# REMEDIATION OF ENVIRONMENTAL IMPACT OF ACIDIC DAM OF MINES THROUGH MEMBRANE PROCESS

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## ABSTRACT

Mining Industry is assuming a sustainable position day after day. Looking for higher efficiencies, new energy sources, and improving the social-economical life in the communities which are surrounding the mines are just a few examples. In particular, water has been one of the most sensible resources being discussed in the mineral market once its dependence is quite high due the high level of consumption in mining process. On the other hand, what is a need for a standpoint in the opposite side and according to the process it needs to be removed to guarantee the ore removal. Based on that, more and more mining companies are moving to reuse process in order to make a lower impact in water demand. Here it is not only the environmental impact over the table but also the economic aspect due the cost of cubic meter of water. Additionally there is a conflict with other activities as the human presence that either demands its consumption. There is a trend where mining companies are reporting the flow balance in order to measure the water use. Clearly the companies will be obligated to inform how much is the intake, the discharge and the quality of water coming back to water sources. Under that question there is a significant evolution during the last years where the level of recovery is over 85%, but there is a room to be improved. The reject has been another issue of concerning once the level of metals is decreasing according the time due the exhaustion of the mine. The challenge is to convert waste residual matter to resource and the application of new technologies can be an important tool. Tailing dams can be a source of process optimization besides to mitigate an environmental risk. In this particular case, they deserve a special attention once they have a large footprint and often being significant environmental liability for a mining project. On the other hand, mining clean up and recovery of remote mining areas are taking a priority role once the environmental impact can persist for a very long time largely. Abatement of acid mine drainage (AMD) is of increasing scientific and technical interest because of stringent regulations regarding environmental pollution. Acidity and dissolved heavy 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). This paper details an industrial scale application using Nanofiltration membranes where Acid Mine Drainage from waste rock piles dam in a uranium mine (Brazilian Nuclear Industries) located in Caldas, Brazil has been treated in order to adequate a permeate water stream according the local legislation.

**KEYWORDS:** acid mine drainage; sulfate; membranes; nanofiltration.

# 1. INTRODUCTION

## 1.1. Acid Mine Drainage

Acid Mine Drainage (AMD) is produced when sulfide-bearing material is exposed to oxygen and water. The production of AMD usually – but not exclusively – occurs in iron sulfide-aggregated rocks and it is characterized by low pH and high concentrations of heavy metals and other toxic elements. Although this process occurs naturally, the major producer of such effluents is the mining industry. Waters draining active and, in particular, abandoned mines and mine wastes are often net acidic (sometimes extremely so). Such waters typically pose an additional risk to the environment by the fact that they often contain elevated concentrations of metals (iron, aluminum and manganese, and possibly other heavy metals) and metalloids (of which arsenic is generally of greatest concern). In 1989, it was estimated that ca. 19,300 km of streams and rivers, and ca. 72,000 ha of lakes and reservoirs worldwide had been seriously damaged by mine effluents, although the true scale of the environmental pollution caused by mine water discharges is difficult to assess accurately (JOHNSON *et al*., 2004).

Also referred to as acid rock drainage (ARD), AMD emanating from mine waste rock, tailings, and mine structures, such as pits and underground workings, is primarily a function of the mineralogy of local rock material and the availability of water and oxygen. Because mineralogy and other factors affecting AMD formation are highly variable from site-to-site, predicting the potential for AMD can be exceedingly challenging and costly. AMD can severely contaminate surface and groundwater, as well as soils.

Acid mine drainage (AMD) may form in underground workings (groundwaters) of deep mines, although this is generally of minor importance when a mine is in active production and water tables are kept artificially low by pumping. However, when mines are closed and abandoned, and the pumps turned off, the rebound 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).

Releases of AMD have low pH, high specific conductivity, high concentrations of iron, aluminum, and manganese, and low concentrations of toxic heavy metals. Because most treatment technologies are either inadequate or too expensive, quite commonly, significant AMD is left untreated. The reactions of acid generation are best illustrated by examining the oxidation of pyrite (FeS2), which is one of the most common sulfide minerals.

