

Performance Evaluation of Freeze Crystallization for removal of Water and Sodium Sulfate from Mine Wastewater

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Abstract— Mine water treatment aims for zero waste generation. Freeze crystallization was evaluated for treatment of reverse osmosis brine rich in sodium sulfate. The aim was to recover potable water and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. A chiller was used to cool the brine to freezing temperature. Only ice was produced while Na_2SO_4 was below its saturation level, about 45 g/L (as Na_2SO_4). With further ice removal, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ started to crystallize. As water recovery increased from 0 to 80%, it was noticed that: (i) The freezing point decreased from -2°C at the start of ice formation, to -4°C when $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ started to crystallize, (ii) ice purity was determined by measuring TDS, which increased from 2 000 mg/L to 3 000 mg/L and (iii) Energy utilization amounted to 10 kWh/m³ during cooling to the freezing point and to 100 kWh/m³ when ice and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ were formed.

Keywords— Freeze desalination, Mine water, Sodium sulfate, Ice purity, Energy utilization

I. INTRODUCTION

Currently industrial brines and mine water are managed by prioritizing their disposal rather than treatment. Brines produced from mining, during metal processing, and other industrial activities in South Africa are mainly stored in lined ponds. Those ponds lose water through evaporation during the warm, dry season. During the rainy season there are high risks of spillages as rain water may result in overflowing of the ponds. Serious damage to the environment may result subsequent to these spillages of brine, which is highly saline. As a result, the dependence on natural evaporation, a technique which is popular in South Africa, is not recommended. It is also inadequate in terms of environmental safety and human health. Nano filtration and reverse osmosis (RO) have also been employed for desalination of mine water producing clean water and brine. Owing to new requirements for zero waste disposal, continuation of research is necessary to overcome shortcomings related to current methods of brine treatment [1]. This research may lead to new alternative methods and/or technologies for brine treatment.

Manuscript received October 20, 2020. This work was supported in part by the S.A Department of Trade, Industry and Compensation (dtic)

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Several methods such as RO, Electrodialysis and Freeze Desalination (FD) are some of the technologies being utilized for treatment of highly saline mine water. RO is widely used for desalination of both seawater and mine water. Although RO can recover up to 90 % potable water, one of its major disadvantages include membrane fouling/scaling which reduces the efficiency [2]. These limitations result in generation of sludge and brine which is mainly disposed of in evaporation ponds and sludge being disposed of at a high cost. This reiterates the need for treatment of brine being stored in ponds to meet zero waste disposal requirements. Freeze Desalination (FD) is the technology that is energy efficient, cost effective and environmentally friendly. Other advantages include, not being vulnerable to corrosion and fouling [3]. It can be implemented in the treatment of the brine generated from RO in particular for mine related water streams. It will further recover more potable water from RO brine in the form of ice and simultaneously crystallize out the salt in the form of Na_2SO_4 which can be sold [4].

The ROC (Reverse Osmosis/Cooling) process was developed for the treatment of brines from desalination processes, such as RO. The objective was to increase recovery of water by up to 99% and also recover salts such as sodium sulfate in the process. In so doing the generation of both sludge and brine were reduced. In the ROC process, brine is treated with sodium carbonate and sodium hydroxide in the pre-treatment stage to allow selective precipitation of metals (CaCO_3 , MnO_2 and $\text{Mg}(\text{OH})_2$). After pre-treatment, the sodium rich water is passed through a membrane stage to produce drinking water and brine. The brine has a concentration high enough to allow Na_2SO_4 crystallization upon cooling.

Overall, combining the three stages, sodium alkali pre-treatment, Reverse Osmosis desalination and Cooling crystallization, yields the following improvements to current technologies: (i) reduced RO membrane scaling – long membrane life, (ii) increased water recovery – no brine generation, (iii) elimination of mixed sludge generation – no sludge disposal costs, and (iv) production of saleable products from polluted water [5]. This study will focus on the recovery of reusable water and/or commercial salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) from mine waste water and by so doing it will seek to improve the quality of recovered water and lower the amount of generated waste.

A. Crystallisation

The crystallization of sodium sulfate hydrates is an exothermic process. This means that crystallization and dissolution of hydrates could be monitored through temperature measurement of a saturated solution undergoing cooling/heating cycles [6]. Crystallisation is a phase change in which a component is recovered from a solution, melt or vapour phase in crystalline form. It is a process which is dependent upon the thermodynamic driving force for nucleation and crystal growth [7].

B. Product quality

Crystal size distribution generally indicates quality of the product forming crystallisation process. The larger the crystals the higher the quality of the product. In ice formation, larger crystal size results in a more rapid filtration rate and purer ice crystal recovery. Recirculation enhances crystal growth by allowing crystal lattices to increase in size resulting in larger crystals [7].

