Direct Cooling of Brine with Primary Refrigerant During Freeze Crystallization

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Abstract

To achieve zero waste disposal, this study explores pipe freeze crystallization as a cost effective and energy efficient solution for brine treatment. The key objectives were to assess chiller capacity, evaluate the impact of brine composition on salt and ice recovery, and measure energy consumption. Results showed that the chiller operated at 43.7 kW, enabling the recovery of 519.9 kg/day of $Na_2SO_4·10H_2O$ (60%) from high TDS (131.9 g/L) brine at a flow rate of 200 L/h. For lower TDS (117.5 g/L) brine, 119.4 kg/day of $Na_2SO_4·10H_2O$ and 313.2 kg/day of ice were recovered. The total energy required for cooling, salt crystallization, and ice formation was only 5.7 kW, demonstrating the efficiency of this method compared to conventional brine management techniques.

Keywords: Industrial wastewater treatment, brine treatment, zero waste, salt recovery, ice recovery, energy efficiency

Introduction and Background

In coal washing plants, water is used to separate coal fines from coal and transport them to waste disposal sites, where fines settle in dumps, and water returns through penstocks or seepage to the washing plant. Since the dump walls are built from coal discard with high pyrite (FeS_2) content, the leachate generated contains Fe^{2+}, Fe^{3+}, Al^{3+}, Mn^{2+}, Ca^{2+}, Mg^{2+}, Na^+, SO_4^{2-}, and Cl^- (Qureshi *et al*. 2016; Seo *et al*. 2017). This acid wastewater must be neutralised to prevent acid corrosion and undergo desalination to remove gypsum forming compounds before being safely discharged into public water systems. To achieve zero waste disposal, brine from desalination cannot be stored in evaporation ponds. Instead, it requires advanced treatment technologies such as crystallization. A study supported by the Wader Programme of the WRC demonstrated that coal leachate with a total dissolved solids (TDS) concentration of 12,540 mg/L can be effectively neutralised with Na_2CO_3 to produce stable water (Maree *et al*. 2021). Additionally, $Fe(OH)_3$ sludge was processed for pigment recovery. The neutralised water, free of scale forming compounds like gypsum, $CaCO_3$, and metal hydroxides, was then treated with reverse osmosis, yielding purified water and a concentrated brine stream with a TDS of 90 g/L. This brine was further treated using a low temperature crystallization approach to recover $Na_2SO_4·10H_2O$ and clean water through ice formation.

Crystallization based separation presents a more energy efficient and sustainable alternative to evaporation or distillation for saline wastewater treatment. It provides several advantages, including: i) it enables zero waste operations by concentrating brines to the point of selective salt crystallization, ii) it allows different salts to be recovered based on their solubility differences (Lewis *et al.* 2010; Randall *et al.* 2009, 2011), and iii) it consumes substantially less energy, only 123 kWh per ton of ice, compared to the 715 kWh per ton of water vaporised through evaporation (Table 1). Researchers have demonstrated that $Na_2SO_4{\cdot}10H_2O$ can be efficiently recovered through cooling with a secondary refrigerant (Maree 2018). A 300 L/h Pipe Freeze Crystallization (PFC) plant was designed, constructed, and has been operational since 2018 (Fig. 1). The plant consists of key components such as an 18 kW chiller, a cooler reactor with a high density polyethylene (HDPE) pipe heat exchanger (120 m long, 32 mm diameter), a clarifier, and an ice filter. The efficiency of the PFC system depends on several factors, including i) the recycle flow rate of the secondary refrigerant, ii) pipe dimensions, iii) feedwater temperature, iv) freeze temperature, v) TDS concentration, vi) SO_4^{2-}/Cl^- and SO_4^{2-}/SO_3^{2-} mole ratios, vii) refrigerant type, and viii) ambient temperature. Fig. 1 illustrates the variations in salt recovery over a 66-month period, which correlate with changes in these key process parameters.

Objectives

The primary objectives of this study were to evaluate the chiller capacity required for effective cooling, assess the impact of brine composition on the recovery of salt ($Na_2SO_4{\cdot}10H_2O$) and ice, analyse energy consumption across different operating conditions, and determine the purity of recovered ice. These factors are critical for optimising the efficiency and scalability of the crystallization process while ensuring minimal energy use and maximum resource recovery.