## 1.2. Nanofiltration

Nanofiltration is a separation technique that considers membrane. Reported pore diameters for these membranes range from around half a nanometer to several nanometers, and the membranes are charged when in contact with aqueous solutions. Separation takes place on the basis of charged and size. As a consequence species whose effective diameter is one nanometer or greater will be removed. Multivalent ions are removed to a greater extent that singly charged ions. Under circumstances where removal of multivalent rather than monovalent ions is important, Nanofiltration offers a more cost-effective option than other membrane technologies, as reverse osmosis, once the equipment can be operated at significantly lower pressures to obtain the same permeation rates.

Nanofiltration membranes can be simple polymers or composite membranes in which barrier layer is a fully aromatic crosslinked polyamide. Such a membrane typically consists of a thick, porous, non-selective layer formed in a first process step, which is subsequently overcoated with an ultrathin barrier layer on its top surface in a second process step (PETERSEN, 1993)

## 2. 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 km2. The location map is shown 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 courses 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/year. The mine covers an area of 2.0 km2. 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 E) for the purpose of mining operations (FERNANDES *et al*., 2008).

**Figure 1. Basin Nestor Figueiredo and INB location.**

Chemical composition of the rocks is shown in Table I. 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).

**Table I. Average composition and Standard Deviation of rocks from the three ore bodies of Poços de Caldas mine.**

| Element | Body A | Body B | Body E |
|---|---|---|---|
| Fe-tot (%) | 2.6±0.60 | 4.88±3.68 | 2.61±1.06 |
| F (mg/kg) | 1488±172 | 4178±2957 | 2013±803 |
| U (mg/kg) | 89±57 | 538±958 | 279±619 |
| S (mg/kg) | 8616±2544 | 18,961±18,025 | 5637±5321 |

Source: Waber *et al*. (1991).

The Poços de Caldas Project was intended to produce 500 t $U_3O_8$ year and 275 t/year 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) and the tailing dam. After 15 years (1982–1997) the uranium mining and milling operations have ceased. However, 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 BaCl2 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 water-bodies will result in unacceptable doses to members of the public. (FERNANDES *et al*., 2008).

## 3. 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 has been to remove MnSO4 from an acid mine drainage water source that is stored in a dam named Basin Nestor Figueiredo (BNF) and whose volume capacity is 750 m3. Currently INB faces a process of site clean-up and it must to adequate manganese content  of the dam according the local legislation (CONAMA 430/11) that limits to < 1 mg/L for environmental disposal. In order to achieve the current value, INB spends tons of Ca(OH)2 on a daily basis where lime precipitation has been considered.  The precipitated 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 financially, ecologically and socially. 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:

**Table II. Process considered at INB.**

| | |
|---|---|
| Configuration | 1 stage |
| Vessels | Codeline 8” |
| Elements per Vessel | 1 |
| Type of Element | Polymide thin film |
| Manufacturer | Dow-Filmtec |
| Model | XUS 229323 |
| Feed water | Acid mine drainage at 1500μS/cm @ 25oC |
| Typical RO feed | SDI < 3 |
| Feed capacity per unit | $10m^3$/h |

### 3.1. Pre-Treatment

The water coming from BNF is driven to a lead-lag multimedia filtration system (Fig.2). The reason for the multimedia filtration has been for colloidal removal so that the Silt Density Index (SDI15) before Nanofiltration membrane has been below 5 (100% of time). The Silt Density Index or SDI is an important empirical test used to characterize the fouling potential of a Nanofiltration feed water stream. The SDI test is based on measuring the rate of plugging a 45 micron filter using a constant 30 psig feed pressure for a specified period of time. SDI15 refers to a silt density index test which was run for 15 minutes.

The cylindrical multimedia filters used for this purpose were made of carbon steel and hard rubber inner coating. The vessels (height x diameter: 1.5 m x 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 m3/h/m2 and pressure operation was 21 psi. It was used inlet and outlet connection of 2 inches and PVC pipes. 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 5µm (effective) cartridge filter prior to the 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.

