Treatment of copper leachate for the recovery of valuable products

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Abstract

Copper leachate containing 13 500 mg/L Al^{3+}, 8 500 mg/L Mg^{2+} and 109 000 mg/L SO_4^{2-} requires to be treated. The purpose of this investigation was to identify a process configuration for the recovery of clean water and saleable products such as $Al_2(SO_4)_3$, $Al(OH)_3$ and $MgSO_4$ from copper leachate. It was predicted from OLI software that: 40% of the water can be recovered before $Al_2(SO_4)_3$-crystallization will occur and 80% before $MgSO_4$-crystallization will commence. Pilot studies showed that the TDS can be reduced from 119 000 mg/L to 2 100 mg/L. The total cost, including capital redemption cost, was estimated at R207.32/m³. The value of the products were estimated at R550.37/m³.

Key words: Aluminium sulphate, Freeze crystallization, Leachate treatment, Magnesium sulphate, Mine water, ROC process

Introduction

The *Waste Act, 2008* and *National Water Act, 1998* of South Africa were enacted to promote cleaner production, waste minimization, water reuse, recycling and waste treatment, with disposal seen as a last resort (IWMSA, 2000). The Act stipulates that acids should be neutralized to have a pH between 6 and 12 before discharge onto a landfill site. The TDS content of brine or waste with a high salt content should not exceed 50 000 mg/L and the TDS from leachables should not exceed 100 000 mg/L (Gazette, 2008). Copper leachate is an example of such a waste stream and has a pH of 3.2 and contains 8 520 mg/L Mg^{2+}, 510 mg/L Ca^{2+}, 86.6 mg/L Cu^{2+}, 509.5 mg/L Fe^{2+}, 509.2 mg/L Fe^{3+}, 13 538 mg/L Al^{3+} and 109 408 mg/L SO_4^{2-}. Current methods of water treatment remove the adverse impacts, providing clean water for discharge, but leaves behind a concentrated waste that requires further treatment or disposal as a hazardous waste. Freeze desalination can be used for treatment of such highly saline solutions to: (i) produce water of a good enough quality and (ii) enable product recovery from a concentrated brine stream.

The potential of freeze desalination of sea water to produce drinking water was derived from the natural phenomenon of pure ice formation from frozen sea water (Nebbia & Menozzi, 1968). This led to the realization of the possibility of using freezing to produce fresh water from brackish water, industrial brines and a range of other saline water streams (Schroeder, 1980; Khawaji, et al., 2008). The major benefit of freeze crystallization, over current brine treatment technologies e.g. distillation and evaporation ponds, derives from the much lower heat of fusion of ice (333 kJ/kg) compared to the heat of evaporation of water (2500 kJ/kg). The **ROC (Reverse Osmosis/Cooling) process** was developed for the treatment of brines from desalination processes, such as reverse osmosis (**Figure 1**) (Mtombeni & Maree, 2014; Mtombeni, et al., 2016). In the ROC process, brine is treated with chemicals such as Na_2CO_3 and/or NaOH in the pre-treatment stage to allow selective precipitation of metals ($CaCO_3$, MnO_2 and $Mg(OH)_2$). After pre-treatment, the sodium- and magnesium-rich water is passed through a membrane stage to produce drinking water and brine. The brine has a Na_2SO_4-concentration which is high enough to allow Na_2SO_4 crystallization upon cooling/freeze desalination.