Methods and Materials

Saline water with a composition of approximately 75 g/L Na_2SO_4 and 75 g/L NaCl was used as the feedstock for this study. The experimental setup consisted of an 18 kW chiller containing a refrigerant mixture of 30% MeOH/70% H_2O, a cooler reactor equipped with an HDPE coil pipe, and a supporting metal skeleton to ensure structural stability, and a clarifier. The chiller was responsible for lowering the temperature of the secondary refrigerant to -10 °C, which was then circulated between the chiller and the cooler reactor. A long HDPE pipe, submerged in the secondary refrigerant, facilitated the controlled cooling of the saline water, circulating between the cooler reactor and clarifier, enabling the crystallization of $Na_2SO_4{\cdot}10H_2O$ and the formation of ice (Fig. 2).

The plant was operated continuously to evaluate the impact of brine composition on salt and ice recovery, energy consumption, and ice purity. TDS and chloride concentrations were analysed following Standard Methods (American Public Health Association 2012) to monitor water quality changes. Additionally, OLI ESP software simulations were conducted to predict the equilibrium concentration of Na_2SO_4 in the brine under varying cooling

Table 1 Comparison of energy consumption between freeze crystallization and evaporation/distillation.

Parameter	Unit	Freezing	Evaporation/Distillation
Flow (m/t)	m^3/h	1	1
Flow (m/t)	kg/s	0.28	0.28
T_1	°C	25	100
T_2	°C	-2	25
C_p	kJ/kg.K	4.18	4.18
H_v	kJ/kg	330	2 260.00
Energy for cooling/heating ($E = m/t.C_p.dT$)	kWh/t	31.35	87.08
Energy for freezing/evaporation ($E = m/t.H_v$)	kWh/t	91.67	627.78
Total Energy	kWh/t	123.02	714.86

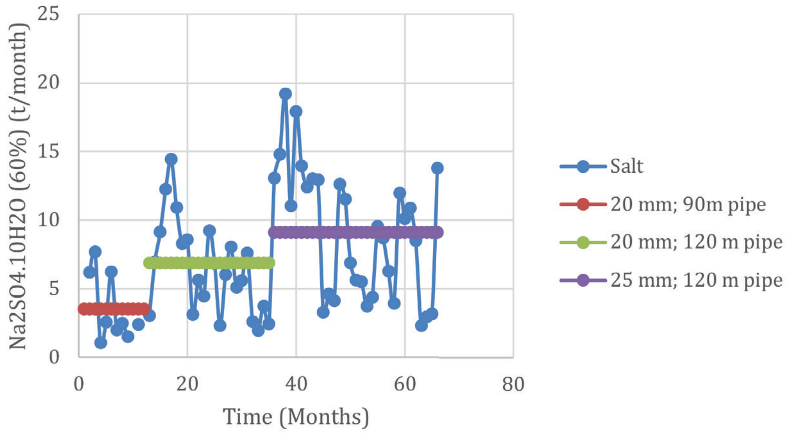

Figure 1 Salt recovery with cooling over time (from More et al. 2025).

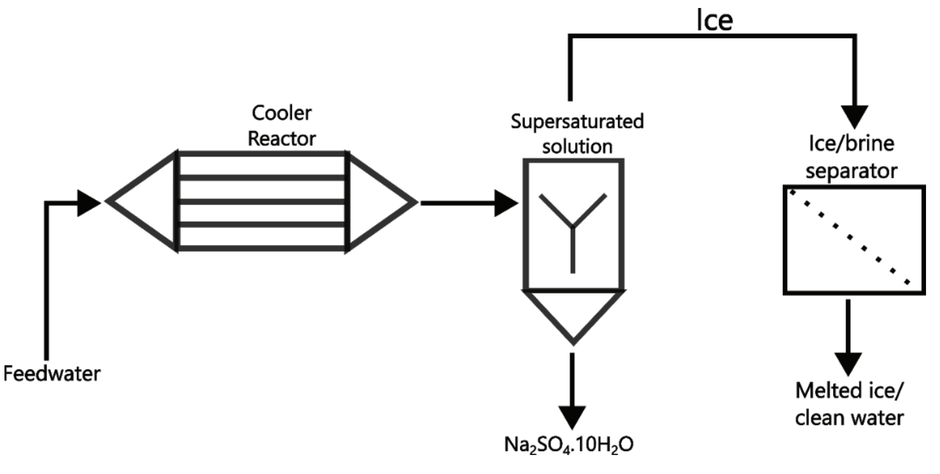

Figure 2 Schematic diagram of the experimental setup.

conditions. These simulations were validated by comparing predicted crystallization outcomes with actual experimental results, ensuring the accuracy of the process modelling and optimisation.

