# MAXH$_2$O DESALTER technology treats calcium sulfate saturated wastewater, a perfect solution for treating acid mine drainage wastewater

**ALEX DRAK, ROI ZAKEN PORAT AND TOMER EFRAT**
**IDE Technologies**
**Kadima, Israel**

**MARCO KERSTHOLT AND GERARD VAN HOUWELINGEN**
**Royal Haskoning DHV**
**Amersfoort, the Netherlands**

KEYWORDS: Acid mine wastewater treatment, MAX$H_2$O DESALTER, reverse osmosis, Crystalactor® technology, calcium sulfate precipitation.

## ABSTRACT

(Acid) mine drainage ((A)MD) is a big problem for the mining industry. The formation of (Acid) mine drainage is caused by the oxidation of sulfide minerals which, depending on the buffer capacity of the rocks, leads to either highly acidic, metal-rich water with high sulfate content or neutral/slightly acidic water with moderate metal content and high sulfate concentration. Both types of (A)MD have high sulfate concentration and high scaling potential, predominantly of gypsum. Sulfate is considered a more significant long-term water quality issue for mining operations, and its control levels are based primarily on secondary drinking water recommendations of approximately 500 mg/L. Two methodologies are mainly used, stand-alone or in combination, to remove sulfate from acid mine water: separation, which are membrane separation; or salt precipitation, for example formation of gypsum.

Conventional membrane separation systems, as a solution for sulfate removal from acid mine wastewater, have several drawbacks that limit the maximum possible system recovery, and even prevent their use in these applications. Conventional membrane systems will also encounter operational challenges when required to handle variable feed quality and variable recoveries, as well as at high supersaturation conditions of calcium sulfate ($CaSO_4$).

A recently developed MAX$H_2$O DESALTER technology overcomes these limitations, making it the perfect solution for treating acid mine wastewater. Its many benefits allow this technology to address the different challenges successfully, such as calcium sulfate scaling, and bio and organic fouling potential. The developed system enables operation of a reverse osmosis (RO) system with feed water quality varying from 1,000 mg/L to 70,000 mg/L TDS, and at water recoveries from 25% to 99.9%. The developed system removes sulfate ions by crystallization of calcium sulfate in the Crystalactor®, an integrated salt precipitation unit, while concentrating the wastewater in the RO system. The only limiting factor of the system becomes the RO brine osmotic pressure, not supersaturation of calcium sulfate.

This paper presents the results from a recent pilot conducted with acid mine drainage wastewater. The results show that the system can reach a recovery of over 90%, at which the calcium sulfate saturation index theoretically reaches over 3,000%, which typically leads to immediate calcium sulfate precipitation on the RO membrane. In practice, continuous crystallization of the calcium sulfate in the integrated salt precipitation unit maintained the

saturation index in the range of 1 - 800%-1,200% during operation. The system operated without the addition of chemicals other than antiscalant, and produced pellets of more than 90% dry solids content, which do not require further sludge dewatering treatment. Depending on the effluent requirements, the obtained RO brine stream can be partially or completely blended with RO product, further increasing the total recovery of the system.

These results show the significant advantage of the developed system as a treatment alternative for acid mine wastewater. The developed system saves operational costs by decreasing chemical consumption and the amount of sludge to be discharged, and investment costs by the high recovery that can be achieved.

## INTRODUCTION

Water supplies around the world are becoming increasingly scarce due to increasing global populations, increasing industrial processes, pollution and inequitable water distribution. Mining industries are one of the major contributors to environmental pollution. Water issues at mine sites can arise from various sources including process wastewater and seepage from tailing facilities, waste dumps, metal-concentrate processing facilities, ponds and other mine facilities. (Acid) mine water drainage ((A)MD), characterised by neutral to low pH and high salt and heavy metal content, is recognized as one of the more serious environmental problems in the mining industry. (A)MD is produced when sulfide-bearing material is exposed to oxygen and water. The longer this type of wastewater goes untreated, the more costly and insurmountable the problem becomes (Akcil et al., 2006).

Sulfate, typically the predominant ion, is introduced into mine water as a result of the oxidation of sulfide-bearing ores (often pyrite). Calcium is often present at elevated levels as, during underground (A)MD processes, nearby dolomitic rocks dissolve into the water to neutralize the formed acid from the sulfide oxidation. These two ions, which are close to the saturation threshold, make the treatment process of (A)MD extremely difficult. Sulfate control in mine water primarily follows one of two often combined methodologies; (1) Removal of salts from water by membrane separation; (2) Removal of sulfate by salt precipitation (Bowel 2004).

The recent demand for low sulfate concentration of 250-500 mg/L makes it difficult for existing technologies to meet the challenge while remaining economically viable. Therefore, it is necessary to develop new technologies to address the new challenges.

