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Desalination: Freeze Crystallization

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Desalination: Freeze Crystallization

Throughout spring 2019, me and five other team members worked on task 4 for the WERC competition. Task 4 required recovery of 50% of the feed water by the method of freeze crystallization on a 5 wt% Aluminum Sulfate, 5 wt% Magnesium Sulfate, and 90 wt% water. The recovered water was required to meet EPA standards (250 mg/L of sulfates) after processing. A bench scale process was used to model a full scale process that was scaled up to 100 gallons per minute. The bench scale processed 1 gallon of the brine solution. The bench scale process was comprised of an inner and outer vessel. The inner vessel held our brine solution which was agitated using a variable speed agitator. The outer vessel contained our refrigerant which was a saturated calcium chloride solution and ice. The refrigerant was pumped in order to provide agitation. Calcium chloride solution was used because it was the safest refrigerant to pump. The operating range of our experiment was determined using the magnesium sulfate phase diagram, which was -4-0 degrees Celsius. After multiple experiments, it was determined that the recovered water from the solution contained around 2-5 wt% salts. The full scale process was modeled using concentric plate coils that would grow 1.5 inches on each plate. Our bench scale apparatus could only generate a half an inch of ice because the ice layer acts as an insulator. For the full scale process, the refrigerant temperature would need to be decreased from -4 to -8 degrees Celsius in order to account for the reduced heat transfer through the ice. Once an inch of ice is formed, the refrigerant temperature would need to be dropped to -12 degrees Celsius in order to maintain a constant flux to the bulk brine solution. Multiple bench scale batches were used in order to recover 75% of the original water. The yield needed to recover from the bench scale solution was 75% because we decided to run the recovered water through a small reverse osmosis (RO) unit. The water that was recovered from the RO unit met the EPA standards and was ready to be tested using a conductivity meter. Only two thirds of the recovered ice that was fed to the RO unit was recovered and met the EPA standards which is why 75% must be recovered from the freeze crystallization process.

The net present value (NPV) for the freeze crystallization process was around (\$22 million). This high NPV required us to look into alternative methods. The first alternative method analyzed was a 5 stage multiple effect evaporation (MEE) process. This process was initially analyzed because as a group we thought the stand alone reverse osmosis process was not viable because salt water has 3.5 wt% salts. Our brine solution consisted of 10 wt% salts but because of the salts high molecular weights, they have a low molar percent. The MEE process was modeled using Aspen in order to check my hand calculations for the energy and mass balances. The NPV for the MEE process was (9.2 million). The stand-alone RO unit was the one we recommended to Freeport-McMoran because its NPV after 10 years was around (3.0 million).

Throughout this WERC project I primarily worked on the MEE process on Aspen. I also worked on a majority of the bench scale experiments in order to gather experimental data. The experimental data (wt% salts in recovered water) was used to generate a full-scale model for this process. After an in depth analysis of this task, we recommended the stand alone reverse osmosis process to Freeport-McMoran instead of the freeze crystallization process. If this experiment were to be repeated, we would try to achieve more accurate temperature control.

WERC 2019

Task #4

March 18, 2019

Freezerbacks

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1.0 Executive Summary

The Freezerbacks researched, designed, and economically evaluated a full-scale freeze crystallization process as well as two alternative full-scale processes: 5 stage multiple effect evaporation and reverse osmosis. All three processes were designed to treat hyper-saline mine water that was sent into evaporation pond systems. These systems were designed for Freeport-McMoRan's mines that need to treat impacted water.

The Freeport-McMoRan copper mine in Miami, Arizona was visited in order to gain insight about the problem. The mine is no longer actively mining copper and is in the process of reclaiming land used. An essential part of restoring the land is treating impacted water that is currently being recirculated throughout the process before discharging. Current methods, evaporation ponds, are neither time nor cost effective. Ultimately, the water needs to be purified to the EPA standard of the maximum concentration level of sulfates (250 mg/L). After the feed has been processed, a waste stream will be disposed of via existing evaporation ponds.

The deciding factor between the processes is the economics and total recovery. Multiple effect evaporation can be modified to recover more than 50% of water therefore reducing the footprint for the evaporation ponds. Although the heat of vaporization for water is about six times greater (40.65 kJ/mol) than the heat of fusion for water (6.02 kJ/mol), the capital cost for freeze crystallization is greater, and the process is unused on an industrial scale. Reverse osmosis will purify 50% of the water with a simpler system and cheaper overall cost. All processes are being presented as viable, with preference for the reverse osmosis.

A batch bench scale system was constructed to model freeze crystallization. It was designed to process one gallon of salt solution in a single vessel. The bench scale process overall recovered 72% of the water with a final salt composition that ranges from 1.44 wt.% to 5.10 wt.%. For full-scale design purposes, 2.5 wt.% recovery was assumed. Reverse osmosis further purified the melted ice to EPA standards.

A thorough evaluation was conducted by generating a full-scale economic analysis for each process, taking into consideration the advantages and disadvantages of each. Important factors taken into consideration were capital and operating costs, complexity, total recovery of water, and concentration of sulfates in the water recovered.

In the freeze crystallization process, impacted water is pumped through two units in a semi-batch process where ice is formed on concentric plate coils in vessels. A total of 75% water is first recovered by crystallization and then the recovered water is passed through a reverse osmosis membrane (RO) to recover 50% of the initial brine water at environmental specifications. The net present value (NPV) after 10 years of operation is \$(21.4 million) with a 50% total recovery of water. The multiple effect evaporation process is a 5-stage process in which heat from steam is used to evaporate water. This process results in a recovery of 75% pure water with a net present value of \$(9.44 million). The reverse osmosis process will require two stages and a total of 21 elements. Reverse osmosis proved to be the most economical with an NPV of \$(2.96 million) and a 50% purified water recovery compared to the other two processes.

2.0 Introduction

In the mining industry, usage of large volumes of water enables mines to conduct multiple processes within one location. Hypersaline brine waters exit the processes of the mine to be utilized for other roles; some of these roles include leaching, recirculation, and extraction operations. These waters are highly concentrated with salt components and are released to different sections of the mine. The salts of highest concentration in the brine are aluminum sulfate and magnesium sulfate heptahydrate, along with low concentrations of many other elements.

There are multiple ways to recover purified water from the brine solution: freeze crystallization, evaporative processes, and reverse osmosis. The impacted water in the mine must be purified to meet regulations before being discharged. Freeze crystallization is a process which can be used to recover purified water. For this task, the sponsor (Freeport-McMoRan), has requested an evaluation of a freeze crystallization process for recovering 50% of the impacted mine waters. Multiple effect evaporation and reverse osmosis were also investigated as, potentially, less costly processes.

3.0 Explanation of the Task

The task consists of designing a process to recover salts from the brine using freeze crystallization. The maximum amount of aluminum sulfate and magnesium sulfate heptahydrate

allowed equates to a conductivity of 1000 mS/cm. The water recovered must be at least 50% of the initial feed.