### 3.2. Nanofiltration unit

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. 3

**Fig. 2. Multimedia filters**

**Fig. 3. NF containerized unit**


**Fig. 4. Nanofiltration System**

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. 4). 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 $\left(r = \frac{\text{Permeate flow}}{\text{Feed Flow}}\right)$. 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).

### 3.3. 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 400ft² and manufactured by The Dow™ Chemical Company through its subsidiary FILMTEC™.

### 3.4. 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.

### 3.5. Key contaminant removal

The results from the diary analysis showed that membrane acted in efficient level, considering the removing results were higher than 95 % for contaminant key elements, except for Uranium that showed 87,0% removal. The table III presents the average removal results for analyzed elements.

The best results were the aluminium, manganese (Figure 5) and fluoride (Figure 6) removals. The membrane performance for sulfate removal was significant, taking into account the great concentration in the feed – around 1,000 mg/L (Figura 7).

**Table III. Average removal of higher concentration elements using nanofiltration system. 3. Average removal of rare earth elements present in the effluent after treatment through nanofiltration system**

| Specie | Average |
|---|---|
| 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) |

| Specie | Average |
|---|---|
| Lanthanum | 99,5 ± 0,2 (n= 6) |
| Cerium | 99,5 ± 0,2 (n=6) |
| Praseodymium | 96,7 ± 0,2 (n=5) |
| Neodymium | 99,4 ± 0,2 (n=6) |
| Samarium | 98,4 ± 0,1 (n=6) |
| Yttrium | 99,4 ± 0,3 (n=7) |

Note: RSD: Relative Standard Deviation and n = number of samples

Furthermore, the membrane was efficient in rare earth elements removing. Some of them were analyzed and the average results are shown in table 3.

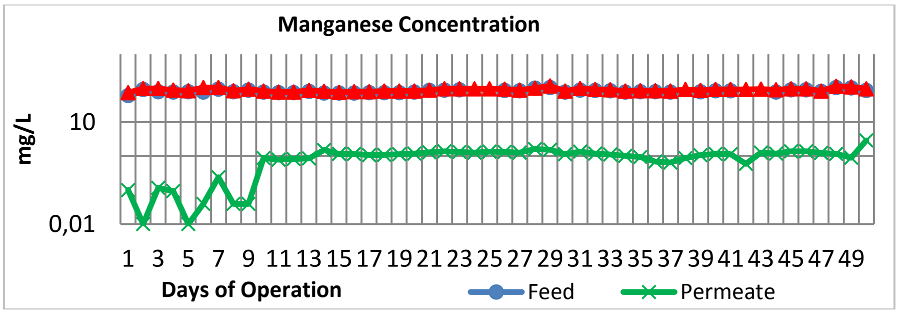


**Figure 5. Manganese concentration in feed, permeate and reject during the nanofiltration operation.**

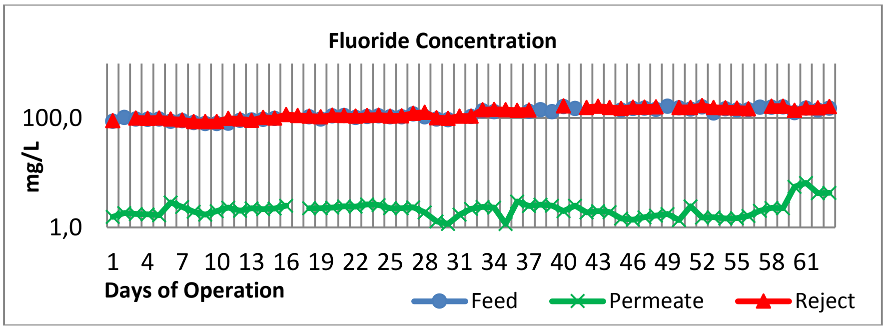


**Figure 6. Fluoride concentration in feed, permeate and reject during the nanofiltration operation. The Fluoride has been reduced to around 2 mg/L even with the feed ranging from 80 to 160 mg/L.**