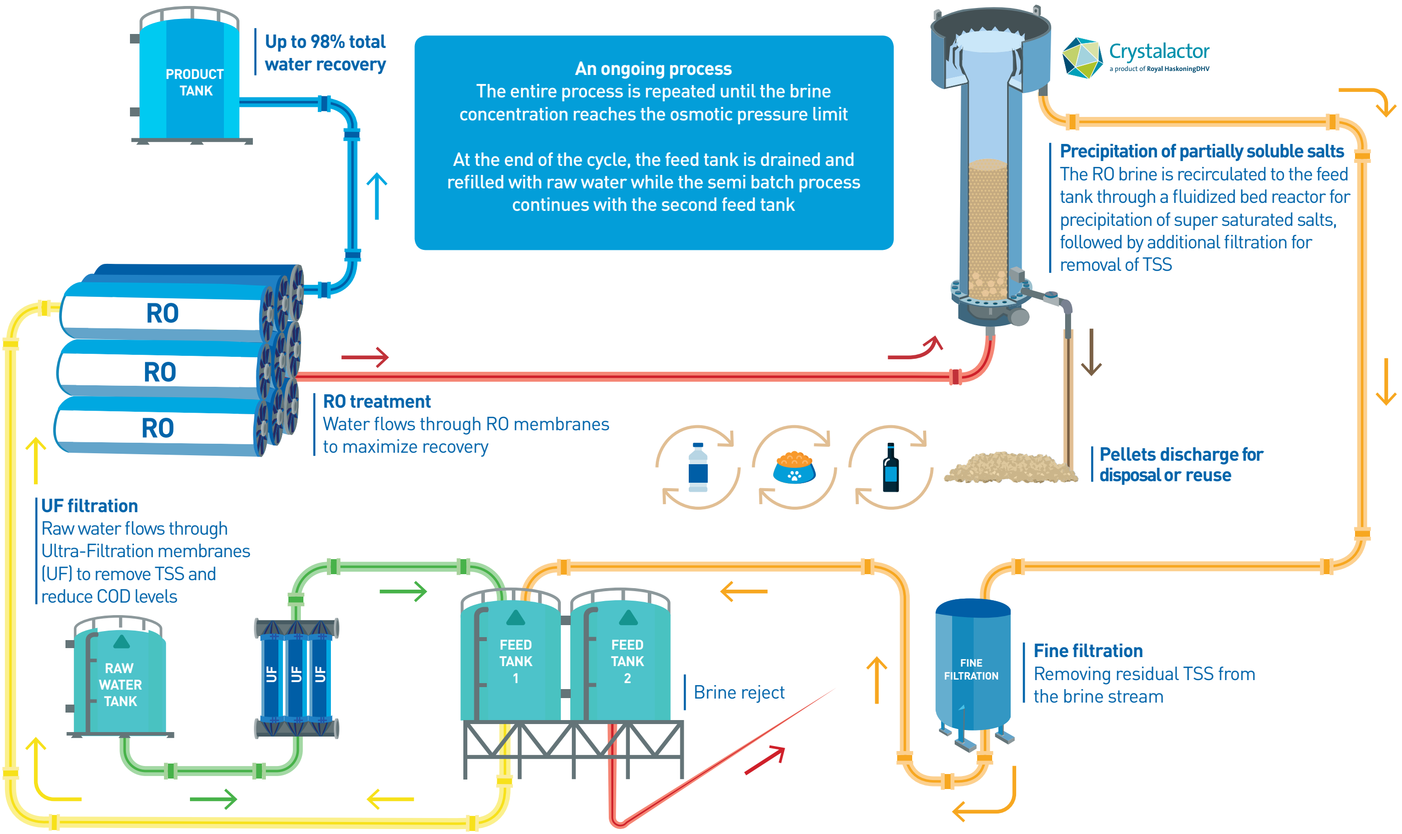
The main challenge of minimizing quantity of produced wastewater is the wastewater chemistry. As the concentration of wastewater salts increases, there is an increased risk of treatment process failure due to the precipitation of salts on all available surfaces. Brine disposal is a problem in many situations. A recently developed technology, containing an RO system with an integrated salt precipitation unit, overcomes this limitation. The technology provides a solution for difficult industrial wastewater and brackish water, and successfully overcomes the various challenges, e.g. scaling by sparingly soluble salts, and organic and bio fouling.

The developed technology was successfully tested for minimization of brackish water and industrial wastewater concentrates. The recovery of these concentrates was limited by calcium carbonate and silica scaling (Drak et al., 2018). This paper presents the results of the minimization of calcium sulfate enriched concentrates.

## INNOVATIVE BRINE MINIMIZATION TECHNOLOGY – TECHNOLOGY DESCRIPTION

The developed system contains an RO system with an integrated salt precipitation and removal unit. The process provides a solution for difficult industrial wastewater and brackish water requiring high recovery operation and successfully overcomes the different challenges, e.g., scaling of sparingly soluble salts, and organic and bio fouling. The integrated salt precipitation and removal unit removes only the salts that can harm the desalination process and, without the addition of chemicals, produces scaling pellets of more than 90 percent dry solids content, which do not require further sludge dewatering treatment. In addition, the reverse osmosis unit is operated at high shear velocity, minimizing the negative effect of concentration polarization, thus improving the RO process efficiency. The developed process minimizes the brine quantity to the maximum threshold limit of the osmotic pressure, with minimum operational expenditures (Drak et al., 2016).