The solution is composed of 50 grams of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 50 grams of $\text{Al}_2(\text{SO}_4)_3$, and distilled water to prepare one liter of solution. One gallon of this solution is used. The approach of dealing with this task is as follows:

- Identify potential freeze crystallization designs for removing these two salts from water
- Develop a full-scale process which recovers 50% of water meeting EPA standards of under 250 mg/L for sulfates from a 100 gpm feed stream
- Develop a lab-scale process to test the crystallization cycle of a full-scale freeze crystallization process
- Determine possible market opportunities for the products in the system
- Perform an economic analysis on the potential processes
- Select the most economically feasible and energy efficient process to recover purified water

4.0 Site Overview

The Freezerbacks visited the Freeport-McMoRan copper mine in Miami, Arizona to learn about the process of copper mining and better understand the task. The Miami mine occupies 17 square miles of land 90 miles east of Phoenix, Arizona and is undergoing reclamation activities on portions of the operation. This mine is no longer actively mining new copper ore but is leaching remaining ore with sulfuric acid. Copper leaching requires large volumes of water to complete the process, which becomes contaminated with high concentrations of salts. The Freeport-McMoRan Miami mine is a zero-discharge facility; therefore, all water is either recirculated through the process or stored in ponds onsite. There is currently four large pit lakes onsite to store water; one of which has clean, usable water. This clean pit lake is shown in Figure 1. The other three pit lakes contain impacted water. In addition to the water in the pit lakes, there is a very large amount of hypersalinated brine being recirculated through the process. For the mine to reach a point of closure, contaminants in the water need to be removed to safely discharge all process water into nearby natural streams.



Figure 1: Pit lake at the Miami, AZ mine

Fresh water is essential to the daily operation at the mine, making it an incentive to treat the hypersaline waters. Freeport-McMoRan has already spent millions of dollars on shutdown procedures and is investigating processes to reduce overall cost throughout reclamation and cleaning impacted water.

5.0 Freeze Crystallization Research Methodology

Freeze crystallization is not currently utilized in industry, therefore experiments were conducted to gain understanding of the process ^[15]. Several different designs for freeze crystallization were considered. To identify the most practical option, vital parameters to be satisfied were complexity, capital cost, and scalability. However, a comprehensive examination of the various designs yielded an assortment of problems for the purification of the solution.

One of the main restrictions for freeze crystallization is the small phase envelope where operation must occur for the solution to produce purified water. As seen in Figure 2, by freezing the solution within a phase envelope of -4 to 0 °C and a composition of 0-20 wt.%, ice is formed without magnesium sulfate ^[16]. However, operating with such constraints is difficult and limits

how fast ice can form due to the small temperature difference between the freezing surface and the bulk solution.

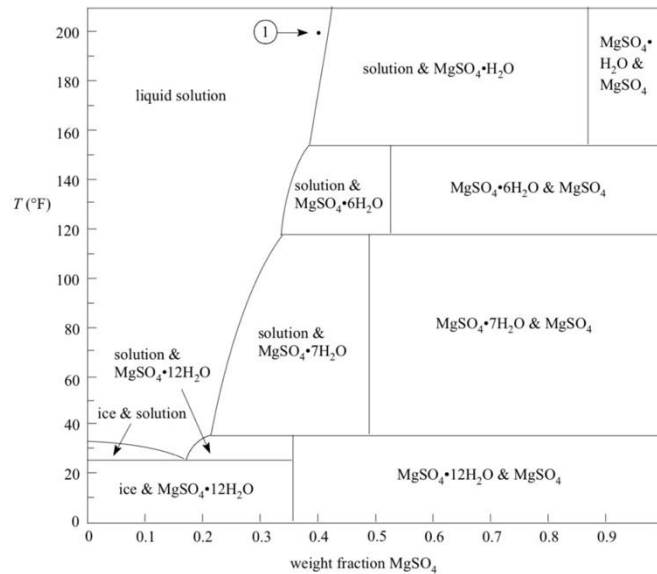


Figure 2: Phase Diagram of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and Water ^[16]

Because separating the salts is difficult, research into the marketability of the salt mixture was conducted. Magnesium sulfate is widely used in agriculture to increase the uptake of nitrogen and phosphorous.^[14] This is important because both are essential nutrients for plants. The high solubility of magnesium sulfate heptahydrate (710 g/L at 20 °C) makes it the perfect compound for magnesium deficient soil.^[14] Aluminum sulfate can also be used for plants by reducing the soil pH, making it acidic.^[10] However, few plants can tolerate aluminum sulfate because aluminum sulfate will cause aluminum toxicity.^[10] Aluminum sulfate becomes more soluble with lower pH making land non arable.^[4] This makes the marketability of salts uneconomical considering the mixture is applicable to a small niche market.

The first design consideration for the full-scale design was a scrape surface crystallizer and a belt filter. The scrape surface crystallizer forms ice crystals on the outer wall, then scrapes them off into a slurry. Subsequently, a belt filter separates the solid and liquid. Creating a slurry of ice and brine is possible in refrigerated vessels. However, once the slurry is created, the ice crystals need to be washed using pure, low-temperature water. The washing step requires a pressurized belt filter, a large volume of wash water, and an enclosure for the belt filter to keep the ice crystals at a maximum of -1°C . If the ice crystals reach above 0°C at any point during the

wash cycle, the ice would begin to melt and not be recoverable. This design was not chosen due to its complexity.

The next design consists a single vessel that recover over 72.5% purified water to allow the use of reverse osmosis. However, during the design process, it was found that this level of recovery was unrealistic within a single vessel. Due to the necessary agitation in the vessel, an annulus and two elliptical heads are required. These spaces, along with the plate coils themselves, take up a fixed volume in the vessels where ice is unable to form. This loss of volume ultimately led to the rejection of a single vessel design.

6.0 Bench Scale Operations

6.1 Experimental Procedure

The bench-scale design tests the freeze crystallization process. The bench scale apparatus is shown in Figure 3 and the process flow diagram in Figure 4. In this design, the 5-gallon pail is filled with approximately 12 liters of saturated calcium chloride (CaCl_2) solution. A 5-quart vessel is placed on a stand inside the 5-gallon pail, stabilized by a weighted container, and filled with the brine solution. A variable speed agitator is positioned on the stand and inside the inner vessel. The agitator blends the solution to uniformity inside of the vessel. Ice is added to the annulus of the outer vessel to lower the temperature of the CaCl_2 solution. This solution serves as the refrigerant for the crystallizer and removes heat from the solution inside the inner vessel for crystallization. To provide even heat transfer, the CaCl_2 solution is agitated with a regenerative centrifugal pump. The suction to the pump comes from a bulkhead fitting at the bottom of the 5-gallon pail. The discharge from the pump enters the annulus of the apparatus through four holes in the side of a vertical, flattened copper pipe with a velocity of four feet per second (fps). The pump discharge has a spill back stream with a valve that can be used to adjust the flow rate into the annulus. A single element reverse osmosis system follows the freeze crystallizer to further purify the salts.