C. Eutectic freeze crystallisation

The concept of freezing a solution in order to separate water and solutes is not a new one. Many authors have described such a method as a means of separation. Eutectic Freeze Crystallization (EFC) uses these concepts and focuses on a specific area of freeze crystallization, namely, operating at the eutectic point of two components (ice and salt). Different salt-water systems have different eutectic compositions and temperatures. The eutectic point of a solution is defined as the composition of a solution that has the lowest crystallisation temperature of any other composition of the same solution or simply as the composition and temperature below which both solvent and solute crystallise out of solution [7]. The principle of the EFC concept can be described using a typical phase diagram of a binary aqueous solution, shown in Figure 1. The concentration of dissolved solids in waste waters is usually very low, a few grams per litre, thus ice will generally crystallize first. The phase diagram used to describe the EFC process therefore has the starting position on the left side (Fig. 1) of the eutectic point because this is the region where ice crystallizes first [1].

D. Freeze desalination

Freeze desalination is an alternative method, based on salt rejection from water during freezing. Salt rejection in freeze desalination is due to the small dimensions of the ice crystal lattice that excludes the salt ions during partial freezing instead of being incorporated in the crystal lattice of the ice. The rejection of salt ions out of the solid phase (ice) is highly related to the hydration free energy and hydrated or ionic radius of the salt ions. Hydration free energy is the energy which indicates the stability of the hydrated ions compared to their unhydrated counterparts. Ions with smaller energy of hydration have less association with water, and hence are more likely to be rejected from the ice phase [3]. Freeze desalination is a natural phenomenon based on that ice crystals are essentially made up of pure water, and have the properties of pure water. Salt ions exert a freezing point depression effect as shown by molecular simulations [3].

II. MATERIALS AND METHODS

A. Feedstock

A30 g/L Na_2SO_4 solution was used as feed.

B. Equipment

Chiller, cooling reactor, clarifier and ice separator at the Brine Treatment Plant, based at *A-Thermal Retort Technologies* (Olifantsfontein) was used for the cooling process to recover water and Na_2SO_4 via ice formation.

C. Software

OLI Software was used to predict the aqueous behavior of various compounds in solution [8].

D. Procedure

The following approach was followed:

A 15 kW Chiller was utilized to cool a secondary refrigerant (water/ methanol mixture) to between -4°C and -8°C . Cooling down of brine, rich in sodium sulfate, to temperatures between -3°C and -5°C was achieved by passing it through a heat exchanger and further cooling down of the brine to between -4°C and -6°C for ice formation to recover clean water. The slurry from the heat exchanger was pumped into the clarifier to allow separation through settling as the salt crystals that have formed have higher density. For ice formation, the ice slurry was pumped directly to the ice separator where the ice was trapped on a net.



Fig. 1: Schematic diagram of the Freeze Crystallization unit (15 kW Chiller, Heat exchanger for TDS cooling and ice separation, Clarifier for salt/liquid/ice separation)

III. RESULTS AND DISCUSSION

A. Water quality

The feed water had a TDS of 12 540 mg/L. The TDS values of the ice samples were less than 3 900 mg/L and became lower over time. The sample collected after x min had a TDS of 3 868 mg/L and after y min' 2 989 mg/L. The raised TDS concentration was ascribed to larger ice crystals being formed over time. If this TDS concentration is too high for reuse of the water it can be retreated in the RO plant. The brine concentration increased with time from 13 430 to 14 070 mg/L.

The brine increased slightly in concentration, but also contained some precipitate. *OLI Software* showed that the precipitate that formed was $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. As water recovery increased from 7.2% in Sample 1 to 57.3% in Sample 3, the saturation level of Na_2SO_4 was exceeded, resulting in the crystallization of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (Table 2). It was noted that: (i) Na_2SO_4 remained in solution up to its solubility level of 44 310 mg/L Na_2SO_4 , (ii) the enthalpy increased from -3 886 864 to -836 444 Cal/kg when 80% water was removed through ice formation. For water with zero Na_2SO_4 content, the enthalpy drop was from -3 816 720 Cal/kg to -763 343 Cal/kg. This showed that the additional energy needed owing to the exothermic energy released from $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ was insignificant compared to what was needed for ice formation.