The operation principle of the technology is the recirculation of treated water through the RO system at high shear velocity, and continuous precipitation and removal of supersaturated salts from the recirculated brine. This significantly reduces the salt concentration build up near the RO membrane wall, thus prevents the precipitation of sparingly soluble salts on the membranes. The brine



**Up to 98% total water recovery**

**An ongoing process**
The entire process is repeated until the brine concentration reaches the osmotic pressure limit

At the end of the cycle, the feed tank is drained and refilled with raw water while the semi batch process continues with the second feed tank

**Precipitation of partially soluble salts**
The RO brine is recirculated to the feed tank through a fluidized bed reactor for precipitation of super saturated salts, followed by additional filtration for removal of TSS

**RO treatment**
Water flows through RO membranes to maximize recovery

**Pellets discharge for disposal or reuse**

**UF filtration**
Raw water flows through Ultra-Filtration membranes (UF) to remove TSS and reduce COD levels

Brine reject

**Fine filtration**
Removing residual TSS from the brine stream

flows through the salt precipitation unit downstream to the RO membranes, where it reduces the saturation of sparingly soluble salts, thus enabling continuous cycles through the RO system, until reaching maximal brine osmotic pressure.

The salt precipitation unit used in this process has decades of experience in potable water softening (Van Ammers et al., 1986) and has been applied for recovery of phosphate, heavy metals and fluoride as well (Van Dijk et al., 1991). The principle of fluidized bed reactor operation is as follows: the reactor is partially filled with suitable seed particles of 0.5 – 0.2 mm size; the RO brine is pumped upward through the bed of particles to maintain this in a state of fluidization. The seed particles are used as crystallization sites; they provide the high surface area that lowers the energy required for precipitation. The antiscalant that prevents the scaling in the RO elements, together with sparingly soluble salts, adsorbs and precipitates on the seed particles, creating the salt-coated crystals. As the crystals become progressively heavier, they gradually travel towards the bottom of the bed. Periodically, without interrupting the operation of the reactor, the lower portion of the bed, with 1.0 – 0.8 mm size crystals, is discharged into a transportable container with a perforated bottom, and fresh seed material is introduced. No filter or other mechanical dewatering equipment is required; the dry solids concentration in the obtained crystals is more than 90% and they can be used for soil neutralization, road building, as an animal feed additive, in cement making and other applications (Giesen et al., 2009).

**The advantages of the developed process are:**

- The low and independent instantaneous RO recovery, per cycle, that allows operation with a single stage RO system, with good flux balance between elements, lowest lead element flux and highest cross-flow and concentrate flow velocities
- The ability to achieve different total recovery levels in the same system; the brine recirculation can be stopped at any recovery, at any RO brine level
- The ability to operate with variable feed water TDS levels
- Low bio-fouling potential due to the variable salt concentration or variable osmotic pressure to which the membrane elements are exposed during the operation
- Low organic fouling potential due to high cross-flow velocity (feed to brine) in RO membranes,
- Low scaling tendency and the ability to dissolve scale, due to the under-saturated water conditions to which the last elements are exposed at the beginning of every cycle

## CASE STUDY – DESCRIPTION

The developed technology was tested with mine wastewater that is metal-rich water with a high sulfate content and high calcium sulfate scaling potential. The wastewater composition, together with product water requirements, are presented in Table 1. The major challenge of this wastewater was supersaturation with respect to calcium sulfate. An additional challenge with this type of wastewater is the presence of metals and organic material that prevents a conventional RO system from reaching high recovery.

**Table 1: Mine Water Quality and Product Requirements**

| No. | Quality Parameter | Units | Mine Wastewater | Product Requirements |
|---|---|---|---|---|
| 1. | pH | | 5.70 | 9.0 – 5.5 |
| 2. | Alkalinity | ppm as CaCO3 | <5.0 | |
| 3. | Total dissolved solids | ppm | 3,157 | < 500 |
| 4. | Conductivity at 25C | microS/cm | 3,960 | |
| 5. | Calcium | ppm | 294 | |
| 6. | Magnesium | ppm | 1.3 | |
| 7. | Sodium | ppm | 734 | |
| 8. | Potassium | ppm | 35.6 | |
| 9. | Chloride | ppm | 96 | < 200 |
| 10. | Fluoride | ppm | 0.62 | < 1.0 |
| 11. | Sulfate | ppm | 2,020 | < 250 |
| 12. | Boron | ppm | 0.49 | < 0.75 |
| 13. | Total suspended solids | ppm | 12.8 | |
| 14. | Turbidity | NTU | 18 | |
| 15. | Iron | ppm | 1.96 | |
| 16. | Aluminum | ppm | 0.858 | < 5.0 |
| 17. | Manganese | ppm | 0.082 | < 0.2 |
| 18. | Copper | ppm | 0.587 | |
| 19. | Dissolved organic carbon | ppm | 6.1 | |
| 20. | Chemical oxygen demand | ppm as O2 | 35.0 | |
| 21. | Oil and grease | ppm | 1.39 | |
| 22. | | Calcium sulfate saturation index | % | 57% at 25 C |

The pilot, used for the study, is designed for the production of 600 L/d of treated permeate. The pilot is designed to simulate the process conditions of a full-scale unit. A picture of the pilot main components is presented in Figure 2. The RO installation is presented on the left, and the salt precipitation reactor in combination with the gravity sand filters on the right.