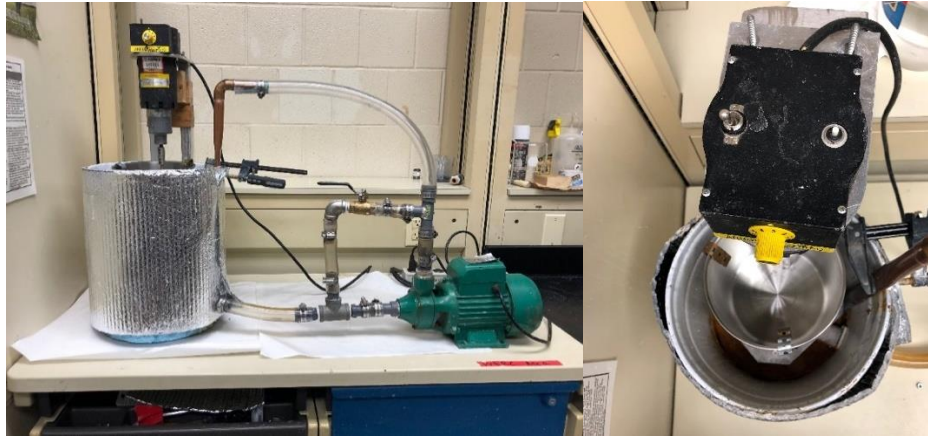


Figure 3: The Freezerback's Bench-Scale Apparatus

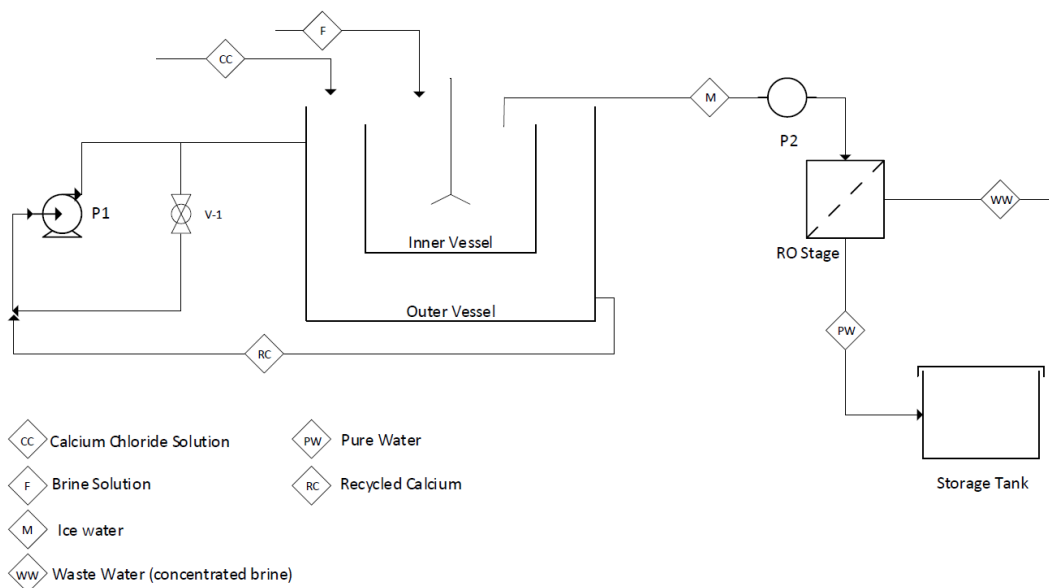


Figure 4: Bench-Scale Apparatus PFD

Once the inner vessel has formed approximately ½” of ice, the system is turned off and the agitator is taken off the stand so the inner vessel can be removed. The remaining brine is drained into a temporary storage container, and the ice is washed with distilled water. The wash is recycled into the brine solution. The ice is then scraped off the sides of the inner vessel to be recovered. Following this, the brine is returned to the inner vessel and the crystallization process repeats. A batch process was used to keep the flux constant as it would be in the full-scale design. A total of four batches are run for approximately an hour each in order to recover 72.5%

water at a salt concentration of 3.5 wt.%. This ensures that reverse osmosis would be an option, and the subsequent water losses would be managed.

6.2 Safety Content

One of the main safety considerations for this bench scale experiment is the potential for spills due to multiple liquid transfers. Always wear the proper PPE when operating the apparatus. When a spill occurs, be sure to notify those in the area and clean up the liquid immediately. Be sure that no electrical equipment encounters the liquid. All solutions used in this experiment contain high concentrations of salts. The high concentration is corrosive and harmful to the skin; therefore, it is always important to wear nitrile gloves. Maintain the integrity of the apparatus by ensuring there are no leaks. Lastly, because there are sharp edges on the weighted bucket, use caution when handling them. If a process upset occurs, shut down all electrical equipment safely and evacuate the lab.

6.3 Experimental Results and Evaluation

The bench scale batch process simulates the surface of one plate coil in an agitated vessel. One and a half inches of ice are required to recover the necessary amount of water. However, as the ice layer grows, it acts as an insulating layer. To keep the growth rate of ice constant, the outer refrigerant temperature needs to be lowered gradually to -12°C . The refrigeration method of the bench scale can maintain a temperature range between -4 and -2°C which only allows for a half inch of ice formation. This simulates the wall of one plate coil within the full-scale vessel by removing the insulating layer of ice systematically. Additionally, the concentration of salts in the brine will increase as more water is crystallized out, as it would be in the full-scale.

Seven bench-scale experiments were conducted. The experimental results, shown in Table 1, indicates the importance of the refrigerant temperature and the wash procedure. It is important to keep the refrigerant temperature constantly between -3°C and -4°C to keep heat flux through the ice as consistent as possible. An even heat flux lowers the possibility for salts to become entrapped within the outer layer of porous ice crystals and reduces the overall salt concentration in the recovered ice.

The wash cycle proved to be crucial to the final purity of the water. It was determined that the mother liquor was adhered to the porous outer layer of ice crystals. To remove it, the ice was washed four times with distilled water. When the ice was not washed, the concentration of salts increased by 1.5 wt% in the recovered ice. As will be discussed, to recover water of sufficient purity, reverse osmosis will need to follow the freeze crystallization to remove the remaining salts.

Table 1: Bench Scale Experiment Results

Run	1	2	3	4	5	6	7
Total Time Elapsed (minutes)	70 min	70 min	150 min	80 min	60 min	70 min	300 min
Final Weight Percent Salt in the Ice (%)	1.69%	1.44 %	2.58%	3.70%	5.10%	2.24%	4.99%
Refrigerant Temperature (°C)	-2	-2.5	-1.4	-1.6	-1.5	-2.8	-5.0

One deficiency of the bench-scale experiment is the instability of the refrigerant temperature. This method causes a wide range of temperature fluctuations throughout the experiment, if ice is added in large amounts. There is up to a five-degree temperature drop once the ice is added. The full-scale design will operate within a much smaller, consistent, well controlled, temperature range. This will result in lower salt concentrations in the ice crystals in the full scale process.

The data gathered from the bench-scale experiments proved that recovering over 72.5% of the water with 3.5 total wt.% salts is reasonable. Performing the bench scale experiments demonstrated the importance of keeping the temperature of the refrigerant constant. A wash cycle must be included to remove the mother liquor that is adhered to the ice crystals. This wash water is recycled back into the brine feed to ensure the water used can be recovered.

7.0 Full-Scale Designs

7.1 Freeze Crystallization

The Freezerbacks have developed a process that meets all task specifications. A semi batch process with an overall rate of 100 gpm is set as part of the design basis. The vessels designed for this process obtain slightly more than 50% recovery. After the brine has been

processed through all vessels, the overall recovery (including the wash water) is 75%. The reverse osmosis system that follows the freeze system reduces the total recovery to 50%.

