

Solar Evaporation of Brine

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Abstract

The leachate from coal and waste dumps is highly polluted with mine water, creating significant environmental challenges. Current methods involve storage in evaporation ponds, aiming to reduce immediate impacts. This research proposes an innovative approach using the combination of evaporation, to decrease leachate volume, oxidation of Fe^{2+} to Fe^{3+} with iron-oxidizing bacteria and pH adjustment by using $\text{CaCO}_3/\text{Ca}(\text{OH})_2$. Key findings include solar evaporation, oxidation achieving a 1:2 molar ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$ to recover magnetite using sodium or calcium alkalis, and improved sludge separation characteristics. This method enhances acid mine water treatment efficiency, reduces energy costs, and simplifies management, making it a promising strategy for sustainable practices in mining and environmental management.

Keywords: Leachate, evaporation, solar heating, Fe(II) oxidation, magnetite

Introduction

The mine water produced in South Africa by gold mines and coal mines, discloses that the existing and previous gold mines in Gauteng produce 350 ML/d. This is produced by the Western (40 ML/d), Central (82 ML/d), Eastern (102 ML/d) and Far Western (126 ML/d) Basins (Mogashane *et al.*, 2020). The coal mines in Mpumalanga produced 200 ML/d of mine water of which 100 ML/d is further treated with reverse osmosis to produce water of drinking quality and brine that are stored in evaporation ponds (Maree *et al.*, 2013). Storage of brine in evaporation ponds is not encouraged by Department of Water and Sanitation as ground water can be contaminated when the plastic liners get damaged (Ahmed *et al.*, 2000).

Leachate from mine tailings, which typically contains high concentrations metal ions, is often subjected to evaporation processes to effectively reduce its overall volume. To facilitate this, water spray cannons are employed, creating micro-sized droplets

that are dispersed into the atmosphere, thereby promoting evaporation. While this method can help in concentrating the leachate and minimizing the volume of waste, it has significant drawbacks (Jiang *et al.*, 2023). One major concern is that the saline-rich spray produced during this process can be carried by wind, potentially impacting neighboring areas. This unintended dispersal can lead to soil and water salinization, adversely affecting local ecosystems and agricultural lands. Consequently, while evaporation strategies may seem beneficial for waste management, careful consideration of their environmental impacts is essential (Nalukui and Besa, 2024).

In South Africa and elsewhere, brine from desalination plants is typically stored in evaporation ponds; however, this practice is not favored by authorities due to the potential leakage of plastic liners, which raises significant concerns about environmental contamination and long-term sustainability. Similarly, in mining operations, the management of leachate containing high levels of iron ions is

critical, especially after the oxidation process. Efficient recovery of magnetite from this oxidized leachate can significantly mitigate its environmental impact while transforming it into a valuable resource. By implementing effective recovery techniques, both practices address the need for sustainable waste management. This approach not only enhances resource utilization but also reduces the overall volume of waste generated, promoting a more responsible and environmentally friendly mining and desalination industry (Mos, 2018).

Maree has proposed a system for the evaporation of iron rich acid mine water and brine and for the recovery of good quality water and salt (Fig. 1), existing out of the following stages: (i) Solar heating of the brine in a coil shaped pipe, (ii) Evaporation of the brine in a pipe system, (iii) Condensation of humid air through cooling with ambient air or melted ice from freeze crystallization units. The purpose of this investigation was to evaluate and to improve the proposed design.

Objectives

The following objectives were set for the project: (i) Evaluate process configuration

for solar evaporation (ii) Determine rate of heating in a pipe (iii) Determine effect of temperature and air volume on vapor fraction.

Materials and Methods

Feedstock. Leachate from a waste coal dump and tap water was used for paper and laboratory studies.

Equipment. HDPE pipes of different diameter, steel plate and thermometer were used.

Experimental. The effect of the following parameters was investigated: (i) Solar heating of the brine, (ii) Evaporation of the brine in a pipe system.