**Figure 2: Pilot unit**

The pilot is operated at the following process parameters:

- Reverse Osmosis permeate flux - < 40 LMH
- Reverse Osmosis instantaneous (local) recovery - < 15%
- Reverse Osmosis total recovery –90%-95%
- Salt precipitation reactor hydraulic loading rate - 100 – 60 $m^3/hr/m^2$
- Gravity media filter hydraulic loading rate - < 12 $m^3/hr/m^2$

## CASE STUDY – RESULTS

This section presents the continuous operation of the pilot with mine wastewater. Figure 3 shows the total recovery achieved in the pilot study. It can be seen that in every cycle, recovery above 90% was achieved. RO feed pressure, at the end of the cycle, was only 25 – 28 bar, meaning that further increase in recovery is possible. Since about 70% of the salts in the wastewater are calcium and sulfate that are partially removed in the salt precipitation reactor during the process, the recovery of the system can be significantly increased until reaching the limit of the osmotic pressure. In order to reduce the duration of each cycle for operation at recoveries higher than 90%, it is probably worth splitting the system into two systems, each operating at 90% recovery and providing a total recovery of about 99%.

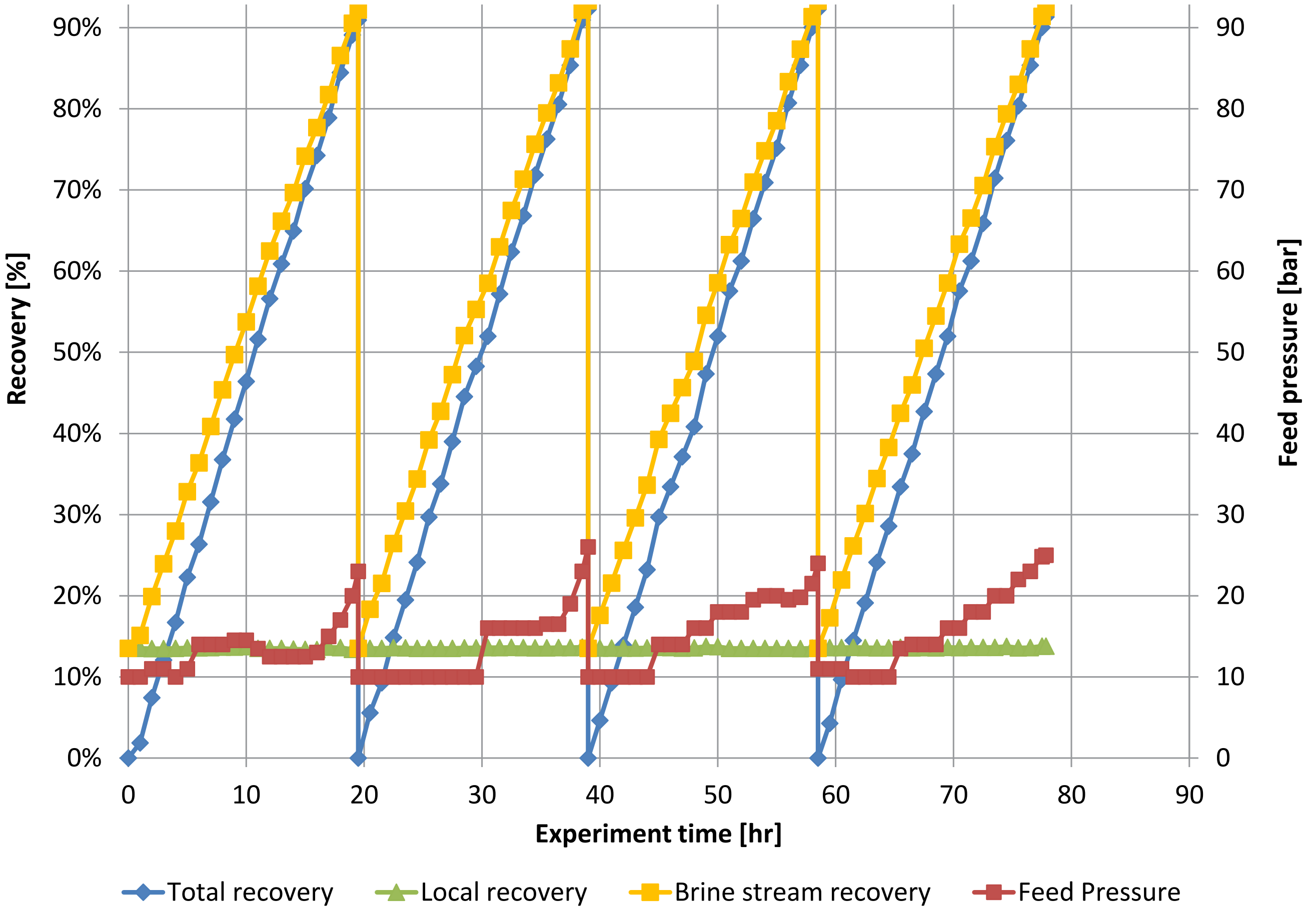


Figure 3: Achieved Recovery and Feed RO Pressure during the Pilot Study

Figure 4 shows the sulfate concentration changes during the pilot study. The green triangles are the theoretical sulfate values in case there is not removal of calcium sulfate during the process. The blue rhombuses are the actual sulfate values measured during the study. It can be seen that theoretical sulfate concentrations would reach the values of 27,000-32,000 mg/L while the actual sulfate concentrations measured are 15,000-17,000 mg/L. Part of the sulfate reduction can be attributed to calcium sulfate crystallization in the salt precipitation unit.