B. Energy utilization

Table 3 shows the theoretical energy needed for cooling 1 t/h of water from 25°C to -2°C and for freezing 1 t/h. For cooling, with a COP of 3, Energy utilization amounts to 10.45 kWh/t water and for freezing to 91.7 kWh/t ice. Table 4 shows the actual energy utilization when energy utilization was calculated in two ways: (i) Using the mass of water or ice cooled, time period and temperature drop in the case of cooling, and (ii) kWh measurements, time and mass of water cooled or mass of ice formed. For cooling, the COP value was calculated to be 2.05 (average of 4.77 and 1.37). For Freezing the COP value was calculated to be 0.46 (average of 0.48 and 0.44). It is expected that with more results and longer operation periods the COP for cooling will stabilize at 3 and for freezing at 1.

C. Feasibility

The total costs of waste transportation and disposal amounts to R2 350/m³ (Table 5). With Freeze Crystallization, these costs can be reduced down to R112.72/m³ (Table 6). These costs can be reduced significantly if the salt is processed to saleable form. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, for example, can be processed to Na_2CO_3 where Na_2SO_4 has a selling price of R700/t, and Na_2CO_3 a selling price of R5 000/t.

IV. CONCLUSION

It is recommended that Freeze Crystallization be used for treatment of leachate from mine dumps, solid waste disposal sites and brine streams from industrial and seawater desalination plants with the aim to recover saleable products such as water, $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, $\text{Al}_2(\text{SO}_4)_3$, CaSO_4 , Na_2SO_4 and MgSO_4 .

ACKNOWLEDGMENT

The authors express their gratitude to *A Thermal Retort Technologies* for making the freeze crystallization plant available and the South African Water Research Commission for financial support through its Wader Programme. Dr Fritz Carlsson is thanked for proof-reading and editorial input.

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TABLE I. WATER QUALITY OF FEED, BRINE AND MELTED ICE SAMPLES WITH INCREASED WATER RECOVERY - ACTUAL RESULTS

Parameter	Unit	Feed	Brine			Ice		
			Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
Water recovery	%		0.0	20.0	80.0	0.0	20.0	80.0
<i>Solution</i>								
pH		9.3	8.9	8.8	8.8	9.0	9.0	9.1
TDS	mg/L	12 540.0	13 430.0	13 550.0	14 070.0	3 868.0	3 480.0	2 989.0
EC	mS/cm	22.1	23.2	23.6	26.0	7.8	6.8	6.0
Volume	L	200.0	185.5	141.6	85.3			
Ice	kg		14.5	58.4	114.7			
Ice recovery	%		7.2	29.2	57.3			

TABLE II. OLI PREDICTED VALUES OF VARIOUS PARAMETERS DURING WATER REMOVAL THROUGH ICE CRYSTALLIZATION

H2O (mg)	H2O (mg)	Temperature [°C]	pH	Specific Electrical Conductivity - Aqueous (µmho/cm)	SO42- Aq (mg)	Na(+1) Aq (mg)	Na2SO4 Aq (mg/L)	Na2SO4.10H2O (Mirabilite) (mg)	Na2SO4 (mg)	Enthalpy - Total (cal)	Enthalpy - Solid (cal)	Enthalpy - Aqueous (cal)
1 000 000	1 000 000	0	8	12 592	20 317	9 711	30 028	0	30 000	-3 886 864		-3 886 864
920 000	920 000	0	8	13 389	20 317	9 711	32 640	0	30 000	-3 581 530		-3 581 530
840 000	840 000	0	8	14 311	20 317	9 711	35 748	0	30 000	-3 276 196		-3 276 196
760 000	760 000	0	8	15 391	20 317	9 711	39 511	0	30 000	-2 970 863		-2 970 863
680 000	680 000	0	8	16 676	20 317	9 711	44 159	0	30 000	-2 665 530		-2 665 530
600 000	595 378	0	8	16 717	17 849	8 532	44 310	8 266	30 000	-2 360 671	-26 640	-2 334 031
520 000	510 620	0	8	16 717	15 308	7 317	44 310	16 776	30 000	-2 055 825	-54 070	-2 001 756
440 000	425 861	0	8	16 717	12 767	6 102	44 310	25 287	30 000	-1 750 980	-81 500	-1 669 480
360 000	341 102	0	8	16 717	10 226	4 888	44 310	33 798	30 000	-1 446 135	-108 930	-1 337 205
280 000	256 343	0	8	16 717	7 685	3 673	44 310	42 309	30 000	-1 141 289	-136 360	-1 004 930
200 000	171 585	0	8	16 717	5 144	2 459	44 310	50 820	30 000	-836 444	-163 790	-672 654

TABLE III THEORETICAL ENERGY CONSUMPTION FOR COOLING WATER AND FOR FREEZING (80%)