Results and Discussion

Chiller Capacity

The chiller's primary refrigerant transferred cooling energy to the secondary refrigerant through copper spirals in the chiller bath, which in turn cooled the brine through an HDPE coil heat exchanger in both the cooler reactor and clarifier. Temperature sensors placed at key points in the system monitored temperature variations, confirming the effectiveness of heat exchange between the chiller bath, secondary refrigerant, and brine. The chiller capacity was determined under zero load conditions by temporarily removing the HDPE heat exchanger from the cooler reactor. This assessment provided insight into how efficiently the system could maintain low temperatures necessary for crystallization.

As shown in Table 2, the chiller's energy transfer capacity decreased from 43.73 kW to 8.19 kW as the temperature dropped from 7.4 °C to -12 °C. This decline was reflected in the coefficient of performance (COP), which fell from 3.6 to 0.7 due to increased heat losses at lower temperatures. The system's efficiency was constrained by the flow rate of the secondary refrigerant and the length of the HDPE coil. Although the recycle pump had a capacity of 20,000 L/h, only 6,200 L/h could be processed through the chiller bath without overloading the cooler reactor. Increasing the length of the HDPE pipe and improving insulation could enhance heat transfer efficiency, allowing for better cooling performance and improved crystallization rates.

Salt Recovery

The brine treatment plant was specifically designed to remove Na_2SO_4 through cooling, facilitating the crystallization of $Na_2SO_4 \cdot 10H_2O$. A secondary refrigerant mixture (50% methanol and 50% water) was continuously recycled between the chiller bath and the cooler reactor at a rate of 6,200 L/h. The brine was cooled by passing through a 120 m long HDPE pipe (32 mm OD), which was submerged in the cooler reactor. This setup enabled efficient heat exchange and facilitated salt precipitation. The brine was then recycled between the HDPE coil in the cooler reactor and a 1,000 L clarifier, where the crystallized salt settled and was subsequently removed.

During a typical operational week (2024-12-23 to 2024-12-29), the system processed brine with a high TDS concentration at a rate of 200 L/h (Table 3). The feedwater contained 131.9 g/L TDS, with 63.2 g/L NaCl and 68.6 g/L Na_2SO_4. As the brine was cooled from 25 °C to -2.0 °C, $Na_2SO_4 \cdot 10H_2O$ crystallized, reducing Na_2SO_4 concentrations from 68.6 g/L to 40 g/L, yielding 519.9 kg/ day of $Na_2SO_4 \cdot 10H_2O$ (60%). The total energy consumption for cooling and salt production amounted to 7.9 kW, closely matching the measured electrical energy consumption of 7.33 kW. The cold energy generated by the chiller was calculated at 12.5 kW. Additionally, chloride concentrations were reduced from 61 g/L in the feed to 12 g/L in the melted ice, indicating substantial impurity separation. These findings confirm that the system operates efficiently, with salt recovery rates aligning closely with OLI simulation predictions.

Ice Recovery

The primary goal of brine treatment plant was to remove Na_2SO_4 through cooling. With a chiller capable of reaching -30 °C, tests were conducted to assess ice recovery alongside salt crystallization. These findings were critical for upgrading the plant to recover not only $Na_2SO_4 \cdot 10H_2O$ but also NaCl and ice. During a typical operational week (2024-08-19 to 2024-08-25), the system processed brine at 171 L/h with a high TDS concentration (Table 3). The feedwater contained 117.5 g/L TDS, composed of 98.9 g/L NaCl and 18.6 g/L Na_2SO_4. As the brine was cooled from 20 °C to

***Table 2** Determination of the chiller capacity.*

Time	Temperature		Volume		Energy		COP
	Chiller Bath	Cooler Reactor			Electrical	Thermal	
h	°C	°C	L	kWh	kW	kW	
0.00		7.40	1 696	0.00	0.0	0.00	
0.33	-3.00	-1.70	1 696	4.11	12.3	43.73	3.55
0.83	-4.30	-3.60	1 696	8.59	10.3	21.14	2.05
1.33	-5.70	-5.10	1 696	14.74	11.1	15.02	1.36
1.83	-7.40	-7.10	1 696	24.04	13.1	12.67	0.97
2.33	-8.60	-8.30	1 696	27.49	11.8	10.78	0.91
2.83	-10.90	-9.70	1 696	34.24	12.1	9.67	0.80
3.33	-11.60	-11.10	1 696	41.16	12.3	8.89	0.72
3.83	-12.50	-12.20	1 696	45.99	12.0	8.19	0.68