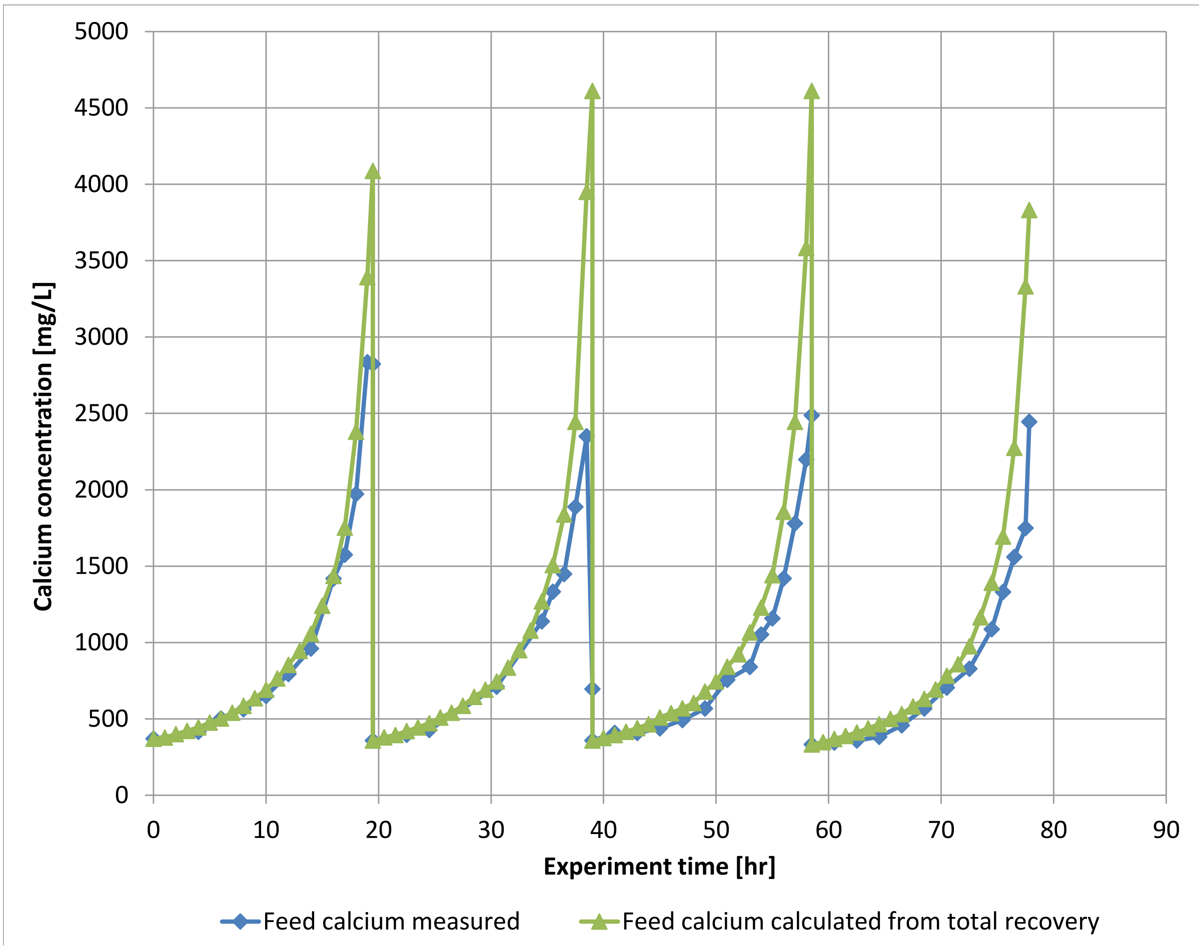


Figure 4: Sulfate Concentration Changes during the Pilot Study

Figure 5 shows changes in the calcium sulfate saturation index during the pilot study. The yellow circles are the theoretical calcium sulfate saturation index that would be achieved if no calcium sulfate was removed during the process. The blue rhombuses are the actual calcium sulfate saturation index achieved in the study, and calculated based on measured calcium and sulfate concentrations. It can be seen that actual calcium sulfate saturation index at the end of the cycle was around 1,000%-1,200% for a very short period of time. This high supersaturation of calcium sulfate, without scaling on the RO membrane, was achieved by maintaining a constant antiscalant concentration in the recirculated RO brine. The antiscalant used in this study was phosphonate based antiscalant, specifically designed to prevent calcium sulfate precipitation in RO membranes. According to the antiscalant manufacturer, the maximum calcium sulfate supersaturation that can be achieved in the presence of antiscalant without scaling in RO membranes during continuous operation is 800%. Due to the cycle operation of the developed technology, the RO membranes are exposed to high supersaturation of calcium sulfate for a very short time. This short time is probably insufficient for calcium sulfate to start the scaling process on the RO membrane. In addition, the lower than saturation conditions prevailing in the RO membrane at the beginning of the cycle can remove/dissolve the crystals that precipitate at the end of the previous cycle.