The purpose of this investigation was to validate a process configuration as shown in

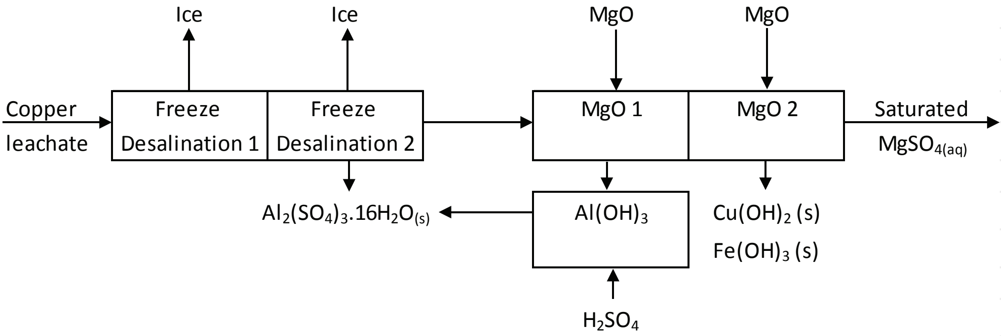

Figure 1 *Process configuration for treatment of copper leachate*

Figure 1 for the recovery of clean water and saleable products such as $Al_2(SO_4)_3$, $Al(OH)_3$ and $MgSO_4$ from copper leachate.

Methods

Modelling

The *OLI ESP* software program was used to predict the water quality after treatment with (i) alkalis such as Na_2CO_3 and NaOH (OLI, 2015) for removal of metals, (ii) freeze crystallization to further concentrate the brine to the level where $Na_2SO_4.10H_2O$ crystallizes. *OLI* is an aqueous equilibrium chemistry estimator with an interactive and self-instructive interface for clarifying reactions, having the ability to work with all kinds of common equilibrium reactions, with a strong solution algorithm, possessing expressive and easily understandable displays for results, and the ability to produce results in multiple formats according to different uses. The *Stream Analyzer* of OLI was used to perform single point equilibrium calculations, multiple point survey calculations for calculating a complete trend analysis for characteristics such as temperature, pressure, pH and composition effects, and simple mix and separation capability. The calculations provide liquid- and solid-phase separations for a specialized model.

The *OLI Analyser 9.0 System* was used to simulate the reactions by running a simulated AMD sample with assumed values of temperature, pressure, and pH. The base titrants used were NaOH, Na_2CO_3 and MgO. The temperature was assumed to be 25°C, the pressure, 1 atm and the pH was varied as desired with the different alkalis. Once the input values were run in the *OLI Systems Chem Analyzer*, a calculated summary of the simulated results would appear. This could be used to predict the actual reactions to use in the treatment methods according to the specific characteristics. Thus it was used to optimize a neutralisation-precipitation-desalination process for AMD.

Feedstock

Copper leachate containing 8 520 mg Mg^{2+}, 510 mg Ca^{2+}, 86.6 mg Cu^{2+}, 509.5 mg Fe^{2+}, 509.2 mg Fe^{3+}, 13 538 mg Al^{3+} and 109 408 mg SO_4^{2-} per L of water, was prepared artificially.

Equipment and Procedure

A Tecumseh 971 W (input power) reciprocating compressor (Model: AJE2444ZHZ [CAJ2464Z]) with a refrigeration capacity of 727 W, was used to cool the primary refrigerant, R-404A. The primary refrigerant was recycled through a heat exchanger in the water bath to cool the secondary refrigerant (30% methanol/water mixture) to -10°C or as required. Leachate was cooled to freezing point by passing it though a second heat exchanger, submerged in the water bath containing the secondary refrigerant. The ice/brine mixture was passed through a static brine/ice separator. The separation was based on the density difference between water and ice. The separator consisted of an ice column (110 mm diam; 1.2 m height) and a drain pipe (50 mm diam.) inside the ice column. Ice/brine slurry was pumped upwards through the ice column under low pressure using a peristaltic pump. The drain pipe was perforated, to allow brine to flow by gravity to a sump directly underneath the drain pipe. The lower section of the drain pipe had 12 mm holes covered with a 1 mm mesh wire gauze. Due to continuous deposition of ice crystals at the base of the column, the ice column moved to the top where a portion was harvested as product. The feed line to the ice column was provided with a pressure gauge to monitor pressure. Pressure build-up was an indication of excessive ice accumulation in the separator instead of normal upward ice movement in the ice column.