Analytical. Standard procedures were used to collect samples at various phases, filter them (Whatman No. 1), and measure their concentrations of Fe(II), Fe(III), pH, Ca, and alkalinity (APHA, 2012). Metals were analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-OES) (iCAP-7000 Series, ANATECH, South Africa). The pH/EC meters were calibrated before the start of each set of experiments and during the experiment using calibration buffers.

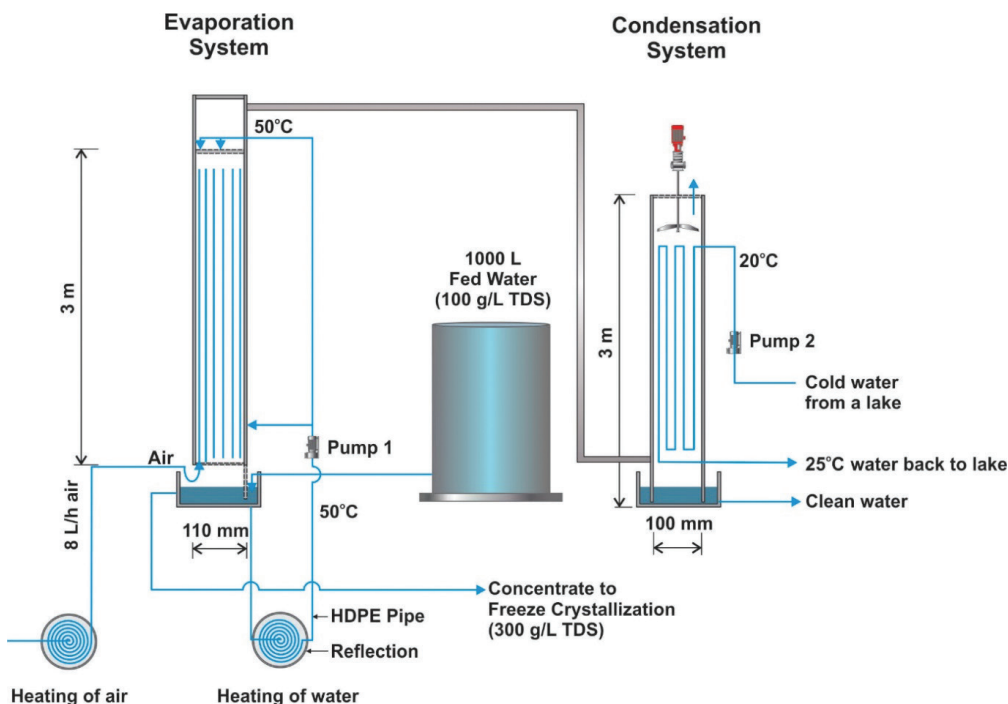


Figure 1 Process configuration for solar evaporation.



OLI Software simulations. The OLI ESP software program was used to predict the conditions needed for evaporation of the leachate (OLI, 2021). OLI is an aqueous equilibrium chemistry estimator with an interactive and self-instructive interface for clarifying reactions, the ability to work with all kinds of common equilibrium reactions, a strong solution algorithm, expressive and easily understandable displays for results, and the ability to produce results in multiple formats according to different uses.

Results and Discussion

Up-concentration of saline waters

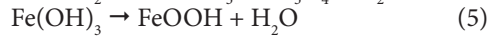
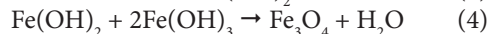
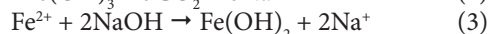
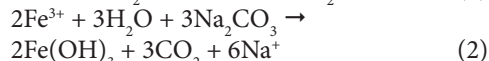
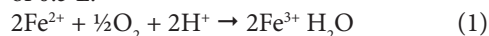
The up concentration of saline waters needs a combination of treatment steps, depending on its chemical composition. For mine water rich in metals with a low pH, metals need to be removed through pH adjustment. For brine from desalination plants, up concentration through evaporation can be applied directly.