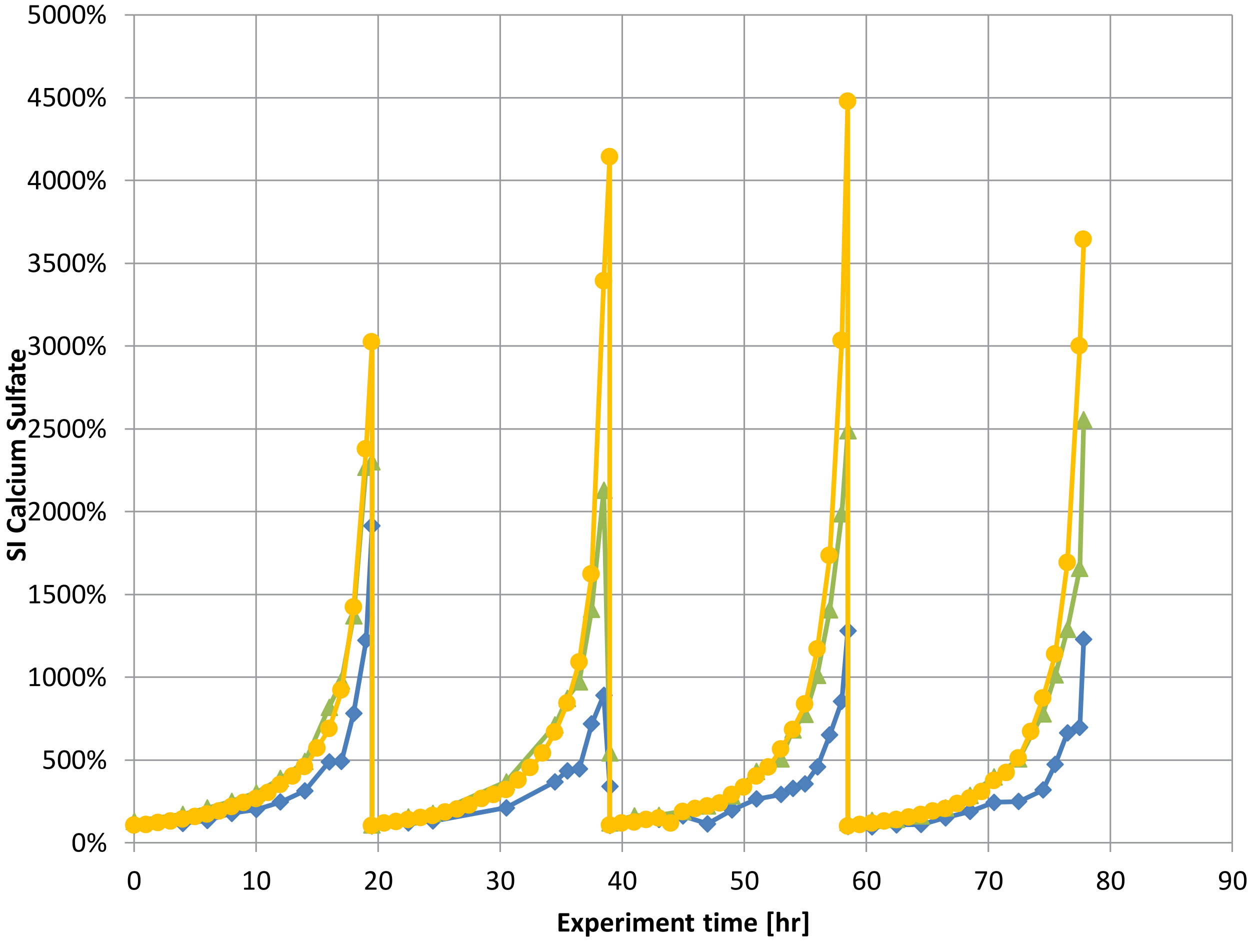


**Figure 5: Calcium Sulfate Saturation Index Changes during the Pilot study**

Figure 6 shows the changes in the concentration of antiscalant during the pilot study. The green triangles are the theoretical antiscalant concentration as phosphate, in case of there is no deactivation of antiscalant. The blue rhombus are the actual antiscalant concentration as phosphate kept in the recirculated RO brine. Antiscalant was continuously added during the pilot study in order to maintain constant phosphonate concentration of approximately 1 ppm as phosphate in the recirculated RO brine. This concentration was sufficient to prevent scaling of calcium sulfate in the RO membrane. The difference between the theoretical and actual antiscalant concentrations are the amount of antiscalant that was adsorbed on the pellets in salt precipitation reactor.