The hypersaline brine enters the process at ambient conditions and is pumped at 2000 gpm into one of two 75 cubic meter crystallizers to begin the recovery process. The time required to fill the vessel is approximately 10 minutes. The plate coils in each vessel function as condensers or evaporators depending on if they are melting or crystallizing, respectively. Both vessels in unit 1 and 2 exchange heat by a compression refrigeration system that connects the plate coils of the two vessels in each unit. Figures 5 and 6 show a block flow and process flow diagram of the full-scale freeze crystallization process.

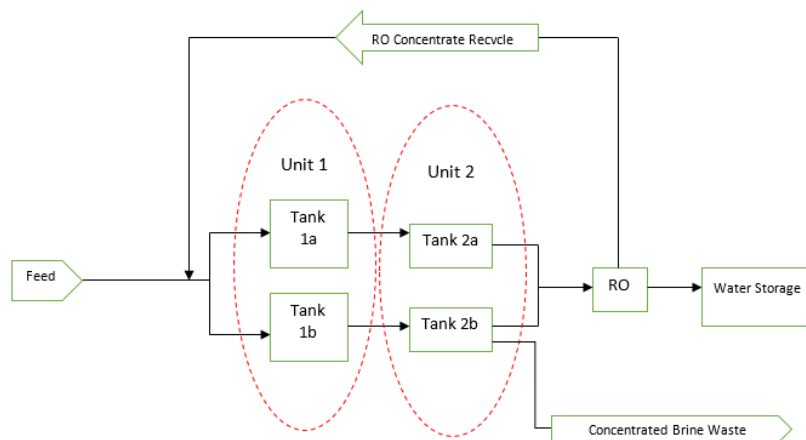


Figure 5: Block Flow Diagram of Full-Scale Freeze Process

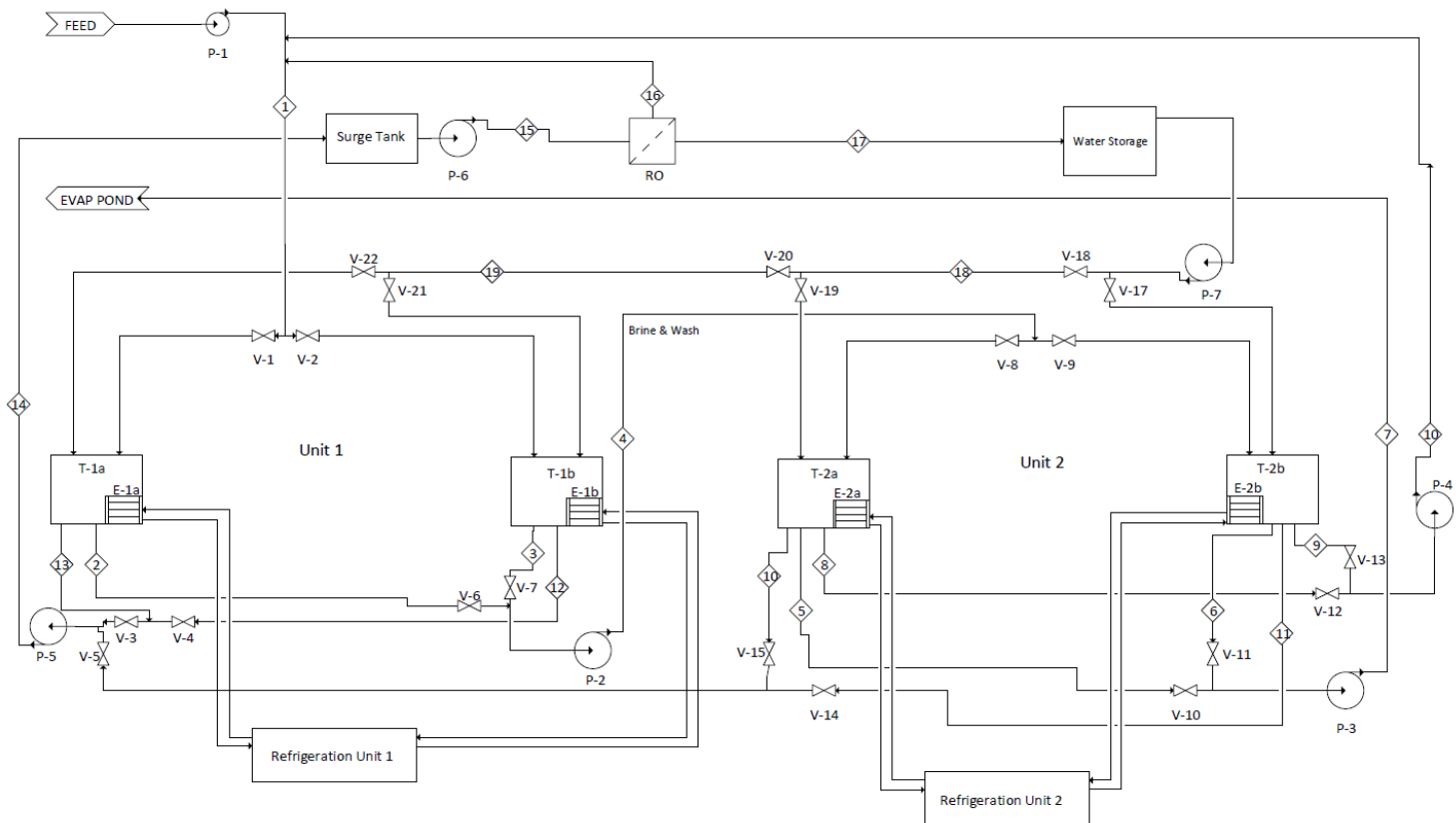


Figure 6: Full-Scale Process Flow Diagram of the Freeze Crystallization

As the ice crystals grow on the plate coils of one vessel, the second vessel in unit 1 will have already completed this step and begins the melting process. Once a vessel has formed one and a half inches of ice over the course of five hours, the remaining brine is drained and pumped to unit 2 at 2000 gpm where it undergoes a second round of freeze crystallization in a smaller vessel. The remaining ice in unit 1 is washed with 500 gpm of pure, recovered water for three minutes. This wash water is pumped to unit 2 to be crystallized. The exiting brine from unit 2 is sent to an evaporation pond, and the wash water is recycled to the feed. The recovered ice from unit 2 is melted and then pumped with the recovered water from unit 1 to the reverse osmosis unit for further purification. Approximately 15,000 gallons of recovered water is pumped from the two vessels after a batch into the surge tank and then pumped at 100 gpm through the reverse osmosis system. Once the water is purified, it is sent into a storage vessel for the mine to use as needed or discharged. The concentrated brine waste exiting the RO has a salt concentration of 10 wt% and is recycled back into the feed source.

Unit 1 contains two tanks that are four meters diameter and six meters tall. The smaller unit contains two tanks that are both three meters diameter and six meters tall. A diameter limit of four meters was set so the vessels can be transported on the highway after fabrication. Inside of each vessel in unit 1 are ten concentric cylindrical plate coils that are spaced four inches apart with an agitator in the center annulus. Figure 7 is a sketch of a unit 1 vessel. Unit 2 vessels contain seven plate coils. The 48", 150 kW, unit 1 agitators create turbulent flow and agitation within the annuli of the individual plate coils. Unit 2 vessels will require a 36", 50 kW agitator. In each vessel, one and a half inches of ice will be grown on each side of the plate coils which will leave a one-inch diameter channel for liquid brine to flow.

