Remediation of environmental impact of acidic dam of mines through membrane process

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Abstract Mining industry is assuming sustainable position looking for higher efficiencies. Water is the most sensible resources being discussed in the mineral market once its dependence is quite high due to consumption in mining process. The challenge is to convert waste residual matter into resource and the application of new technologies can be an important tool in this development. Conventional treatment methods for such sites with no production or process improvement prove to be too expensive to be economically attractive. This paper details an industrial scale application using nanofiltration membranes on acid mine drainage water from waste rock piles dam. This source from legacy uranium mine (Brazilian Nuclear Industries) located in Caldas, Brazil has been treated and discharged in order to comply with the local legislation.

Keywords manganese, uranium, nanofiltration, acid mine drainage (AMD)

Introduction

Acid Mine Drainage (AMD) stream is the result of exposure of sulfide containing material with oxygen and water. The production of AMD usually occurs in iron sulfide-aggregated rocks and typically it is characterized by low pH and high concentrations of (semi)-metals as well as other potentially toxic elements (1). Although this is a natural process, the mining industry is the major producer of AMD waters. Waters draining active mines, abandoned mines and mine wastes are often net acidic. Such waters typically pose an additional risk to the environment because they often contain high concentrations of metals (iron, aluminum and manganese, and other metals and metalloids, incl. arsenic).

Acid mine drainage (AMD) may form in underground chambers of deep mines, when a mine is in active production this is generally of minor importance because the water tables are kept artificially low by pumping. However, when mines are closed and abandoned, and the pumps are turned off, the rise of the water table can lead to contaminated groundwater being discharged, sometimes in a catastrophic event such as the one that happened at the Wheal Jane mine in 1992 when a range of contaminants entered the environment (Younger *et al.* 2004; Neal *et al.* 2004).

Abatement of acid rock drainage (ARD) is of increasing scientific and technical interest because of stringent regulations regarding environmental pollution. Acidity and dissolved (semi)-metals released from different sources of mine waste including underground and open pit mines, mine waste rock deposits, and tailings heaps and ponds result in a deterioration of soil and water quality (Sand *et al.* 2006).

Nanofiltration is a separation technique that considers membrane with a reported pore diameter in the range of half a nanometer to a few nanometers. These membranes are charged when in contact with aqueous solutions and as such, separation takes place based on charge and size. As a consequence, species with an effective diameter of one nanometer or greater will be removed. Multivalent ions are removed to a greater extent that single charged ions. Under the circumstances where removal of multivalent ions rather than monovalent ions is important, nanofiltration offers a more cost-effective option than other membrane technologies, as reverse osmosis, because the equipment can be operated at significantly lower pressures to obtain the same permeation rates.

Description of the Study Site

The Poços de Caldas mining site is located in the Minas Gerais state, in the southern region of Brazil (latitude 21°45'S and longitude 46°35'W), 180 km northwest from São Paulo city and 360 km southwest from Rio de Janeiro the two major cities in the country. It occupies an area of about 15 km^2. The location map is presented in Fig. 1, where the city of Poços de Caldas (200,000 inhabitants) is located 20 km north from the mining site. The two major water sources which receive the releases of the mining and milling operation are the Antas River that flows in the direction of Poços de Caldas city and the Soberbo river which flows in the direction of the city of Caldas. Average annual precipitation is 1800 mm/a. The mine covers an area of 2.0 km^2. The mineralized zone was located at about 200 m below surface and the mine area was divided into three different ore bodies (A, B and C) for the purpose of mining operations (Fernandes *et al.* 2008). Bacia Nestor Figueiredo (BNF) is the place where the treat AMD came from indicated in the Fig. 2.

Fig. 1 *INB mining location.*

Fig. 2 *Bacia Nestor Figueiredo*

Chemical composition of the rocks is shown in Table 1. Attention must be called to the high contents of sulfur, occurring as pyrite that varies from 5637 to 18,961 ppm. The occurrence of pyrite in the rock has an important bearing in the generation of acid drainage as discussed previously in this text (Fernandes *et al.* 2008).