Parameter	Symbol	Unit	Cooling	Ice	Total
Water flow	q	t/h	1.00	1.00	
Water flow	q	kg/sec	0.28	0.28	0.28
Heat coef	Cp	kJ/(kg.°K)	4.18	330	
Temp dif	dT	K	25	-2	
M.Cp.dT/t	E	kJ/sec	31.35	91.67	123.02
Power	P	kW	31.35	91.67	123.02
Flow	q	m ³ /h	1.00	1.00	1.00
E consump		kWh/t	31.35	91.67	123.02
COP			3.00	1.00	1.00
E consump		kWh/t	10.45	91.67	123.02
Cost		R/kWh	1.00	1.00	1.00
Cost		R/t	10.45	91.67	123.02

TABLE IV. TEMPORAL BEHAVIOR OF VARIOUS PARAMETERS DURING ICE AND SALT PRODUCTION WITH FREEZE CRYSTALLIZATION

Time	d Time	Volume	Temp	Ice	Acc Ice	Energy utilised	Power	Energy utilized Calc 1	Energy utilized Calc 2	Energy utilized _{theo} , COP = 1	COP1	COP2	Energy measured	Energy reading
						m.Cp.dT	m.Cp.dT/t x 3600	Px1000/3600	kWh/t/ m _{water}					
Cooling							kW	kWh/t	kWh/Time/ t _{water}				kWh	kWh
h	h	L	°C	kg		kJ								
0.0		126.00	20		0								0	19 690.4
0.5		126.00	7		0	6 846.8	3.80	13.69	16.3	31.4	2.29	1.93	2.05	19 692.5
1.0		126.00	2		0	9 480.2	2.63	9.48	28.4	31.4	3.31	1.10	3.58	19 694.0
1.5		126.00	1		0	10 006.9	1.85	6.67	37.0	31.4	4.70	0.85	4.66	19 695.1
2.0		126.00	0		0	10 533.6	1.46	5.27	46.7	31.4	5.95	0.67	5.88	19 696.3
0.0		126.00	8		0	0.0	0.00	-					0.00	19 713.0
0.5		126.00	2		0	3 160.1	1.76	6.32	13.8	31.4	4.96	2.27	1.74	19 714.7
1.0		126.00	0		0	4 213.4	1.17	4.21	22.5	31.4	7.44	1.39	2.84	19 715.8
Average											4.77	1.37		
Ice formation														
						m.Hv	m.Hv/t x 3600	Px1000/3600x 1000/m _{ice}	kWh/Time/t _{ice}					
3.5	2.0	126.00	1	14.46	14.5	4 771.8	0.66	165.00					2.89	19 699.2
6.0	2.5	126.00	4	16.21	30.71	5 349.3	0.59	132.00	301.0	91.7	0.69	0.30	7.77	19 704.1
9.0	3.0	126.00	-1	18.98	49.69	6 263.4	0.58	110.0	354.6	91.7	0.83	0.26	14.50	19 718.8
10.0	1.0	126.00	-1	8.74	58.43	2 884.2	0.80	330.0	204.8	91.7	0.28	0.45	16.29	19 720.6
12.0	2.0	126.00	0	14.05	72.48	4 636.5	0.64	165.0	264.8	91.7	0.56	0.35	20.01	19 724.3
13.0	1.0	126.00	0	13.19	85.67	4 352.7	1.21	330.0	124.3	91.7	0.28	0.74	21.65	19 726.0
14.0	1.0	126.00	0	13.8	99.47	4 554.0	1.27	330.0	211.6	91.7	0.28	0.43	24.57	19 728.9
15.5	1.5	126.00	0	15.25	114.72	5 032.5	0.93	220.0	164.6	91.7	0.42	0.56	27.08	19 731.4
Average											0.48	0.44		

Note 1 - Energy utilized Calc 1 - Calculated from mass ice produced and time period

Note 2 - Energy utilized Calc 2 - Calculated from kWh reading

TABLE V. DISPOSAL COST OF WASTE

Cost item	Unit	R/t	R/m ³
Waste disposal cost	R/t	1 000	1 000
Waste transport cost	R/t	1 500	1 350
Total			2 350

TABLE VI. FEASIBILITY OF THE FREEZE CRYSTALLIZATION PROCESS

Cost item	Unit	Cooling	Freezing	Capital cost
Capacity	t/h	0.30	0.24	0.30
Electricity	kW/m ³	10.45	91.67	102.12
Electricity cost	R/kWh	1.00	1.00	
Capital cost	R			1 090 800
Capital cost	R/ML/d			51 171 221
Capital redemption cost (120 months; 8% interest/a)	R/m ³			20.41
Flow	R/m ³	1.00	0.80	
Electricity cost	R/m ³	10.45	73.34	83.79
Labour (6 x R8000/person/month)	R/m ³			3.16
Management, Admin and Insurance (5%)	R/m ³			5.37
Total	R/m ³			112.72