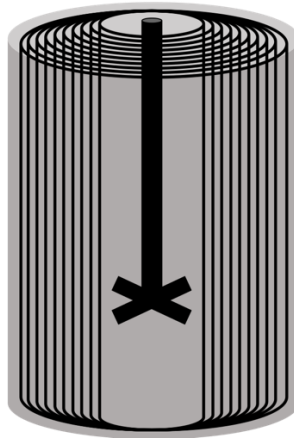


Figure 7: Sketch of Refrigeration Unit 1 Vessel

The larger vessels require 65 kW of compressor power, and the smaller vessels require 95 kW. Each tank requires a residence time of approximately five hours for the ice layer to form. The outer refrigerant is initially -4°C . The process controls operate based on the time elapsed to lower the temperature of the refrigerant as the ice forms. This ensures that there is a constant flux through the surface where the ice is forming.

The recovered water is pumped into a reverse osmosis (RO) membrane process after it leaves the surge tank. Dow Chemical's Water Application Value Engine (WAVE) is utilized to simulate using Reverse Osmosis in a full-scale process. The water is pumped to the two stage RO system at 25°C , 100 gpm, and 650 psia. Stage one has two pressure vessels and eight elements, and stage two has one pressure vessel and four elements. The element type is SW30HRLE-400i because of its high rejection. The feed going into the RO system has a

concentration of 2.5 wt.% (25,000 mg/L), and the water recovered from the RO is 0.001 wt.% (9.67 mg/L) salt. This RO unit recovers 67% of the feed sent to it. The concentrate leaves the RO system at 9.9 wt.% and is recycled back into the feed storage pond for the freeze crystallization. The Freezerbacks have determined that the salt concentrations produced in a full-scale freeze crystallization process may be lower due to the optimized operational control. This process is recommended to follow the freeze crystallization if needed. If the salt concentration is decreased below the EPA standard of 250 mg/L, reverse osmosis will not be necessary.

The safety concerns for the freeze crystallization are the low temperatures and the refrigerant that is used in the process, Freon (R-134A). According to the SDS for R-134A, it is not classified as a dangerous substance but typical first aid measures apply. It should not be inhaled or ingested and Personal Protection Equipment (PPE) should be utilized to protect the eyes and hands. Skin should not be in contact with the refrigerant or the hypersaline brines because the cold temperature and saturation will dry out the skin.

7.2 Multiple Effect Evaporation

Multiple effect evaporation (MEE) is a process that uses steam produced by a steam generation boiler which provides the feed and operate the 1st stage. In this feed forward process, the steam required to heat downstream stages is supplied from the upstream stages. The vapor generated by each stage, except the last stage, is fed to the shell side of the evaporator in the next stage. The inlet pressure to the first effect is 60 psia and the outlet pressure of the last effect is atmospheric, 14.7 psia.

A multiple effect evaporation system was designed to recover 50% to 75% of the water in the feed. Five effects were used to reduce the amount of energy required to reach a 50% yield of water while minimizing cost. An Aspen model was used to determine the energy requirements for yields up to 75% of water. A distilled water yield of 50% was examined in order to directly compare with the freeze crystallization process, however a 75% yield was only marginally more costly. It was determined that purifying 75% of the feed water outweighed the extra cost and would be used in the full-scale process.

Refer to Figure 8 for a PFD of the MEE process. The feed is pumped at 100 gpm into the evaporator and heated from ambient to 72°C in a shell-and-tube heat exchanger (S&T), which

uses the 5th stage steam. The feed then enters the 1st Stage Evaporator where it is heated from 144°C to 170°C by use of 3100 kg/s of steam, flashing 10% of the feed. The recirculating brine is pumped at 220 gpm through the 1st stage evaporator exchanger. This pump provides the circulation required to control the outlet condition of the recirculating stream so that no vaporization occurs within the heat exchanger, in order to avoid two-phase flow within the exchanger. The outlet pressure within the heat exchanger is controlled by a back-pressure control loop at the exit. The stream from the top of the V/L separator controls the brine outlet flow by manipulating a valve in the brine discharge line. All intermediate stages of the evaporator operate in an analogous manner to the 1st stage, except the steam necessary to vaporize the feed is provided by the vapor exiting the top of the V/L separator of the preceding stage.

The 5th stage operates in an analogous manner to the intermediate stages, except the exiting brine leaves the 5th stage and goes to preheat the feed. The pressure in the shell side of the exhaust steam feed preheater is controlled by using a steam trap in the condensate discharge line. The amount of purified water produced is controlled by sensing the volumetric flow of exiting brine waste and using a flow controller to manipulate a valve in the steam line to the shell side of the 1st stage evaporator. The remaining brine, coming out of the bottom of the last effect, is sent to the evaporation pond. The brine solution is comprised of 20 wt% salt and 80 wt% water.

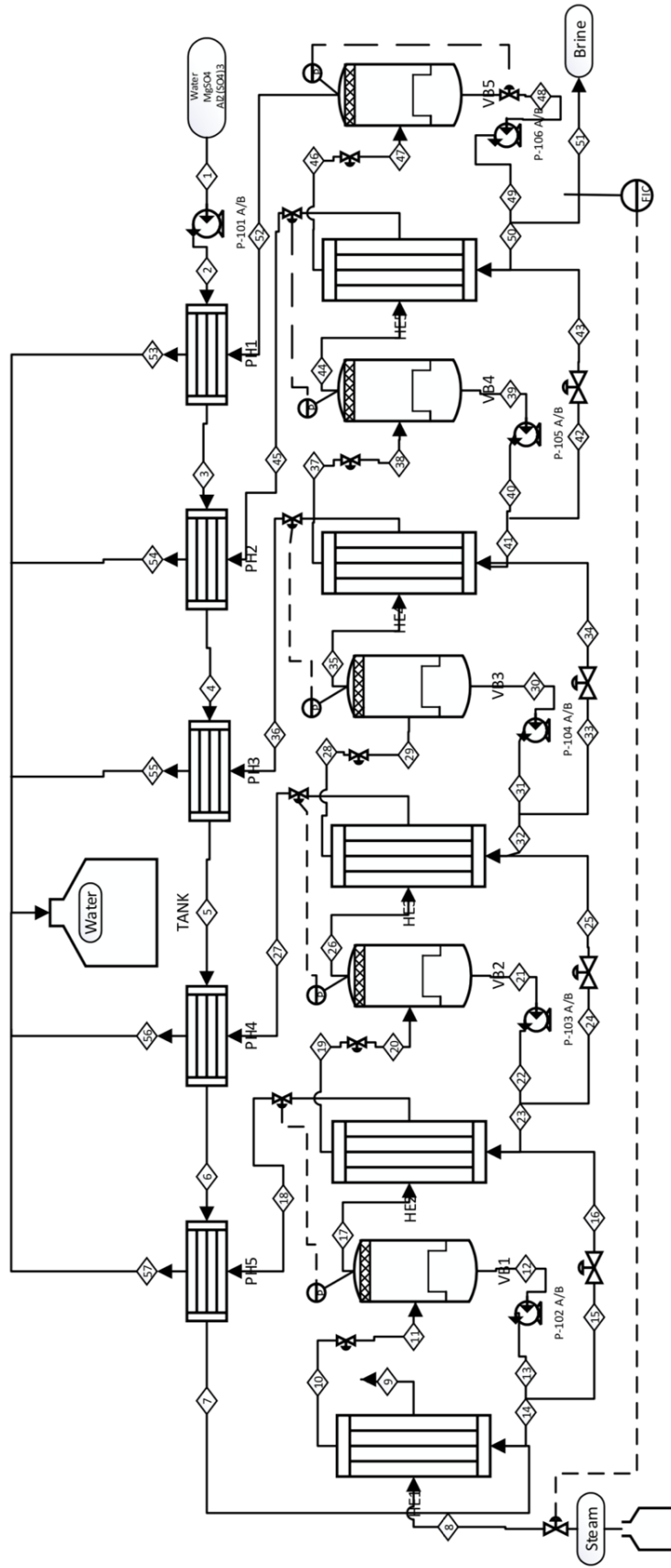


Figure 8: PFD of a 5 Stage Evaporator for Recovering 50 gpm of Pure Water from 100 gpm of Brine Feed