The Poços de Caldas Project was intended to produce 500 t U_3O_8/a and 275 t/a of calcium molybdate as a by-product. The operations gave rise to two main sources of contaminants to the environment; the waste rock piles (WRP)

Element	Body A	Body B	Body E
SiO_2 (%)	55 ± 0.53	53 ± 2.85	55 ± 2.64
Al_2O_3 (%)	21.7 ± 0.64	20 ± 2.96	23 ± 1.14
Fe-tot (%)	2.6 ± 0.60	4.88 ± 3.68	2.61 ± 1.06
F (mg/kg)	1,488 ± 172	4178 ± 2,957	2,013 ± 803
Th (mg/kg)	60 ± 46	96 ± 89	318 ± 962
U (mg/kg)	89 ± 57	538 ± 958	279 ± 619
Zn (mg/kg)	253 ± 47	570 ± 646	592 ± 1,360
S (mg/kg)	8,616 ± 2,544	18,961 ± 18,025	5,637 ± 5,321
Zr (mg/kg)	1,708 ± 873	4,334 ± 7,115	1,009 ± 828

Table 1 *Average composition and Standard Deviation of rocks from the three ore bodies of Pocos de Caldas mine (from : Waber et al. 1991).*

and the tailing dam. After 15 years (1982–1997) the uranium mining and milling operations have ceased while the chemical plant in charge of the liquid effluent treatment is still active. Recently, due to the exhaustion of the capacity of the tailing dam to receive additional wastes, the precipitate from the chemical treatment has been deposited in the mine open pit. The effluent from the tailing dam is treated with $BaCl_2$ to remove radium isotopes from the solution. Regarding the tailing dam, it has already been mentioned that the direct release of untreated effluents into the receiving waterbodies will result in unacceptable doses to members of the public (Fernandes *et al.* 2008).

Results and Discussion

From January 2012 to June 2012 a nanofiltration pilot plant has been the focus of a study in a Uranium site placed in Poços de Caldas, Brazill called Industrias Nucleares do Brasil (Brazilian Nuclear Industries). The aim of the application was to remove $MnSO_4$ from an acid mine drainage water source that was stored in a dam named Bacia Nestor Figueiredo (BNF) and whose volume capacity was 750 m^3. Currently INB faces a process of site clean-up and it must limit the manganese content of the dam according the local legislation (CONAMA 430/11) that limits to < 1 mg/L for environmental disposal. Currently, in order to achieve the current value, INB spends tons of $Ca(OH)_2$ on a daily basis in a lime precipitation process. The precipitate is pumped to open pit and supernatant is released to the environment. The cost of managing waste water after a non-scheduled environmental release is usually very high from a financial, ecological and social aspect. As a result, mining firms worldwide are focused on the early planning and implementation of water-management plans. In order to look for an alternative technology, the following process has been considered at INB:

Number of Units:1/Configuration:1 stage/Vessels: Codeline 8"/Elements per Vessel:1

Type of Element: Polyamide Thin Film/Manufacturer: Dow-Filmtec/Model:XUS 229323

Feed water: Acid mine Drainage at 1500 µS/cm @ 25 °C.

A cartridge polishing filter to remove fine particulate not removed by previous filters

Typical RO Feed: SDI < 3/RO Recovery: 9 % (avg/element)/Feed Capacity Per Unit: 10 m^3/h

Pre-Treatment

The water coming from BNF is driven to a lead-lag multimedia filtration system (Fig. 3). The multimedia filtration has been chosen for colloidal removal so that the Silt Density Index (SDI_{15}) before Nanofiltration membrane reaches less than 5 (100 % of time).

The cylindrical multimedia filters used for this purpose were made of carbon steel and hard rubber inner coating. The vessels (height × diameter: 1.5 m × 0.9 m) were partly filled with layers of : 150 mm of pebble (4.5 mm particle size); 400 mm of sand (0.6 mm – 1.2 mm particle size) and 300 mm of anthracite (0.8 mm – 1.0 mm particle size). The average flow rate was 11 $m^3/h.m^2$ and pressure operation was 21 psi. Each filter was equipped with backwash system and two manometers. The backwash was performed every time the differential pressure has exceeded 3.6 psi.