Magnetite from coal mine leachate

Leachate from a waste coal dump that contained 9 270 mg/L Fe^{2+} , 100 mg/L Fe^{3+} , 328 mg/L Al^{3+} and 600 mg/L Ca^{2+} , 486 mg/L Mg^{2+} , 43 788 mg/L SO_4^{2-} and 200 mg/L Cl^- was treated with the aim to recover magnetite (Fe_3O_4) from Fe^{3+} -rich water (Table 1).

In Step 1, 70% of the water was evaporated at 60 °C through contact with air in a column reactor. Fe^{2+} was oxidised to Fe^{3+} (Eq. 1) due to the presence of 20% O_2 in the air. In Step 2 the Fe^{3+} -rich oxidised water was treated with Na_2CO_3 to precipitate Fe^{3+} as $\text{Fe}(\text{OH})_3$ (Eq. 2). In Step 3, a specific volume of the Fe^{2+} -rich feed water was treated with NaOH to precipitate Fe^{2+} as $\text{Fe}(\text{OH})_2$ (Eq. 3). The volume of Fe^{2+} -rich feed water needed to result in a $\text{Fe}(\text{OH})_3/\text{Fe}(\text{OH})_2$ mole ratio of 2, was calculated to be 0.8 L out of a total volume of 1 L. In Step 4 the product water from Steps 2 and 3 was mixed to form the $\text{Fe}(\text{OH})_2/\text{Fe}(\text{OH})_3$ sludge, which was allowed to settle and separated from the liquid. In Step 5 the $\text{Fe}(\text{OH})_2/\text{Fe}(\text{OH})_3$ mixed sludge was heated to form magnetite (Fe_3O_4) at 100 °C (Eq 4). An OLI simulation was used to determine chemical dosages and to predict water qualities. At a dosage of 45 423 mg Na_2CO_3 , Fe^{2+} was reduced from 9 270 to 60 mg, Al^{3+} from 328 to 1 mg. A dosage of 26 129

mg NaOH was needed to reduce Fe^{2+} from 60 to 1 mg, Fe^{3+} from 1 to 0 mg and Al^{3+} from 1 to 0 mg. The TDS concentration increased from 55 010 mg/L to 212 488 mg/L when 1 L of feed water was evaporated to a final volume of 0.3 L.



Pigment from Coal Mine Leachate

Pigment can be recovered from iron in mine water as an alternative to magnetite. Only Steps 1 and 2 will be needed. Steps 3 and 4 will be obsolete. Step 5 will need higher temperatures for processing $\text{Fe}(\text{OH})_3$ to goethite (yellow pigment) at 200 °C (Eq. 5) or to hematite (red pigment) at 800 °C (Eq. 6) (Rapeta *et al.*, 2024).

Brine

Brine from reverse osmosis plants has a TDS of 30 000 to 90 000 mg/L and contains mainly Na_2SO_4 and NaCl. Such brine is stored in evaporation ponds, which are not environmentally accepted. Such brine can be treated with Freeze Crystallization (FC) for the recovery of water and salt. Since FC required 120 kWh/ton ice, it is advantageous if the RO brine can be concentrated further prior to treatment with FC.

Solar Heating

Evaporation is energy intensive as 2 256 kJ is needed for evaporation of 1 kg H_2O , which amounts to 713.8 kWh/ton H_2O . At an electricity price of R2.00/kWh, evaporation cost (heating from 25 °C to 100 °C + evaporation) amounts to R1 427.50/ t H_2O . This high cost of evaporation with electricity serves as motivation for solar evaporation.

Table 2 shows the effect of pipe diameter on the rate of heating with solar energy in HDPE pipes. It also shows pipe cost. It was noted that water can be heated in a 16 mm ID HDPE pipe within 25 min from ambient temperature (21 to 28 °C) to 49 °C compared to 26 min in a 46 mm Dia. HDPE pipe (Fig.