The amount of water recovered throughout the MEE process was 15,300 kg/s and the yield was 75%. The energy requirement to generate the required steam was 4,270 kW.

Safety considerations for the multiple effect evaporation process involve the high operating temperatures and pressures. No skin should contact the hot equipment when it is running. Steam and natural gas are also highly pressurized. When operating, natural gas should not be inhaled and can be harmful in high doses. Normal PPE should be used along with more protective gloves when operating around the high temperature processes.

7.3 Reverse Osmosis

Reverse osmosis is a pressure-driven process where a concentrated solution is forced against an osmotic pressure through a semi-permeable membrane. The solution passes through the semi-permeable membrane by a solution-diffusion mechanism. The most widely used membrane for RO is a spiral-wound membrane element because of its large membrane surface area to volume ratio^[20]. Molecules larger than the pore openings are rejected from the product stream. RO separates molecules at a limit of 0.1-1nm^[20]. This means RO can remove dissolved materials, all suspended solids, and colloids in the solution. There are hundreds of seawater desalination RO systems currently in use which operate at very high pressures, up to 1050 psi^[24]. An issue with RO is membrane scaling and fouling^[17]. Solutions with high mineral content tend to scale and foul which leads to increased pressure drop, higher energy cost, and membrane failure. Membrane failure will permit contaminants to pass through to the filtered solution. Another issue with RO is the amount of water loss to the rejection stream ranging from 10-70 percent recovery^[17]. The water loss is dependent on pressure drop and pore size but can be reduced with purification of rejected solution.^[17] Figure 9 is the process flow diagram for the full scale reverse osmosis process.

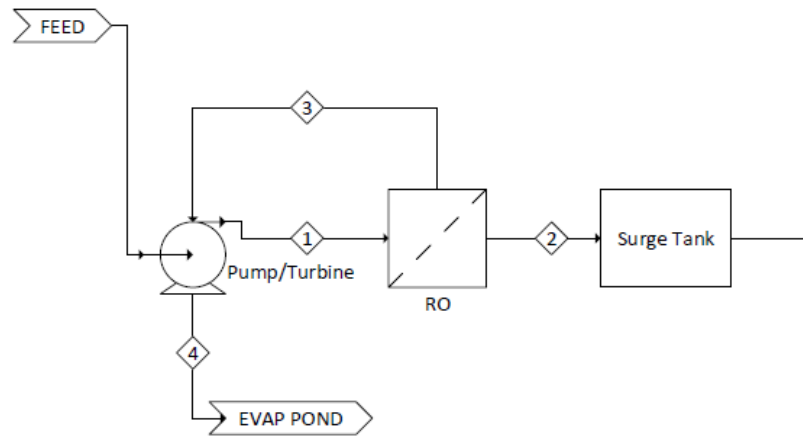


Figure 9: Full-Scale Process Flow Diagram of the Reverse Osmosis System

Using Dow’s WAVE program, an analysis is done using reverse osmosis for producing purified water. If reverse osmosis alone is used to process the 10 wt% brine with 50% recovery, a pressure of 960 psi is required. The waste discharge brine at a pressure of 960 psi can be used to drive the charge pump which lowers the power cost by 40%, conservatively. A recovered water stream with 0.006 wt% (55.6 mg/L) sulfates is produced using two stages and a total of 21 elements. A capital cost of \$420,000 with a \$313,400 annual operating cost was determined for a full-scale operation of these parameters based on the total number of elements in the system, the mixed media pretreatment system, and the installation costs. The system would require one operator per shift and replacement of all elements after 5 years. Reverse osmosis is determined to be optimal for this scenario due to its low cost, prevalence in industry, and ease of operation.

This process is evaluated for a brine solution that contains only magnesium sulfate and aluminum sulfate. However, brine that has been used for mining processing will have many other contaminants dissolved within it. This makes the composition of the brine very important for the effectiveness of this RO system. Dow elements have an operating pressure limit of 1000 psi. If a high enough concentration of other dissolved solids is present in the brine, the membrane pressure will quickly surpass the operating limit. Additionally, the presence of compounds such as aluminum, silica, and certain heavy metal ions may result in fouling. Countermeasures such as pH change or the addition of anti-scaling compounds may be necessary. The Freezerbacks recommend a water analysis at each mine that will require purification of its brine using reverse osmosis. This will ensure that the RO system would work given each specific feed composition.

8.0 Full-Scale Economics

An economic analysis of the freeze crystallization, MEE, and RO full-scale processes were carried out using the Peter and Timmerhaus design book. The equipment costs are shown in Table 2 below. Table 3 shows the FCI for each full-scale process. Following that, Table 4 is a summary of the operating costs. A list of the final costs and evaluations are in Table 5. According to the Arizona Water Company, the industrial cost of water per 1000 gallons is \$3.12 which was used to calculate the annual water savings. The pumps and piping required to transport the feed from the ponds to the process are not included in this project definition report. While the freeze crystallization process requires the least amount of energy, it resulted in the largest net present value (NPV) due to the high equipment cost and therefore the high FCI. Freezerbacks recommend the reverse osmosis process that recovers 50% purified water with an NPV of \$(2,960,000). Even though this system operates at a high pressure and would require brine analysis before implementation, it is the simplest and least expensive process to meet the task specifications. This allows the mine to maximize reclamation and treatment schedule while minimizing costs.