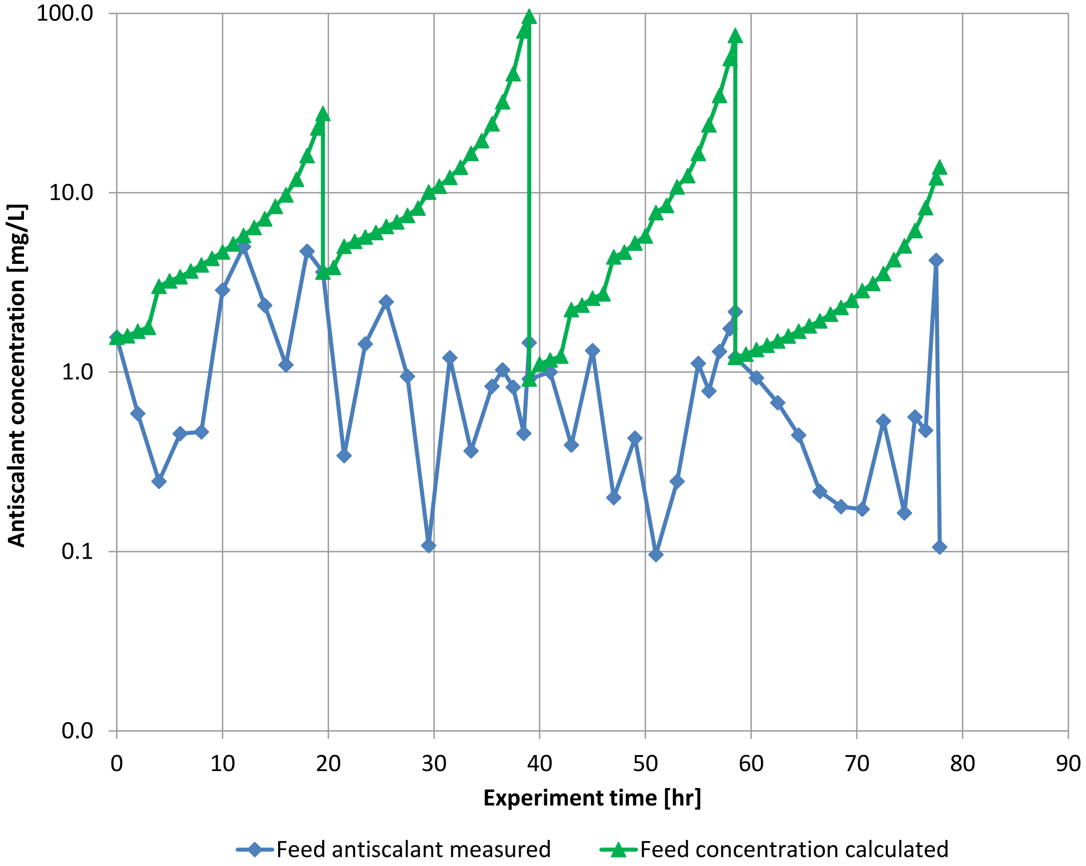


Figure 6: Antiscalant Concentration Changes during the Pilot Study

At the end of the pilot study, samples of pellets were analysed by High Resolution Scanning Electron Microscopy (HR SEM). The pictures of pellets taken during the HR SEM analysis are presented in Figure 7.

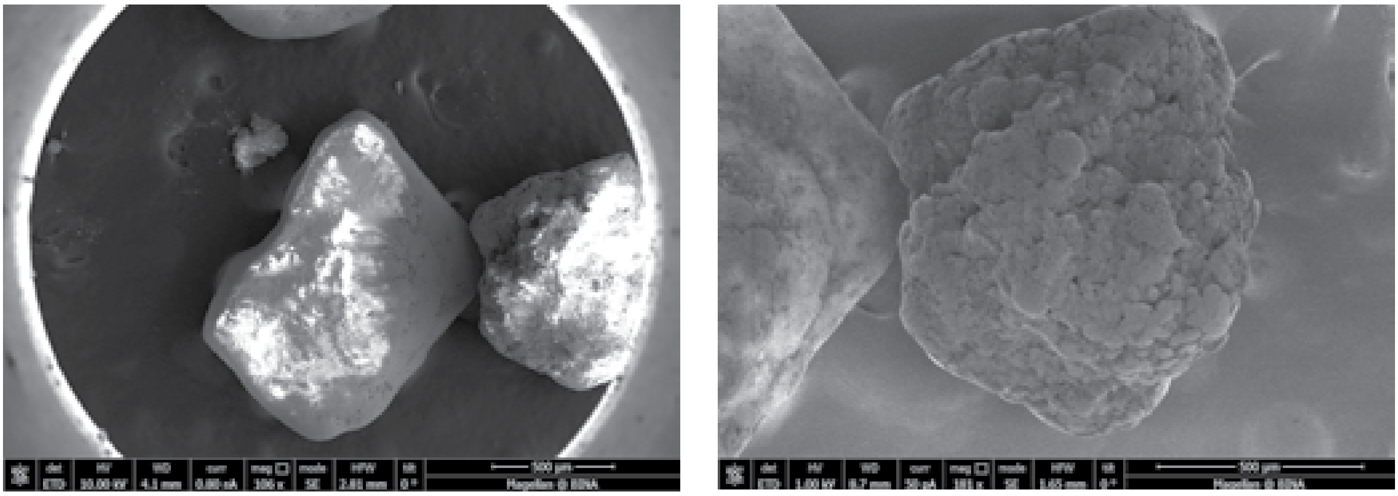


Figure 7: Pictures of Pellets from HR SEM Analysis

HR SEM analysis revealed phosphorus and sulphur atoms on the produced pellets. This is proof that antiscalant absorbs on the pellets and calcium sulfate precipitates on the pellets.

Table 2 presents the partial product water analysis done in several tests. It can be seen that the produced RO product meets the client product water requirements.