Table 3 *Energy balance between heat transfer from the secondary refrigerant to the brine.*

Parameter	Unit	Salt recovery							
No		1	2	3	4	5	6	7	Average
Date		23-Dec-24	24-Dec-24	25-Dec-24	26-Dec-24	27-Dec-24	28-Dec-24	29-Dec-24	
TDS Feed	g/L	150.5	150.0	100.0	117.5	127.0	149.0	129.0	131.9
Cl^-	g/L	45.4	44.5	20.4	34.4	41.1	46.3	37.4	38.5
NaCl	g/L	74.6	73.1	33.5	56.5	67.5	76.0	61.4	63.2
Na_2SO_4 Feed	g/L	75.9	76.9	66.5	61.0	59.5	73.0	67.6	68.6
Na_2SO_4 Treated	g/L	47.7	45.9	35.4	26.3	20.8	53.0	50.9	40.0
Na_2SO_4 OLI	g/L	10.9	11.0	15.4	12.8	11.7	10.9	12.2	12.1
q1	L/h	6 200	6 200	6 200	6 200	6 200	6 200	6 200	6 200
Chiller bath	°C	-8.2	-8.1	-8.1	-7.6	-7.7	-8.1	-7.2	-7.8
Cooler Reactor	°C	-6.0	-6.2	-5.9	-5.9	-5.7	-5.5	-5.3	-5.8
E1 = q1.Cp.dT	kW	13.32	11.33	12.84	10.25	12.00	15.79	11.81	12.5
q2	L/h	200	200	200	200	200	200	200	200
Feed	°C	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
Treated	°C	-3.2	-2.1	-2.5	-2.2	-0.2	-2.7	-1.3	-2.0
Salt (60% $Na_2SO_4 \cdot 10H_2O$)	kg/d	513.0	562.0	565.0	630.0	703.0	363.0	303.0	519.9
Ice	kg/d	0	0	0	0	0	0	0	0.0
E2a q1.Cp.dT	kW	6.44	6.19	6.30	6.22	5.76	6.34	6.02	6.2
E2b m.Hv (Salt)	kW	1.65	1.80	1.81	2.02	2.26	1.17	0.97	1.7
2Ec m.Hv (Ice)	kW	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0
E2 Total	kW	8.09	8.00	8.12	8.24	8.01	7.51	6.99	7.9
E3	kWh	176.0	176.0	176.0	176.0	176.0	176.0	176.0	176.0
E4	kW	7.33	7.33	7.33	7.33	7.33	7.33	7.33	7.3
		Ice recovery							
No		8	9	10	11	12	13	14	Average
Date		19-Aug-24	20-Aug-24	21-Aug-24	22-Aug-24	23-Aug-24	24-Aug-24	25-Aug-24	
TDS Feed	g/L	114.0	108.0	110.8	126.0	84.4	136.6	142.8	117.5
Cl-	g/L	59.6	65.2	43.1	48.2	53.6	73.7	78.3	60.2
NaCl	g/L	97.9	107.1	70.8	79.2	88.0	121.0	128.6	98.9
Na_2SO_4 Feed	g/L	16.1	0.9	40.0	46.8	-3.6	15.6	14.2	18.6
Na_2SO_4 Treated	g/L	7.1	-9.1	36.9	46.8	-3.6	15.6	-17.5	10.9
Na_2SO_4 OLI	g/L	6.1	0.9	6.1	6.1	0.0	5.9	5.9	4.4
q1	L/h	6 200	6 200	6 200	6 200	6 200	6 200	6 200	6 200
Chiller bath	°C	-14.7	-14.6	-13.2	-14.3	-14.9	-12.9	-13.5	-14.0
Cooler Reactor	°C	-12.6	-12.3	-10.2	-11.6	-12.3	-11.3	-10.8	-11.6
E1 = q1.Cp.dT	kW	13.02	13.80	17.96	16.03	15.31	10.01	16.09	14.6
q2	L/h	171	171	171	171	171	171	171	171
Feed	°C	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
Treated	°C	-6.1	-7.6	-7.3	-8.1	-7.4	-8.7	-6.5	-7.4
Salt (60% $Na_2SO_4 \cdot 10H_2O$)	kg/d	140.0	156.0	47.9	0.0	0.0	0.0	492.0	119.4
Ice	kg/d	201	257	115	438	449	550	183	313.2
E2a q1.Cp.dT	kW	5.10	5.40	5.35	5.50	5.35	5.61	5.19	5.4
E2b m.Hv (Salt)	kW	0.45	0.50	0.15	0.00	0.00	0.00	1.58	0.4
2Ec m.Hv (Ice)	kW	0.77	0.98	0.44	1.67	1.71	2.10	0.70	1.2
E2 Total	kW	5.55	5.90	5.50	5.50	5.35	5.61	6.77	5.7
E3	kWh	176.0	176.0	176.0	176.0	176.0	176.0	176.0	176.0
E4	kW	7.33	7.33	7.33	7.33	7.33	7.33	7.33	7.3

