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ORIGINAL PAPER

Efficient suspension freeze desalination of mine wastewaters to separate clean water and salts

A. Adeniyi[1] · **R. K. K. Mbaya**[1] · **M. S. Onyango**[1] · **A. P. I. Popoola**[1] · **J. P. Maree**[2]

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Abstract Suspension freeze desalination is a promising technique for producing clean water from mine wastewaters. The principle is that growing ice crystals reject impurities during freezing. As a result, pure water is separated from mine wastewaters as clean ice. Actually, there is a need for improved techniques to increase water yield and purity. Here we tested ice formation in complex synthetic solutions during cooling and addition of seed. Solutions included: pure distilled water, 50, 33 g/L NaCl and 17, 50 g/L Na_2SO_4, 50 g/L NaCl and 50 g/L Na_2SO_4. Results show that heat of crystallization was the highest with pure distilled water at 8859 J, whereas the lowest heat of crystallization, of 4608 J, was for the solution of 50 g/L NaCl and 50 g/L Na_2SO_4, indicating that the presence of the salt enhances ice formation. As an application, we designed a new flow diagram, which, in addition to heat exchanger and ice filter, now includes a fluidized bed reactor for salt crystallization and recovery, and a separate heat exchanger for ice crystallization.

Keywords Freeze desalination · Mine water · Fluidized bed reactor · Salt recovery · Ice recovery

Introduction

Freezing process is an alternative method to produce pure water from mine wastewater which is a serious pollution issue globally. The freezing process expels dissolved salt from water crystals, so that melting the ice crystals will produce fresh water. The potential of freezing processes in treatment of mine water has been emphasized by many authors (Jusoh et al. 2009; Lewis et al. 2010; Adeniyi et al. 2012; Mtombeni et al. 2013). Williams et al. (2013) identified major advantages of using the freezing process as a very high separation factor, high energy efficiency due to low latent heat of fusion, generic applicability, no additives and the fact that core technology is readily available. Apart from these, there is the possibility of using ice to cool hot mines and the use of low-cost materials because the process is operated at low temperature.

One of the major barriers for commercialization of freezing processes is the control of the crystallization process for high ice yield and purity. Ulrich and Strege (2002) stated that if the crystallization process is not controlled, then nucleation starts stochastically leading to formation of products of various qualities. Niedermeier et al. (2011) also explained that heterogeneous ice nucleation is stochastic in contrast to homogeneous ice nucleation which is initiated by the presence of ice at a specific temperature. The presence of other ionic salts and impurities in the mine wastewaters makes the formation of ice to be described as heterogeneous nucleation. For ice formation in a complex salt solution, control of both the concentration of salts and supercooling of the solution may be necessary. This is because it is not possible to control a crystallizer by controlling temperature alone (Ulrich and Strege 2002).

✉ A. Adeniyi
adeniyia@tut.ac.za; amosadeniyi7@yahoo.com

[1] Department of Chemical, Metallurgical and Materials Engineering, Tshwane University of Technology, Private Bag X680, Pretoria 0001, South Africa

[2] ROC Water Technologies (Pty) Ltd, Pretoria, South Africa

The solubility characteristic of a solute in a particular solvent is the most important property for determining the best method for causing crystallization and the ease or difficulty in growing crystals (Seader and Henley 2006). Since most brine samples from mines are high in sodium chloride and sodium sulphate (Juby et al. 1996), a solution of sodium chloride and sodium sulphate was investigated in this work. Solubility of sodium sulphate varied widely with temperature, while that of sodium chloride is almost constant with temperature. At 0 °C, solubility of sodium chloride is 35/100 g water and that of sodium sulphate is 4.9/100 g water. We studied here freeze desalination in order to develop a new process diagram that will facilitate pure ice recovery and also salt recovery for potential economic reason.

Experimental

Five synthetic waters were used for the experiments: pure distilled water, 50 g/L NaCl solution, 33 g/L NaCl + 17 g/L Na_2SO_4 solution, 50 g/L Na_2SO_4 solution and 50 g/L NaCl + 50 g/L Na_2SO_4 solution. Equipment used for the experiment was the Tshwane University of Technology freeze desalination laboratory unit (Fig. 1). The unit consists of the following: ice slurry generator with a refrigeration capacity of 0.67 KW that is achieved by circulating the refrigerant (R404a) through a compressor, a heat exchanger and a condenser; a heat exchanger, where the process water contact the refrigerant indirectly; a fluidized bed reactor (FBR) where seeding and clarifying take place; and a filter where ice is separated from the process. Xplorer GLX was used for temperature monitoring on the laboratory unit. A Stratos Eco electrical conductivity meter was used for electrical conductivity measurement. Temperature profile for cooling each of the synthetic solution and effect of seeding on sodium sulphate solution was studied using a Vivo RT4 isotherm water bath with ethanol as the cooling solvent at a cooling rate of 0.1 °C/s. AIKARW 20 digital stirrer was used to stir the solution at 255 rpm. An ETI precision thermometer was used for temperature monitoring of the water bath. A stopwatch was used as a time monitor.