Table 2: Equipment Cost Analysis

Freeze Crystallization			Multiple Effect Evaporation (75%)		
Equipment	Quantity	Total	Equipment	Quantity	Cost
Vessels	4	\$480,300	Heat Exchangers	5	\$110,300
Agitators	4	\$147,700	Vapor/Liquid Vessels	5	\$143,400
Agitator Motors	4	\$168,500	Preheaters	5	\$70,700
Refrigeration Unit	2	\$385,700	Pumps	5	\$37,300
Plate Coils	4	\$56,800	Steam Generator	1	\$49,000
Refrigerant	1	\$711,200			
Pumps	7	\$73,600			
Reverse Osmosis	1	\$132,000			
Total Purchased Equipment Cost		\$2,155,800	Total Purchased Equipment Cost		\$410,700

Table 3: Fixed Capital Investments

Component	Freeze Cost	75% MEE Cost
Purchased Equipment	\$2,155,800	\$410,700
Installation	\$776,100	\$147,900
Instrumentation	\$603,600	\$115,000
Piping	\$689,900	\$131,400
Electrical	\$431,200	\$82,100
Buildings	\$431,200	\$82,100
Yard Improvements	\$172,500	\$32,900
Service Facilities	\$1,293,500	\$246,400
Engineering and Supervision	\$862,300	\$164,300
Construction Expense	\$1,034,800	\$197,100
Contractor's Fee	\$172,500	\$32,900
Contingency	\$2,155,800	\$410,700
Total FCI	\$10,779,000	\$2,053,500

Table 4: Annual Operating Costs Analysis

Component	Freeze	75% MEE	Reverse Osmosis
Labor	\$416,000	\$416,000	\$208,000
Power	\$102,200	\$324,000	\$76,000
Maintenance	\$754,500	\$144,000	\$29,400
Reverse Osmosis	\$48,200	N/A	N/A
Total	\$1,320,900	\$884,000	\$313,400

Table 5: Cost Breakdown of Each Process

	Freeze Crystallization	MEE 75%	Reverse Osmosis
FCI	\$10,779,000	\$2,053,500	\$420,000
Annual Operating Cost	\$1,320,900	\$884,000	\$313,400
Annual Recovered Water Savings	\$26,300	\$39,400	\$26,300
NPV	\$(21,350,000)	\$(9,440,000)	\$(2,960,000)
% Recovery	50%	75%	50%
Salt Concentration (mg/L)	9.67	0	55.61
Annual Duty (kWh)	2.72 million	37.5 million	500,000

9.0 Alternative Methods Considered

As experiments were done with freeze crystallization and evaluations were done on multiple effect evaporation and reverse osmosis, other methods were considered and ultimately deemed inadequate. However, for the purposes of analysis, it is appropriate to give an overview of why these processes were rejected.

9.1 Solar Evaporation Ponds

Freeport-McMoRan is currently utilizing solar evaporation ponds to treat the hyper-saline mine water. This method does not recover any water and the volume percentage evaporated is low. For example, Miami removes approximately 3-10% by evaporation annually into the atmosphere. Generally, solar evaporation ponds have variable efficiencies and take long periods of time to yield necessary inventory reductions. Once the water is no longer recirculating in the process of leaching, there will not be enough space to store all the water in the mine. The current cost to evaporate the water is approximately \$2.50 per 1000 gallons resulting in a total cost of \$16.8 million to evaporate all impacted water. This is a base price that does not include inventory gains over time such as stormwater and groundwater. For evaporation ponds to be effective in preparing for closure, there will have to be quicker evaporation rates because of the large magnitude of water.

One strategy to make the evaporation ponds more effective is to create more shallow ponds. This would require the building of new evaporation ponds onsite with larger surface areas and smaller depths. The capital costs of building efficient evaporation ponds is high for the magnitude of water most mines would be processing. Additionally, a big drawback of evaporation ponds is there is no water recovered. In areas of dry climates, such as Arizona or New Mexico, clean water is a valuable resource. Considering the loss of water as a valuable resource and the high capital costs of building, it was decided that evaporation ponds would not be the optimal solution for Freeport-McMoRan.

9.2 Ion Exchange

Ion exchange is an ideal device to eliminate contaminants in low concentrations ^[18]. In such an instance, the run time for the resin column may be several months ^[18]. Whenever high concentrations of contaminants (10 wt% of solution) are present, the ion exchange cycles

become extremely short ^[18]. Meaning at 10 wt% of solution, the cation exchange and anion exchange resin beds need to be regenerated more often so that they can continue removing contaminants. The solution for the task contains 100 g/L of salt quickly ruling out ion exchange as a feasible process.

10.0 Environmental Considerations

The majority of Freeport-McMoran's mines are located in the arid southwest region where water is scarce and environmental sustainability is a primary focus. All the processes mentioned above are meant to positively impact the environment. The main environmental concern is treating the impacted water so that it can be reused within the mining process or be discharged into local bodies of water.

Locally, Miami, AZ is trying to be diligent to limit both air pollution and global warming progression. The local community wants the water in the aquifers to be pure, so that it does not negatively impact the city's water supply. Also, since Miami, AZ has mountainous terrain combined with a desert climate, it is essential that water is conserved as much as possible.

Something beneficial about this task is that there is no reaction taking place between the salts, chilling solution, or the water. There is no chemical reaction but instead there is only dissolution. Because of this, there are no byproducts (natural or artificial) produced and no other harm affecting the environment besides the salt concentration of the water.

10.1 Regulations

The Arizona Department of Environmental Quality (ADEQ) oversees the environmental regulations given to Freeport-McMoRan on their operations. The ADEQ does not have any specific regulations on magnesium or aluminum sulfate so more input on regulations were drawn from the federal level of the Environmental Protection Agency (EPA).^[1] The EPA has guidelines for industrial water effluent discharge levels. There is no primary maximum concentration level (MCL) guidelines on sulfates so the secondary MCL guidelines were referenced. Sulfate is one of fifteen different elements on this secondary list of maximum concentration levels. The maximum concentration that can be present in discharged water from the mine is 250 mg/L.^[6] Sulfates over this concentration will give a salty taste, can be very drying to skin, and can give

laxative effects. Specifically, in Miami, AZ, there is a push locally to keep the water in the aquifer clean, so the permits are vital for community relations.

10.2 Permitting

State laws given by the ADEQ are permits for aquifers, ground water and surface water ^[1]. Without these permits in Arizona, mines are not allowed to operate. Permits vary from state to state and depend on what type of mining is underway. Due to the Miami site's long operational period, it has been grandfathered in to certain permits such as the Aquifer Protection Permit. Because of a copper mine's leaching ponds and drip system, an Aquifer Protection Permit (APP) is required for newly operating mines. The mine is responsible for ensuring only purified water enters the aquifers which also affects the surface water. The EPA passed the Clean Water Act which requires the Miami mine to have a Storm Water and a Groundwater permit. A Groundwater Permit must be obtained for the Miami mine of Freeport-McMoRan to be allowed to discharge water into the ground. The Stormwater Permit protects the surface water running along the ground. With this, Freeport is required to implement designs specifically to collect surface water from rain so that if the water picks up contaminants in run-off, it can be contained without affecting groundwater or the aquifer. The Clean Air Act that was also passed by the EPA requires the mine to have a permit on the newly implemented scrubber as well as the smelter unit.

11.0 Conclusions and Recommendations

In conclusion, the results of the current evaluations of the bench scale and the full-scale designs show that reverse osmosis is the most economically viable option for implementation in industry. The RO process has a net present value of \$(2.96 million) which is much less than the overall NPV of the freeze crystallization and MEE processes.

Although freeze crystallization uses less energy overall, it requires a higher capital and operating cost due to the cost of refrigeration and narrow operating conditions. Because of the lack of a phase diagram for the aluminum sulfate, there is also some uncertainty for effectiveness of freeze crystallization. Reverse osmosis has been used multiple times in various industries, so it can be more reliably implemented. Freeze crystallization has been researched deeply in South Africa but has never been seen in an industrial setting. Although multiple effect evaporation is

able to recover 25% more water, it has a much higher net present value. MEE should only be chosen if the mine is on a strict time schedule and needs a higher rate of recovery. Due to freeze crystallization being more unreliable and costly in a full-scale process, the Freezerbacks recommend that Freeport-McMoRan utilize the full-scale reverse osmosis in the mines that are applicable to this task.

