11).

4. Discussion and Conclusions

Pilot plant testing of the two alternative water treatment technologies have shown both to be robust under field conditions, reliably meeting all Romanian surface water discharge parameters as specified in NTPA 001/2005. Both technologies could be managed in stable continuous operation under different climate conditions, and for varying feed water qualities. Either technology or possibly even a combination of the two may still be considered for the future treatment of historical ARD flows in parallel with future mining activities at the industrial scale.

Further, both the combined precipitation and nano-filtration processes were optimised during testing for key parameters including pH conditions, residence time, system pressures reagent consumptions and overall process control, providing important data for process design and scale-up. Preliminary cost information for unit processes was also realised, principally through the consumption of key reagents for the two flowsheets for varying feed water properties.

The experience and information gathered during the seven months of pilot trials under "real world" conditions significantly increased the knowledge based required to design a large-scale ARD treatment plant significantly. Both tested technologies are considered as suitable alternatives for industrial scale ARD water treatment. The final process solution will depend largely on the site wide water balance and interaction of the various process streams with the gold ore processing facility.

5. Acknowledgments

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6. Literature

JANNECK, E.; COOK, M.; KUNZE, C.; SOMMER, K.; DINU, L. (2012): Ettringite Precipitation vs. Nano-Filtration for Efficient Sulphate Removal from Mine Water. IMWA, Annual Conference 2012, Bunbury Western Australia, Proceedings, p. 206I-206R. http://www.imwa.info/imwa-meetings/proceedings/264-proceedings-2012.html

Notes:

[1] NTPA 001/2005 – Romanian standard regarding discharge of wastewater into surface water – Approved by Government Decision 188/2002, amended and updated by Government Decision 352/2005.

[2] In chemistry textbooks for construction materials a more common formula for ettringite is:

$$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$$