Analytical

Samples were collected at various stages in the treatment process, filtered (Whatman No. 1) and analysed for pH, conductivity, acidity, Mg^{2+}, Al(III) and SO_4^{2-} using standard procedures (American Public Health Association, 2012). A calibrated Knick Stratos Eco 2505 meter was used to measure electrical conductivity. Ice content was determined by mixing 250 mL ice slurry (mass m_1; temperature T_1) with 200 mL (m_2) warm water (T_2). The mass of ice (m_i) was determined from m_1, T_1, m_2, T_2 and the temperature (T_3) was measured after the ice had melted. Microsoft Excel *Goal Seek* was used to calculate m_i using the following equation:

$$4.18(m_1 - m_i)(T_1 - T_3) + 330m_i + 4.18m_2(T_2 - T_3) = 0 \qquad (1)$$

Results and discussion

Process configuration

OLI software was used to predict the behaviour of copper leachate (1 000 000 mg H_2O = 1L H_2O), containing 8 520 mg Mg^{2+}, 510 mg Ca^{2+}, 86.6 mg Cu^{2+}, 509.5 mg Fe^{2+}, 509.2 mg Fe^{3+}, 13 538 mg Al^{3+} and 109 408 mg SO_4^{2-}. This was treated by freeze crystallization and MgO. **Table 1** shows the chemical composition of the feed water and after treatment for,

Table 1 *Chemical composition of copper leachate before and after treatment by freeze crystallization and MgO dosing (predicted by OLI software)*

Parameter	Water quality (mg)					
	Copper leachate	Freeze Des 1	Freeze Des 2	MgO dosing 1	MgO dosing 2	Sludge separation
Chemical dosing						
MgO				14 406.9	435.8	
Solution						
pH	3.4	3.3	3.0	4.5	8.9	9.0
H_2O (mg)	1 000 000	600 000	200 000	200 000	200 000	200 000
Al^{3+} (mg)	13 523	13 523	6 190	1.0	0	0
Ca^{2+} (mg)	469	266	49	49	49	49
Cu^{2+} (mg)	121	121	121	121	0	0
Fe^{2+} (mg)	510	510	510	510	16	16
Fe^{3+} (mg)	509	509	509	0.5	0	0
Mg^{2+} (mg)	8 522	8 522	8 522	17 209	17 472	17 472
SO_4^{2-} (mg)	109 600	109 113	69 326	69 326	69 326	69 326
TDS (mg)	133 254	132 564	85 227	87 217	86 863	86 863
TDS (mg/L solution)	120 092	186 943	316 445	323 833	322 519	322 519
Mass (mg solution)	1 133 254	732 564	285 227	287 217	286 863	286 863
Cations (meq)	2 277	2 267	1 441	1 441	1 441	1 441
Anions (meq)	2 283	2 273	1 444	1 444	1 444	1 444
Solution						
$MgSO_4$ (mg)				86 535	86 798	**86 798**
$MgSO_4$ (mg/L)				432 675	433 989	433 989
Solids						
Ice (mg)		399 779	360 474	0		
$Al_2(SO_4)_3.16H_2O$ (mg)			**85 554**			
$Al(OH)_3$ (mg)				**17 879**		
$CaSO_4.2H_2O$ (mg)		1 058	1 987			
Cu(OH)2 (mg)					186	
$Fe(OH)_2$ (mg)					795	
$Fe(OH)_3$ (mg)					1.0	
Suspended solids (mg/L)		1 763	437 703	89 397	4 907	