-7.4 °C, the secondary refrigerant temperature increased from -14.0 °C to -11.6 °C, demonstrating efficient heat exchange. This cooling process facilitated the formation of 313.2 kg/day of ice and 119.4 kg/day of $Na_2SO_4 \cdot 10H_2O$ (60%), effectively reducing the Na_2SO_4 concentration from 18.6 g/L to 10.9 g/L (Fig. 3). The experimental results closely matched OLI simulation predictions, confirming the system's efficiency.

The total energy consumption for cooling, salt, and ice recovery amounted to 7.3 kW, aligning well with the measured electrical energy consumption of 7.33 kW. The cold energy generated in the chiller was calculated at 14.6 kW. While the chiller's full 18 kW capacity was not utilised, primarily due to limitations in the flow rate of the secondary refrigerant through the cooler reactor, the system still achieved substantial ice and salt recovery. These results demonstrate that freeze crystallization is a viable and energy-efficient method for recovering ice and salts from high TDS brines, providing both economic and operational benefits.

Conclusions

The study demonstrated that freeze crystallization is an effective and energy efficient method for brine treatment, achieving substantial salt and ice recovery. The chiller capacity was determined to be 43.7 kW at 7.4 °C, supporting stable cooling operations. For high TDS brine (131.9 g/L) at a flow rate of 200 L/h, 519.9 kg/day of $Na_2SO_4 \cdot 10H_2O$ (60%) was recovered, reducing Na_2SO_4 concentration from 68.6 g/L to 40 g/L, with total energy consumption of 7.9 kW. Similarly, for lower TDS brine (117.5 g/L) at 171 L/h, 119.4 kg/day of $Na_2SO_4 \cdot 10H_2O$ (60%) and 313.2 kg/day of ice were recovered, lowering Na_2SO_4 concentration from 18.6 g/L to 10.9 g/L, with a total energy use of 5.7 kW. These findings confirm that pipe freeze crystallization is a viable solution for sustainable brine treatment, optimising resource recovery while minimising energy consumption.

Recommendations

To enhance system efficiency and maximise salt and ice recovery, it is recommended to improve insulation on open pipes to reduce heat losses. Additionally, increasing the length of the HDPE pipe in the cooler reactor from 120 m to 270 m would allow for greater cold energy transfer from the secondary refrigerant to the brine, improving crystallization efficiency. Finally, after implementing these improvements, the plant should be evaluated for NaCl recovery to further optimise the freeze crystallization process and enhance overall resource recovery.

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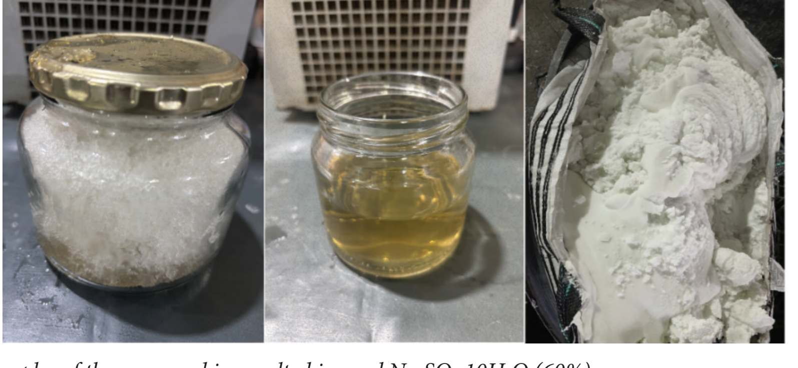

Figure 3 *Samples of the recovered ice, melted ice and $Na_2SO_4 \cdot 10H_2O$ (60%).*

Mdumbe, Zola Shikweni, Akani Chauke, Banele Ntshangase, Josaphat Mulumba, Mxolisi Malale, Thatego Mohlamonyane) for the operation of the plant and monitoring of its performance.

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