*Table 1 Treatment of Fe²⁺-rich leachate through evaporation to form magnetite.*

Parameter	Unit	Feed 1a	Step 1 Evaporation + Fe ²⁺ -oxidation	Step 2 Fe(OH) ₃ formation	Feed 1b	Step 3 Fe(OH) ₂ formation	Step 4 2+3	Step 5 Magnetite
Temp	°C	25.0	60.0	60.0	25.0	25.0	60.0	120.0
H ₂ O	L	1.0	0.3	0.3	0.8	0.8	1.1	
H ₂ O	g	0.0	1.5					
Feed 1								
Na ₂ CO ₃	mg			45 423.0				
NaOH	mg					26 129.0	0.0	
O ₂	mg		1 319.2					
Solution								
pH		5.0			5.0			
Acidity	mg CaCO ₃	43 035.6	43 044.5	166.0	32 675.0	0.0	166.0	
H ⁺	mg	486.6	321.8	1.0	369.0	0.0	0.0	
Na ⁺	mg	0.0	0.0	19 712.0	0.0	15 024.0	34 736.0	
Mg ²⁺	mg	486.0	486.0	486.0	369.0	369.0	855.0	
Ca ²⁺	mg	351.0	100.0	100.0	266.0	266.0	366.0	
Fe ²⁺	mg	9 270.0	60.0	60.0	7 038.0	0.0	0.0	
Fe ³⁺	mg	100.0	9 310.0	1.0	76.0	0.0	0.0	
Al ³⁺	mg	328.0	328.0	1.0	249.0	0.0	0.0	
SO ₄ ²⁻	mg	43 788.0	43 186.0	43 186.0	33 246.0	33 246.0	76 432.0	
Cl ⁻	mg	200.0	200.0	200.0	152.0	152.0	352.0	
TDS	mg	55 010.0	53 991.0	63 746.0	41 766.0	49 058.0	112 741.0	
TDS	mg/L	55 010.0	179 971.0	212 488.0	55 010.0	64 613.0	106 434.0	
Fe ³⁺ /Fe ²⁺								
Cations	me	917.9	905.4	905.0	697.0	697.0	1 599.0	
Anions	me	917.9	905.3	905.0	697.0	697.0	1 602.0	
Vapor								
H ₂ O	g		0.7					
CO ₂				18 855.0				
Solids								
CaSO ₄			853.4					
Fe(OH) ₂				0.0		11 323.0	11 323.0	
Fe(OH) ₃				17 810.0		145.0	17 955.0	
Fe ³⁺ /Fe ²⁺							2.0	
Al(OH) ₃							2.9	2.9
Fe ₃ O ₄								22 696.0

2.a). The pipe cost for heating 1 m³/h from 20 °C to 44 °C at ambient temperature of 29 °C was calculated to be R5 215 in the case of a 50 mm Dia HDPE pipe. Fig. 2.b showed the effect of heat reflection with a steel plate. With a steel plate a higher temperature of 53 °C was reached, compared to 48 °C without

the reflecting plate. Similar runs were carried out to determine the rate of heating air in a pipe. A temperature of 42 °C was reached within 30 min. The lower temperature in the case of air, compared to water, can be ascribed to the smaller heat transfer coefficient of air (10 – 100 W/(m²K) compared to that of water (500 – 10 000 W/(m²K)).

Table 2 Heating of water and with solar energy in a pipe.

Parameter	I.D. (mm)		
	16.0	46.0	106.0
O.D. (mm)	20.0	50.0	110.0
Volume/m (L)	0.2	1.7	8.8
Heating time1 (min)	25.0	26.0	100.0
Volume heated per h in 1 m pipe (L)	0.5	3.8	5.3
Pipe needed for 1 m3/h (m)	2 072.0	261.0	189.0
Pipe price (R/m)	5.0	20.0	60.0
Pipe cost for heating (R/m ³)	10 362.0	5 215.0	11 332.0

Further studies will focus on how the rate of heating can be increased by passing the water through coil pipe, placed in a concave shaped ball, with a reflecting surface, covered with glass, to minimise heat losses to the atmosphere.