(i) removal of water via freeze crystallization for recovery of water and $Al_2SO_4.16H_2O$ and (ii) chemical treatment with MgO for removal of impurities (Cu^{2+}, Fe^{2+}) and recovery of a saturated $MgSO_4$ solution. The chemical composition was expressed in mg in solution and not the conventional mg/L. The reason was because water was removed in addition to chemical compounds. It was shown in Step 1 (Freeze Des 1) that 40% water was removed with no removal of Al^{3+} and Mg^{2+}. The low mass of 469 mg Ca^{2+} in the 1 000 000 mg water was reduced to 266 mg in the remaining 600 000 mg water. This was due to the limited solubility of gypsum. In Step 2 (Freeze Des 2) a further 40% of the water was removed. This resulted in removal of Al^{3+} as the solubility of $Al_2SO_4.16H_2O$ at -1°C was exceeded. Al^{3+} mass in solution was reduced from 13 523 mg to 6 190 mg to produce 85 554 mg $Al_2SO_4.16H_2O$. Ca^{2+} mass was further reduced from 266 mg to 49 mg due to gypsum crystallization.

In Step 3 a dosage of 14 410 mg MgO was applied to precipitate the remaining Al^{3+} as $Al(OH)_3$ at pH4.5. This step offered the benefit that Al^{3+} was completely removed. $Al_2(SO_4)_3$ is used as a coagulant in water treatment. $Mg(OH)_2$ can also be converted to $MgSO_4$ by dissolving it in H_2SO_4. $MgSO_4$ is a valuable product used in fertilizer manufacturing.

In Step 4, the predominant $MgSO_4$ solution was purified by precipitating Fe^{2+} and Cu^{2+} as hydroxides by dosing 435.8 mg MgO. The remaining solution contained 86 798 mg $MgSO_4$. The original 1 L (1 000 000 mg) of water in the 1 133 254 mg copper leachate was reduced to 0.2 L (200 000 mg) of water, representing a $MgSO_4$ concentration of 433 989 mg/L, which is at saturation level. This solution can be sold as is for fertilizer manufacturing.

Freeze crystallization

Freezing point and water quality

Figure 2 shows the time needed to reduce the temperature of 64.6 g of water from room temperature (15°C) to 0°C and to freezing point and ice formation. In the case of the pipe (20 mm diam. 1.5 mm wall thickness) a time of 7.1 min was needed to lower the temperature from 15°C to 0°C. A further 12 min was needed to decrease the temperature from 0°C to -7°C, where after freezing commenced and continued over a period of 23 min. These calculations explained why water is rapidly cooled from room temperature to 0°C compared to the time needed for freezing the water. The energy usage to freeze the 64.6 g water amounted to 21 576 J.

Ice production

Ice slurry was produced by passing copper leachate though a PVC pipe, submerged in a water bath at -8°C and passed through an ice separation system as shown in **Photo 1**. Ice production on a continuous basis can be seen

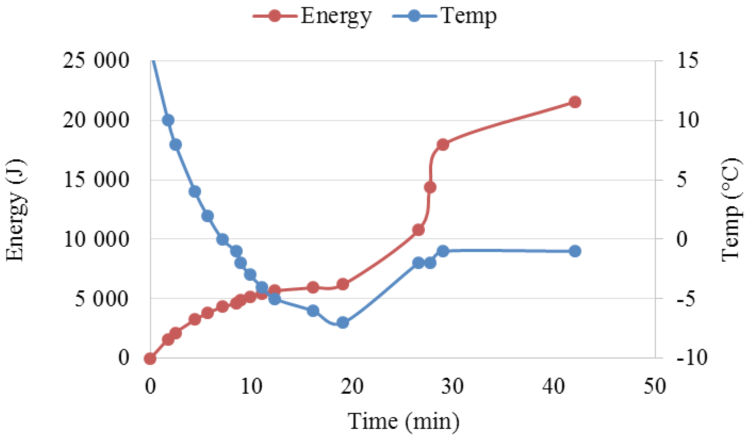

Figure 2 Temperature and energy behaviour during cooling of copper leachate to freezing point

***Photo 1** Ice separation*

in the following link: https://www.dropbox.com/s/bm9olu58r02qalo/Copper%20Leachate.AVI?dl=0

A filter inside the ice separation system allowed brine to be returned by gravity to the recycle stream while ice was forced to move up the column to be harvested. Over a period of 5 hours operation the conductivity of the melted ice decreased gradually from 27 to 7 mS/m. After harvesting and by allowing the ice to mature further by recirculation, the conductivity decreased to 2 mS/m. The purity of the ice is dependent on crystal growth and recrystallization. By running the plant for a longer period, it is expected that the ice purity will improve further. **Table 2** shows that clean ice can be produced. In the copper leachate the TDS content had been reduced from 119 138 mg/L to 2 102 mg/L.