**Table 2: RO Product Water Quality and Product Requirements**

| No. | Quality Parameter | Units | Test 49 | Test 50 | Test 51 | Test 52 | Product Requirements |
|---|---|---|---|---|---|---|---|
| 1. | Total dissolved solids | ppm | 29.2 | 41.2 | 33.0 | 33.0 | <500 |
| 2. | Sodium | ppm | 12.0 | 15.0 | 12.0 | 12.0 | |
| 3. | Potassium | ppm | <1.0 | <1.0 | <1.0 | <1.0 | |
| 4. | Calcium | ppm | 1.2 | 1.2 | 1.0 | 1.0 | |
| 5. | Magnesium | ppm | <1.0 | <1.0 | <1.0 | <1.0 | |
| 6. | Arsenic | ppm | <0.0005 | <0.0005 | <0.0005 | <0.0005 | |
| 7. | Selenium | ppm | <0.002 | <0.002 | <0.002 | <0.002 | |
| 8. | Iron total | ppm | 0.005 | 0.005 | <0.005 | <0.005 | |
| 9. | Manganese | ppm | <0.0005 | <0.0005 | <0.0005 | <0.0005 | <0.2 |
| 10. | Copper | ppm | 0.0014 | 0.0016 | 0.0017 | 0.0011 | |
| 11. | Lead | ppm | <0.0005 | <0.0005 | <0.0005 | <0.0005 | |
| 12. | Chromium | ppm | <0.0005 | <0.0005 | <0.0005 | <0.0005 | |
| 13. | Cadmium | ppm | <0.0002 | <0.0002 | <0.0002 | <0.0002 | |
| 14. | Barium | ppm | <0.002 | <0.002 | <0.002 | <0.002 | |
| 15. | Zinc | ppm | <0.005 | <0.005 | <0.005 | <0.005 | |
| 16. | Aluminum | ppm | 0.005 | <0.005 | <0.005 | <0.005 | <5.0 |
| 17. | Lithium | ppm | <0.0005 | <0.0005 | <0.0005 | <0.0005 | |
| 18. | Silver | ppm | <0.0005 | <0.0005 | <0.0005 | <0.0005 | |
| 19. | Cobalt | ppm | <0.0005 | <0.0005 | <0.0005 | <0.0005 | |
| 20. | Nickel | ppm | <0.0005 | <0.0005 | <0.0005 | <0.0005 | |
| 21. | Strontium | ppm | 0.006 | 0.006 | 0.004 | 0.004 | |
| 22. | Beryllium | ppm | <0.0002 | <0.0002 | <0.0002 | <0.0002 | |
| 23. | Molybdenum | ppm | <0.001 | <0.001 | <0.001 | <0.001 | |
| 24. | Tin | ppm | <0.002 | <0.002 | <0.002 | <0.002 | |
| 25. | Chloride | ppm | 4.0 | 4.0 | 3.0 | 3.0 | <200 |
| 26. | Sulfate | ppm | 12.0 | 21.0 | 17.0 | 17.0 | <250 |
| 27. | COD | ppm | 2.0 | 2.0 | 2.0 | 2.0 | |

**The main findings of pilot study are:**

- The pilot operated continuously with mine wastewater, without scaling on the RO membrane throughout the trials, removing calcium and sulfate in the pellet reactor.
- Recovery of 90%-93% was reached.
- During the entire operation, antiscalant was added to the recirculated solution to maintain the concentration of the anti-scalant at about 1 ppm as phosphate.

## CONCLUSION

The developed technology was successfully tested with mine wastewater enriched with metals and sulfate. The results show that the system can reach recovery of over 90%, at which the calcium sulfate saturation index theoretically reaches over 3,000%, which would typically lead to immediate calcium sulfate precipitation on the RO membrane. In practice, the calcium sulfate saturation index was maintained in the range of 800%-1,200% during operation by its continuous precipitation in the integrated salt precipitation unit. The system operated without the addition of chemicals other than antiscalant, and produced pellets of more than 90% dry solids content, which do not require further sludge dewatering treatment. Depending on the effluent requirements, the obtained RO brine stream can be partially or completely blended with RO product, further increasing the total recovery of the system.

These results show the significant advantage of the developed system as a treatment alternative for acid mine wastewater. The developed system saves operational costs by decreasing chemical consumption and the amount of sludge to be discharged, and investment costs by the high recovery that can be achieved.

The ability of this technology to practically eliminate the recovery limitation of water chemistry by precipitating the sparingly soluble salts on pellets, while operating the RO at high velocity with inherently high shear forces, allows the RO unit to be designed for its maximum production and recovery potential.

IDE Technologies | Your Water Partners

Desalinating Water Since 1965 With Excellence

# REFERENCES

Akcil A., Koldas S., “Acid Mine Drainage (AMD): causes, treatment and case studies”, Journal of Cleaner Production (2006), Volume 14, pp. 1139-1145.

Bowel R., “A Review of Sulfate Removal Options for Mine Waters”, Proceedings of International Mine Water Association Symposium (2004), Newcastle, England.

Drak A., Zaken R., “Minimizing Reject Brine from Desalination Plants”, Water Conditioning and Purification (2018), April Issue.

Drak A., Zaken R., Efrat T., “High Recovery Reverse Osmosis System with Integrated Salt Precipitation Cycle for Industrial Water Treatment Applications”, Proceedings of 77th International Water Conference (2016), San Antonio, USA.

Giesen A., Erwee H., Wilson R., Botha M and Fourie S., “Experience with Crystallization as Sustainable, Zero-Waste Technology for Treatment of Wastewater”, Proceedings of International Mine Water Conference (2009), Pretoria, South Africa.

Van Dijk J.C., Wilms D.A., “Water Treatment without Waste Material: Fundamentals and State-Of-The-Art of Pellet Reactors”, Proceedings of IWSA World Congress (1991), Copenhagen, Denmark.

Van Ammers M., Van Dijk J.C., Graveland A. and Nuhn P.A., “State of the Art of Pellet Softening in the Netherlands”, Water Supply (1986), Volume 40, pp. 223-235.