12.0 Acknowledgements

We would like to acknowledge Freeport-McMoRan for allowing us to tour the Miami, AZ mine and the research labs at the University of Arkansas for granting us designated space to work on our experiment and build our bench scale apparatus. We would also like to greatly thank Professor Robert Cross M.S. and Dr. Tammy Lutz-Rechtin at the University of Arkansas, Sean Wilson, Sam Roose and Brett Waterman of Freeport-McMoRan and Mr. L.H. Boyd, Jr., P.E. of Process Engineering Associates, LLC. Finally, we would like to express thorough gratefulness towards George Fordyce at the University of Arkansas for allowing our designs to be a reality.

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Reference WERC 2019 Task: The Freezerbacks

Sean Wilson

Environmental Engineer, Freeport McMoRan at Miami, AZ

Team Freezerbacks,

Thank you for allowing me an opportunity to audit your project report. Please find the attached draft version including my editorial comments.

I was impressed with your Team's thoroughness and experimental process. Your attention to detail in the experimental design was very good. It was also notable that your attention to safety, cost and environmental considerations made your project more complete.

You will find many direct comments for your attention. I would like to provide more context as follows:

1. Please remember that the project prompt was to help Freeport-McMoRan solve an industry/regional issue. This is not a Miami Operations-specific problem. I have asked that you restructure your report to consider this fact. Acknowledge that you visited Miami Operations to gain insight into the industry and task. The information you learned on your tour helped design, scale and evaluate your experiments. If you speak to the industry as a whole, and use Miami as supporting evidence, you will strengthen your report.
2. Your project report has several sections of information that are either incorrect or misleading in the context that they are being used. I understand where most of your data has come from but in these instances you should speak in more general terms. As an example, Miami is not in shutdown or closure mode. We are not mining new ore but are fully operational otherwise. We are in the process of reclaiming some facilities that are no longer in process. This is a very important distinction to be made. Also, please remove Miami-specific references to volumes and costs. I would encourage you to research FCX.com for our site-specific description as well as those of our sister mines. There you will find a lot of information on site operations and sustainable development efforts (consult the annual Working Towards Sustainable Development report).
3. There are some statements in your Environmental Section 10.0 on permitting and regulations that are not 100% accurate. This is another example of where you should speak to the industry as a whole. Regulations vary significantly between states and other mining operations. Focus on the information presented in the prompt. The environmental benefit is that you are treating impacted waters in a southwest region where water scarcity and environmental sustainability are a significant focus. Freeport is interested in treating these hyper-saline waters to help supply water to operations and/or make them clean enough for permitted discharges.

Please let me know if you have any questions,

Sean Wilson

Environmental Engineer

Freeport McMoRan Miami, AZ

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Audit on University of Arkansas Recovery of Water and Salt from Hyper-Saline Mine Water using Freeze Crystallization

Reference WERC 2019 Task: The Freezerbacks

Sam Roose

Hydromet Operations Superintendent, Freeport McMoRan at Miami, AZ

Hello Team Freezerbacks,

I have finished reviewing your draft report and I have to say that you and your team have done quite a bit of work and have written an excellent report in a very short time frame. Based on my review, I don't see any particular glaring health, legal, or economic issues. Is there anything in particular you or the team were concerned about? If so, let me know and I can give additional feedback. Regarding economics, all of these processes are going to be very expensive just due to the nature of what we are dealing with. Please keep in mind that my expertise is really around operating plants so I am coming at it from that perspective.

One thing I do want to clarify is that Freeport McMoRan Miami Operations does not currently have an APP permit as stated in section 10.2 on page 22. We are in a unique situation here so the APP permit has not been issued to date. That statement should be removed from the report. If you need any clarification on this I can get with Sean Wilson to help explain it in more detail.

I do appreciate the acknowledgement as well. It was our pleasure supporting you and your team on this project and I wish you the best of luck in the competition!

Best Regards,

Sam Roose
Hydromet Operations Superintendent
Freeport McMoRan Miami
sroose@fmi.com

Audit on University of Arkansas Recovery of Water and Salt from Hyper-Saline Mine Water using Freeze Crystallization

Reference WERC 2019 Task: The Freezerbacks

L. H. (Hop) Boyd, Jr., P.E.

Chief Manager, Process Engineering Associates, LLC

Freezerbacks –

I have completed my review of the report. In summary, I found it well written with the conclusions clear and adequately supported by the data. Your group is to be commended.

There are however, some potential improvements and points that you might want to consider, even though time is short. These are:

- It is not clear to me what happens to the concentrated liquor. In both cases, you recover 50-75% of the water in purified or nearly purified form. Thus by mass balance, you have remaining 25-50% water which now has an increased concentration of salts. It is indicated via Figure 5 and perhaps otherwise that this stream is returned to the evaporation ponds. So they now have 25-50% of their original water with an increased salt content still on site – how do they deal with this waste stream?
- The range of options that you considered for this application does not include physio-chemical processes such as enhanced precipitation of sulfates using specialty chemicals. A quick internet search revealed that some technologies exist that could potentially reduce the water sulfate concentration to below your 250 ppm value via precipitation and filtration. The main advantages of these type processes are that they are not energy-intensive, you can get a potentially much higher than 75% clean water recovery, and you can get a resulting dewatered sludge that might be much easier and less costly to dispose of than the concentrated brine streams that result from the crystallization and evaporation options you do consider. If I was the mining company, I would certainly be interested in exploring precipitation/filtration options as well.
- Table 3 Capital Costs – While the factored method you used is appropriate for the level of process engineering completed during this study for estimating the cost of an individual option, care has to be taken when used to compare options. It somewhat defies common sense that, just because equipment costs much more in one option that installation, instrumentation, etc. will cost proportionally more for that option as well. By way of example, let's say a Hastelloy tank costs ten times more than a steel tank of the same weight. Do you really believe that it costs ten times more to pour the concrete pad for the Hastelloy tank than for the steel tank? It does not. Therefore, I have found that when comparing options using a factored cost estimate, the differences in cost are exaggerated. Having said that, the conclusion you reached that the evaporation option is more cost effective than the crystallization option is still valid. This is just FYI in case someone challenges you on these numbers.
- Since Table 2 does not show the equipment costs for the 75% evaporation option that is shown in Table 3, you might want to either show the costs in Table 2 or explain how you got them.
- Figures 5 and 6 PFDs – I'm pretty sure I recognize these as PFDs from process simulations. At any rate, you have included the classic stream identification diamonds. The accompanying mass and energy balance tables that provide the details associated with these stream identifiers in my opinion should be included in the report, even if only as appendices. This is important information. For example, I would be keenly interested in the Figure 6 Stream 51 brine stream composition details, as this could have significant bearing on the ultimate disposition of this stream – this ties into the first bullet point above.

Let me know if you have any questions or comments, and I certainly hope that this qualifies as a “formal audit”. Otherwise, I'll say to you good job, and good luck to the Freezerbacks!

With kindest personal regards,

L. H. (Hop) Boyd, Jr., P.E.

Chief Manager, Process Engineering Associates, LLC

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