Feasibility

A cost-effective process configuration was proposed for treatment of copper leachate by using the following approach: (i) Use freeze crystallization for recovery of water from a highly saline stream, (ii) Precipitate $Al_2(SO_4)_3.16H_2O$ directly with freeze crystallization for as long as $MgSO_4$ remains in solution, (ii) Use MgO to precipitate the last fraction of Al^{3+} in solution (as $Al(OH)_3$) at the stage just before $MgSO_4$ starts to precipitate, (iii) Convert the $Mg(OH)_2$ with H_2SO_4 to $MgSO_4$, and (iv) Use the saturated $MgSO_4$-solution as a final product.

The feasibility of processing copper leachate is calculated in and demonstrated by the results in **Tables 3** - **6**. Electricity cost amounted to R50.07/m^3 (**Table 3**); capital cost to R27.3million for a 68.1 m^3/h plant

Table 2 *Water quality of Feed, melted ice and brine*

Parameter	Chemical composition		
	Feed	Ice	Brine
Cond. (mS/cm)	44.0	2.5	62.0
pH	3.4	3.3	3.2
Al^{3+}	13 500	244	20 195
Mg^{2+}	6 439	95	9 700
Fe^{2+}	471	19	650
Cu^{2+}	2.5	0.0	3.7
Ca^{2+}	21	7	21
SO_4^{2-}	98 706	1 742	147 000
Cations (meq/L)	2 056	36	3 078
Anions (meq/L)	2 056	36	3 063
TDS (mg/L)	119 138	2 107	177 570

Table 3 *Energy cost*

Parameter	Value
Plant capacity (kg/s)	18.92
Electricity usage (80% ice recovery; COP = 1.5; 80% efficiency) (kW)	4 871.36
Electricity usage (kWh/m^3)	71.53
Electricity price (R/kWh)	0.70
Electricity cost (R/m^3)	50.07

Table 4 *Capital cost*

Cost items	Value
Plant capacity (m^3/h)	68.10
Plant capacity (gal/min)	300.00
Chiller capacity (MW)	4.87
Capital cost: Chiller (R/MW)	2 800 000
Capital cost: Chiller (R)	13 639 803
Capital cost: Other (R)	13 639 803
Total Capital cost (R)	27 279 607

Table 5 *Cost of raw materials and value of products*

Chemical	Usage	Price	Cost/Value
	kg/m^3	R/t	R/m^3
Raw materials			
MgO	13.10	4 000	-52.39
H_2SO_4	29.73	3 000	-89.20
Total cost			-141.59
Products			
$Al_2(SO_4)_3.16H_2O$	139.21	2 000	278.42
$MgSO_4.7H_2O$	156.81	1 700	266.58
Water	670.86	8	5.37
Total value			550.37

Table 6 *Feasibility*

Cost item	Value
Capital redemption cost (R/m^3)	-7.88
(1%/month; 120 month)	
Electricity cost (R/m^3)	-50.07
Labour (R/m^3)	-1.41
(10 operators; R7000/Month)	
Maintenance (R/m^3)	-1.37
(3% of Capital cost)	
Other (R/m^3)	-5.00
Chemical cost (R/m^3)	-141.59
Total cost (R/m^3)	-207.32
Value of products (R/m^3)	550.37
Profit (R/m^3)	343.05

(**Table 4**); chemical cost to R141.59/m^3 (**Table 5**); capital redemption cost to R7.88/m^3 (**Table 6**), and the value of water and products ($Al_2(SO_4)_3.16H_2O$ and $MgSO_4$) to R550.37/m^3 (**Table 5**). The combined value of products clearly exceeds the costs by R343.05/m^3 (**Table 6**).