Pre-filtered stream was passed through a 5 µm (effective) cartridge filter prior to the

Fig. 3 *Multimedia filters*

Fig. 4 *NF containerized unit*

Fig. 5 Nanofiltration System

Nanofiltration tests to remove particulate coming from the multimedia filters, which could rapidly foul the membranes. In any industrial application feed pre-treatment could be replaced for an Ultrafiltration to minimize even more the particulate fouling.

Nanofiltration unit (NF)

In order to provide a compact solution it has been established a containerized system with the Nanofiltration membrane and associated automation as showed on Fig.4

That system has considered only one element in the vessel in order to be adequate to small water consumption during the tests but with possibility to leverage the acquired knowledge to larger systems (Fig. 5). The system is able to consider anti scaling in the RO feed stream and also to be prepared to run clean-in-place (CIP) procedure. Several signals were able to be monitored on-line as permeate flow, reject flow and feed pressure. Also analogical data as cartridge filter pressures, dosing pumps flow, and RO differential pressure has been measured.

The system has a centrifugal pump whose feed pressure has been set at 4.5 bar. A pressure control valve in front of the pump was triggered to a pressure transmitter that kept the pressure constant. Another control valve in the concentrate side had the function to keep the recovery of the system $r = \frac{\text{Permeateflow}}{\text{FeedFlow}}$. A differential pressure between the feed and the concentrate was monitored continuously so that the 10 % increasing of that difference would alarm for a cleaning procedure (clean in place – CIP).

Nanofiltration membranes

In this particular case it has been used a membrane named XUS-229323 that has high sulfate removal capacity at brackish water. That membrane has showed excellent performance during the tests. It is a thin film composite (TFC) membrane whose area is 37 m^2 and manufactured by The Dow™ Chemical Company through its subsidiary FILMTEC™.

Recovery

As the considered system had one element, the concept of the project has been to work around 9 –12 % recovery by the element. Considering larger systems where usually number of membranes in the vessels is between five and seven it is possible to leverage similar recoveries for each element inside the vessels so that the expected recovery for a larger system would be around 70 %. This would mean only a reject flow around 30 % of the feed flow.

Key contaminant removal

The results from the diary analysis showed that membrane acted in efficient level, considering the removing results were higher than

Species	Average Removal ± RSD/%
Manganese	98.8 ± 0.7 (*n* =45)
Fluoride	98.1 ± 0.8 (*n* = 55)
Sulfate	95.1 ± 0.5 (*n* = 48)
Zinc	98.1 ± 0.1 (*n* =3)
Calcium	97.9 ± 1.9 (*n*=8)
Aluminium	99.1 ± 0.5 (*n* =8)
Uranium	87.0 ± 5.0 (*n* =45)

***Table 2** Average removal of higher concentration elements using nanofiltration system; RSD: Relative Standard Deviation and n = number of samples*

95 % for contaminant key elements, except for Uranium that showed 87 % removal. The table 2 presents the average removal results for analyzed elements. The best results were the aluminum, manganese (Fig. 6) and fluoride (Fig. 7) removals. The membrane performance for sulfate removal was significant, taking into account the great concentration in the feed – around 1,000 mg/L (Fig. 7).

The results obtained for contaminants removal showed the feasibility of nanofiltration technology with XUS-229323 membrane as the contaminants concentration was reduced to acceptable levels for environmental disposal, especially for manganese and fluoride. In addition, the membrane was able to remove a wide range of elements, including rare earth elements.

Fouling tendency

One of the main concerns, when ARD is treated, is the lifetime of the membranes. During the tests, a very close and efficient operational monitoring occurred so that the correct cleaning was performed at the right time. Based on that, it was decided to autopsy the membranes after the test period. Additionally ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) have been applied in a membrane extract in order to identify what element would have more probability to cause scaling. The ICP-OES results are presented in table 4.

Aluminum and iron were the most important metals whose precipitation has been significant but in levels that did not intrude membrane performance.