Evaporation

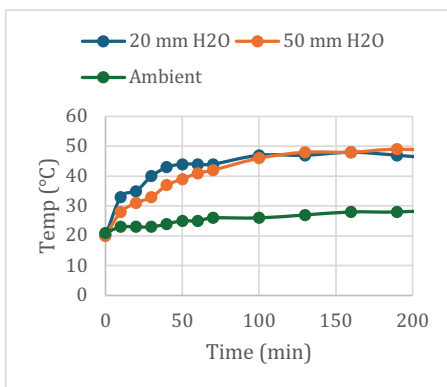
Table 3 shows the effect of temperature and gas volume on the H_2O_{vap} fraction in gas phase (OLI simulation). The cells in bold shows the gas volume and temperature where near 50% of the water was in the gas phase and 50% in the liquid phase. If the target is to do evaporation at 55°C, a mass of 4 000 g N_2 (3 200 L) will need to be contacted with 1 000 g H_2O to produce 433 g of H_2O_{vap} and 567 g H_2O_l . To evaporate 100 L/h water at 55°C, 320 m³/h dry air will be required.

Conclusion

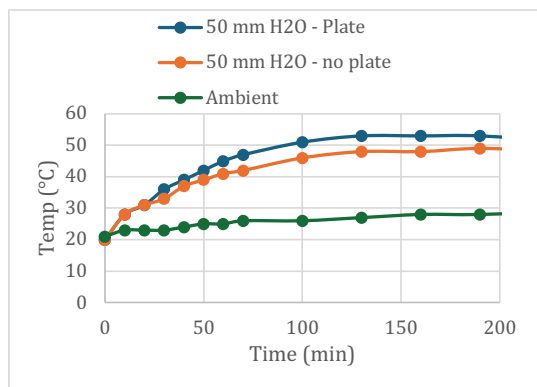
The following conclusion were made: (i) Saline water can be heated in an HDPE pipe. The rate and temperature to achieve is influenced by the pipe dia, pipe length, water feed rate and sun reflection. (ii) Evaporation of saline water is influenced by temperature of the water and air, surface area of the medium and air flow rate. (iii) The estimated cost of solar evaporation amounted to R103/m³. If this can be used to up-concentrate the feed to freeze crystallization, its cost of R614/m³ can be reduced. It is estimated that the cost of freeze crystallization can be reduced by 40% if combined with solar evaporation.

Recommendation

It is recommended to design and construct a 100 L/h unit for solar heating, evaporation and condensation



a. Dia varied with no steel reflection



b. Reflection varied (Dia. = 50 mm)

Figure 2 Heating of water and with solar energy in a pipe (a. Dia varied with no steel reflection, b. Reflection varied (Dia. = 50 mm).

**Table 3** Effect of temperature and gas flow on evaporation from 1 kg water, 50 g Na₂SO₄ and 50 g.

Temperature [°C]	48	55	62	69
H ₂ O – Vap [g] – N ₂ = 0.0 g	0.0	0.0	0.0	0.0
H ₂ O – Vap [g] – N ₂ = 800.0 g	61.0	90.0	134.0	200.0
H ₂ O – Vap [g] – N ₂ = 1600.0 g	121.0	179.0	264.0	390.0
H ₂ O – Vap [g] – N ₂ = 2400.0 g	181.0	266.0	389.0	560.0
H ₂ O – Vap [g] – N ₂ = 3200.0 g	240.0	351.0	506.0	693.0
H ₂ O – Vap [g] – N ₂ = 4000.0 g	298.0	433.0	610.0	798.0
H ₂ O [g] – N ₂ = 0.0 g	1 000.0	1 000.0	1 000.0	1 000.0
H ₂ O [g] – N ₂ = 800.0 g	939.0	910.0	866.0	800.0
H ₂ O [g] – N ₂ = 1600.0 g	879.0	821.0	736.0	610.0
H ₂ O [g] – N ₂ = 2400.0 g	819.0	734.0	611.0	440.0
H ₂ O [g] – N ₂ = 3200.0 g	760.0	649.0	494.0	307.0
H ₂ O [g] – N ₂ = 4000.0 g	702.0	567.0	390.0	202.0

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