A pilot-plant with a capacity of 300 L/h (**Figure 3**) has been designed and is under construction which will be used to demonstrate that brine can be concentrated in two stages: (i) where 40% of the water is removed through ice formation with no removal of Al^{3+} and Mg^{2+} and (ii) where a further 40% of the water is removed together with a portion of the Al^{3+} as $Al_2(SO_4)_3$.

Beaker studies will be carried out on the remaining brine for removal of Al^{3+}, Fe^{2+} and Cu^{2+} with MgO. The following items are shown in **Figure 3**: Feed tank, Chiller, Freezing reactor, Ice/brine/solids separation reactor and Ice/brine separation reactor.

Conclusions

The following conclusions were drawn from the results of this study:

1. With OLI software it was predicted that from 1 113 254 mg copper leachate (1 000 000 mg H_2O + 133 254 mg salt) the following can be recovered: (i) 399 799 mg ice in Step 1 (Freeze Crystallization 1), (ii) 360 474 mg ice, 85 554 mg

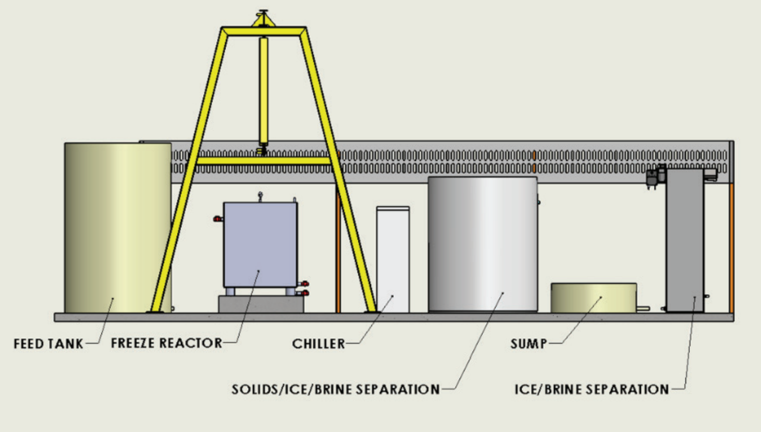

Figure 3 *Schematic diagram of a 300 L/h copper leachate pilot-plant*

$Al_2(SO_4)_3.16H_2O$ and 1 987 mg gypsum in Step 2 (Freeze Crystallization 2), (iii) 17 879 mg $Al(OH)_3$ in Step 3 (MgO dosing 1), (iv) 186 mg $Cu(OH)_2$ and 795 mg $Fe(OH)_2$ in Step 4 (MgO dosing 2) and (v) 86 798 mg $MgSO_4$ (200 mL of a 43% $MgSO_4$ solution) in Step 5 (Final brine).

2. Pure ice with a TDS of 2 107 mg/L was recovered in a laboratory freeze crystallization unit from copper leachate with a TDS of 119 135 mg/L. The TDS of the brine increased to 177 570 mg/L.
3. The total combined running and capital redemption costs were estimated at R207.32/m^3.
4. The total value of water and products ($Al_2(SO_4)_3.16H_2O$ and $MgSO_4$) were estimated at R550.37/m^3.
5. This technology is an improvement on existing desalination technology for the following reasons: (i) It decreases brine volumes by crystallization of dissolved species enabling further water recovery, and (ii) It reduces sludge formation by enabling the selective production of saleable products.

Recommendation

Copper leachate and other brine streams need to be treated on pilot-scale with the focus on recovery of water, $Al_2(SO_4)_3.16H_2O$, $Al(OH)_3$ and a saturated $MgSO_4$ solution or other saleable products.

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