Cleaning Procedures

A protocol of different cleanings has been applied during the test period what leaded to ten CIPs during 2000 hours of operation. It has been defined that oxalic acid cleaning followed by caustic soda cleaning have presented better results in terms of differential pressure recovery. Because the water source was surface water, eventually biocide (DBNPA) cleaning has been considered in shock treatment (by CIP) in order to avoid biofouling growth.

Scaling tendency

We took the opportunity to test 3 different Dow anti scalants (Acumer 4300, 3100 and 1100). One of the results is that that Acumer

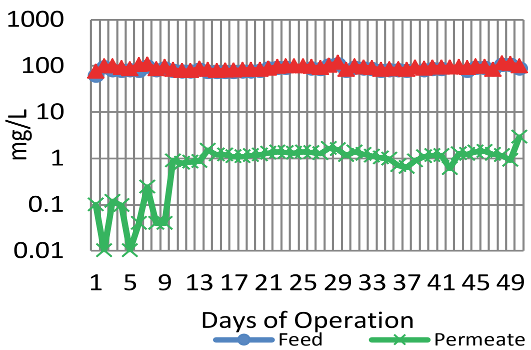

***Fig 6** Manganese feed, permeate and reject*

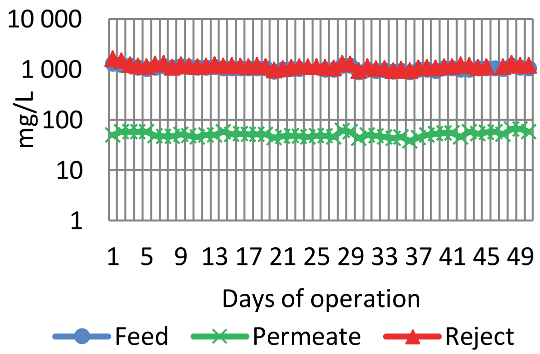

***Fig 7** Sulfate feed, permeate and reject*

Elements	U	Mn	SO_4^{2-}	Fe	Ca	Mg	P	Al	Ti	Ni	Zn	Ba	Cr
mg/L	4.8	2.8	127	13	6.1	2.9	1.2	47	0.4	0.2	3.3	0.13	0.27

Table 3 *Main elements extract of autopsied membrane*

	Parameters	$Ca(OH)_2$ Consumption	pH	Flow Rate	$Ca(OH)_2$ consumption
#	Systems	kg/m³		m³/h	kg/h
1	Conventional Treatment	1.70	11.0	300	510
2	Nanofiltration Reject	1.77	11.1	90	159.3
3	Nanofiltration Permeate	0.04	6.5	210	8.4

Table 4 *Lime Consumption*

4300 has presented lower trend to fouling in comparison to the others (Acumer 3100 and Acumer 1100). Acumer 4300 is a maleic multi-polymeric antiscalant whose molecular weight is around 2000 g/mol and containing 54–56 % of solids content.

Operational Costs and membrane life

Despite of the good permeate quality which can be used in the industrial area or returned to environment according the legislation, the membrane process has showed a very favorable Operational Expense (OPEX) in comparison to the current remediation applied at INB. INB makes use of chemical precipitation using $Ca(OH)_2$ what is generating a significant amount of mud which is a complicated to be handled. Based on the pilot plant test performed at the site, it was possible to define the amount and cost of lime used in the conventional treatment versus the cost of Nanofiltration. The table 5 shows the consumption and pH for the different streams.

According the data, comparing lime consumption in a Nanofiltration system with lime consumption in a conventional physico chemical treatment, the amount of lime used is the same but treating significantly less water. Additionally, a Nanofiltration system occupies 70 % less area than an conventional physic chemical treatment.

Conclusions

1. The membrane considered on the site had a great performance and the nanofiltration system was able to reduce sulfate, manganese and fluoride in order to generate a permeate flow according the local regulation for disposal in the environment or reuse;
2. A correct operational action and a proper pre-treatment design can drag out the time life of the membranes in tough waters as ARD;
3. ACUMER 4300 has been proved as the best anti scalant for this particular water on site;
4. Nanofiltration process has been found to present lower OPEX reducing the occupied area of precipitates;

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