Membranes in Mining: Controlling CaSO₄ Scale in AMD Minewaters

Gregory Gibson*, Max Fazel and Stephen P. Chesters
Genesys International Ltd. UK

Abstract

Membrane technologies are capable of assisting in the treatment of AMD minewaters to produce clean permeate for reuse onsite and the concentrate stream can be used for the recovery of precious metals. Due to the harsh feed conditions associated with AMD waters rapid scaling and fouling can occur. In this mini review the authors have discussed the potential for scaling and fouling, particularly CaSO₄ (gypsum) scale and have presented methods to prevent this using good pre-treatment and frequent cleaning. Genmine AS26 was developed as a low-pH specific antiscalant and Genmine C15 and Genmine C17 are cleaners used for the removal of CaSO₄ scale.

Keywords: Acid mine drainage; Gypsum; Reverse osmosis; Antiscalant; Membrane cleaning

Introduction

The mining industry is the fourth largest consumer of water worldwide. The extraction of precious metals such as gold (33,000 litres/ounce), copper (18,000 litres/kg) and aluminium (8,000 litres/kg) are some of the biggest contributors [1]. The location of these mines is also of importance as many are located in water scarce areas. As well as water shortage issues the environmental aspect of mining is one that is increasingly becoming more prominent, with recent mining disasters at Samarco and Brumadinho offering a stark reality of the consequences of poorly managed and maintained sites [2,3]. During the extraction procedure various chemical processes occur; with the formation of acid mine drainage (AMD) a particular problem. AMD forms in pyrite rich mines beginning a chain of reactions that lead to high levels of iron and sulfate [4]. If left untreated, this process will continue leading to a reduction in pH and an increase in the total dissolved solids (TDS), with this waste usually stored in dams for future treatment. This in itself is an environmental problem as there have been instances in the past of uncontrolled spillages, or the collapse of dams such as seen with Samarco and Brumadinho that are catastrophic to the surrounding areas, often resulting in the pollution of nearby rivers and in these instances there have been multiple fatalities.

By employing desalination techniques such as reverse osmosis (RO) it is possible to treat AMD waters for reuse onsite; in both a process capacity for further metal extraction or even domestically in drinking water for its workers. Szyplinska [1] stated that over 90% of mine water can be reused if treatments such as reverse osmosis and micro-filtration are applied [1]. Due to the high levels of dissolved metals in solution coupled with the typical low pH values seen, most mine waters can be quite challenging in terms of their ability to scale and foul the membrane surface. In this short review the methods of controlling scaling will be discussed, particularly the formation of CaSO₄ (gypsum) scaling as well as the ability to remove scale from the membrane surface by cleaning.

Scaling of Membranes and Methods of Control

The ability to control the build up of scale within an RO membrane plant is of vital importance for the successful and continuous operation of the plant. CaSO₄ is the most difficult scale to deal with as it is pH independent and therefore a change in pH will have no effect on the ability to prevent scale precipitation on the membrane surface. The simplest method of preventing scale formation is to know the water chemistry and what species are likely to exceed their saturation point; and then based on these findings an appropriate antiscalant can be used. Antiscalants are chemicals that are added to water prior to entering the RO plant to prevent scale formation; typically these are polyphosphates or other similar compounds. Antiscalants should be selected based on the chemical composition of the feedwater and used in sufficient quantities to prevent scaling. Cleaners are chemicals that are used to remove existing scale from the membrane surface; typically these are alkaline cleaners such as caustic soda or acidic cleaners such as hydrochloric acid. Cleaners should be used according to the manufacturer’s recommendations and should be avoided as they can damage the membrane surface.
be used. An antiscalant works at the sub-stoichiometric level by one or more closely inter-related mechanisms of threshold inhibition, crystal distortion and dispersion. Threshold inhibition prevents the precipitation of a salt once it has exceeded its solubility product (Ksp), crystal distortion affects the growth and ordering of a crystal causing an irregular shaping and weak structure and dispersion works by the inhibitor chemisorbing onto the crystal surface, giving additional charge, resulting in repulsion and subsequently dispersion [5].

Genesys International Limited has formulated a number of different antiscalants specific to mining including Genmine AS34, Genmine AS45 and Genmine AS26. Genmine AS26 was developed specifically for acidic minewaters and is particularly effective at inhibiting the formation of CaSO₄ scale at low pH. A series of threshold inhibition jar tests where carried out under various conditions; altering the pH, Ca, SO₄ and metal ion concentrations typical of those found in AMD waters. It was found that when other traditional antiscalants performed poorly at low pH, Genmine AS26 gave very good inhibition at high levels of saturation for CaSO₄ (Figure 1).

![Figure 1: Graph showing the performance of Genmine AS26 against other traditional antiscalants at low pH.](image)

**Fouling of Membranes and Cleaning**

Fouling can be described as the deposition of suspended solids within the feed water on the membrane surface and feed spacer. The main sources of fouling in a traditional RO system are bacteria, clay, colloidal silica, organics and metal oxides/hydroxides. Within mining the potential for fouling is even greater as the TDS values of feed waters; particularly iron, aluminium, manganese and sulfate ions are high. If correct pre-treatment is not used, the potential for fouling is further increased. Most traditional antiscalants are phosphonate and/or polycarboxylic based which decrease in performance as the pH is lowered and therefore are largely ineffective against gypsum scaling in AMD waters [6]. By using an antiscalant such as Genmine AS26 the CaSO₄ should stay in solution at low pH up until the limit of the chosen antiscalants capability. Changes in water chemistry that cause the saturation level to go beyond the capabilities of the pre-treatment is one of the primary reasons for the formation of CaSO₄ scale within an RO system. If this happens there will be a noticeable decline in permeate quality and membrane flux, as well as an increase in differential pressure across the membrane. At this point the membrane needs to be cleaned with the correct cleaner(s) in an attempt to remove the specific foulant and restore the permeate flux and salt rejection to previous values as well as improving the quality of the permeate. It is key that the onset of fouling is detected as early as possible as this will ensure that the membranes affected are recoverable. If a RO plant is poorly maintained and scaling and fouling are allowed to occur unabated, the cost of replacing the membranes in a plant can be very expensive. In having a clean in practice (CIP) protocol in place to ensure regular cleaning of the membranes the lifetime of the membranes can be extended.

As already mentioned, CaSO₄ scale is a big problem associated with AMD waters. In a mine with high levels of sulfate, the potential for scaling is even greater. At Genesys International Limited some CaSO₄ specific cleaners have been developed that are very effective at scale removal; called Genmine C15 and Genmine C17 (Figure 2). (Figure 2a) shows the spacer filament in an RO membrane that is completely covered in CaSO₄ scale when viewed under the microscope and (Figure 2b) presents the spacer filament after a 3-hour clean with either Genmine C15 or C17.
**Conclusion**

AMD wastewater in mines has been an ongoing issue for the past number of decades. Through the use of membrane technologies such as RO, this water can be treated for reuse on site thus improving the environmental impact of a mine. The main issue affecting this is the difficult water chemistries encountered in mining such as low pH and high TDS values, resulting in rapid scaling and fouling of the membrane. This mini review has briefly highlighted how through good pre-treatment and the correct choice of antiscalant, the onset for scale formation can be decreased. Genmine AS26 has proven effective at preventing the formation of CaSO₄ scale at low pH and high TDS values. As well as pre-treatment; this review has also shown that CaSO₄ scale can be cleaned using newly formulated products Genmine C15 and Genmine C17 after only a few hours (3 hours) of cleaning in order to restore performance within an RO plant.

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**References**