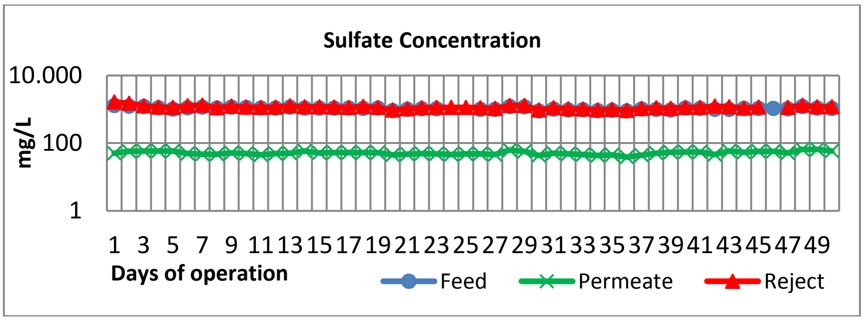


**Figure 7. Sulfate concentration in feed, permeate and reject during the nanofiltration operation. The sulfate has been reduced to 60 mg/L in permeate.**

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, sulfate and fluoride. In addition, the membrane was able to remove a wide range of elements, including rare earth elements.

### 3.6. Fouling and scaling tendency

One of the main concerning when ARD is treated is the time life of the membranes. During the tests it was performed a very close and efficient operational monitoring so that the correct cleaning was performed in the correct time. Based on that, it was decided to autopsy the membranes after the test period. The figure 8 shows the internal side of the element where the leaves surface could be checked. As it can be realized the membranes leaves have presented a very low visual fouling what indicates that the cleaning protocol has been adequate.

| Element | mg/L |
|---|---|
| U | 4,88 |
| Mn | 2,78 |
| $SO_4^{2-}$ | 127 |
| Fe | 12,5 |
| Ca | 6,1 |
| Mg | 2,94 |
| P | 1,27 |
| Al | 46,7 |
| Ti | 0,43 |
| V | 0,01 |
| Cr | 0,2725 |

| Element | mg/L |
|---|---|
| Ni | 0,145 |
| Cu | 0,06 |
| Zn | 3,34 |
| Mo | <0,004 |
| Cd | 0,015 |
| Ba | 0,134 |
| Y | <0,004 |
| La | 0,7 |
| Ce | 0,48 |
| Nd | 0,23 |
| Sm | 0,03 |

**Table. 4 (a) (b). Extract of autopsied membrane**

**Figure 8. Membrane autopsied.**

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 scale in the membrane as showed in table 4 (a) and (b).

Aluminum and iron were the most important metals whose precipitation has been significant but in levels that did not intrude membrane performance. We took the opportunity to test 3 different Dow anti scaling (Acumer 4300, 3100 and 1100) . It has been realized that Acumer 4300 has presented lower trend to fouling when in comparison to the others. Acumer 4300 is a maleic multipolymeric antiscaling whose molecular weight is around 2000 with 54-56% of solids content. Acumer 4300 is an excellent sulfate and carbonate salt inhibitor and it is produced by The Dow Chemical Company™.

### 3.7. 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.
Once the water source was a surface water, eventually biocide (DBNPA) cleaning has been considered in shock treatment (by CIP) in order to avoid biofouling growth.

## 4. CONCLUSIONS

Considering the procedures detailed above, we concluded that the membrane considered in the site had a great performance and it was able to reduce sulfate, manganese and fluorine and to generate a permeate flow according the local regulatory for disposal in the environment or reuse.

We observed that a correct operational action and a proper pre-treatment design can drag out the time life of the membranes in tough waters as ARD. Application of anti-scaling ACUMER 4300 has been proved as the best anti scaling alternative in the particular water in the site. In summary, nanofiltration process has been found to present lower OPEX reducing the occupied area of precipitates and a very efficient technical alternative.

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