The batch process involved cooling of 400 mL of distilled water in the water bath. Temperature change was monitored with time. 16 °C was taken as the starting temperature. This procedure was repeated for each of the prepared synthetic solutions. For the seeded batch process, 400 mL of distilled water was cooled in the water bath. Ice crystallized at −4.5 °C and the crystals were filtered. 400 mL of 50 g/L Na_2SO_4 solution was cooled to −4.5 °C using the water bath. The solution was first seeded with 0.5 g of Na_2SO_4 salt. Na_2SO_4 crystallized out and was filtered. Electrical conductivity of the resulting solution was then taken, and the solution cooled again to −4.5 °C and seeded with 5 g of ice crystal. The ice formed was filtered and weighed. Electrical conductivity of the concentrated solution and the ice was taken after cooling to room temperature.

For the continuous process, 63.75 L of 50 g/L NaCl solution was processed on the freeze desalination laboratory unit at a flow rate of 12 L/min. Evaporating temperature of the refrigerant was set at −13 °C. Samples were taken from the feed tank and the fluidized bed reactor every hour. Ice formed was weighed, and samples were analysed for electrical conductivity. This procedure was repeated for the 50 g/L Na_2SO_4 solution and the 33 g/L NaCl + 17 g/L Na_2SO_4 solution.

Fig. 1 Tshwane University of Technology freeze desalination laboratory unit

Analysis

Heat of crystallization was obtained from the data by the use of Eq. 1.

$$H = mc\Delta T \quad (1)$$

where H is the heat of crystallization (J), m is the mass (g), c is the specific heat capacity (J/g °C), and ΔT is the change in temperature (°C). c For water is 4.179 J/g °C; c for NaCl is 0.853 J/g °C; c for Na_2SO_4 is 0.903 J/g °C. Crystallization is an exothermic process; the heat of crystallization was calculated from an increase in temperature as a result of crystal formation as observed from the temperature profile.

Results and discussion

Behaviour of ice formation in freezing pure distilled water

Water cooled rapidly from 16 °C to a temperature of about 0 °C when the cooling became slower. Water did not freeze at 0 °C because based on the thermodynamics of water, a significant energy barrier must be surmounted before there can be ice formation (Petzold and Aguilera 2009). This was the reason for the continual removal of heat until a temperature of about −5 °C was reached before ice formation began (supercooling). Water appears to be stable during this supercooling region, but the fact that ice formation can be induced by seeding with ice in the region indicated that the region can be considered as metastable. One of the water's unsolved puzzles is the question of what determines the lowest temperature to which it can be cooled before freezing to ice (Emily et al. 2011) because it is difficult to form ice from pure water as it contains no contaminants or particles around which the critical nucleus can form because of the unusual thermodynamics of water.

Effect of sodium chloride on ice formation

The profile for the cooling of 50 g/L NaCl solution was similar to that of pure water except that ice formation was at a lower temperature and also the solution stabilized at a temperature lower than 0 °C (precisely −2.8 °C). This was because of the freezing point depressant effect of NaCl on the freezing of water (Adeniyi et al. 2012). It is important to note that the similar behaviour of this solution with that of pure water was due to high solubility of NaCl in water and also because there was no significant variation of solubility of NaCl in water with temperature. Figure 2f shows that the presence of salts in the solution actually facilitated ice formation during cooling by reducing the heat of crystallization released during ice formation. The presence of sodium chloride in the solution caused a higher reduction in the heat of crystallization. This was the reason why it was easy to recover water from NaCl solution by cooling. NaCl would remain in solution even while ice was being formed.

Effect of sodium sulphate on ice formation

Cooling behaviour of 50 g/L Na_2SO_4 solution was similar to that of pure water and sodium chloride solution in terms of rapid temperature drop before 0 °C and a much slower temperature after 0 °C. However, crystallization of sodium sulphate occurred first at about −5.4 °C. This explained clearly why ice formed from sodium sulphate solution was loaded with sodium sulphate. The temperature profile of solutions of sodium chloride and sodium sulphate changed significantly when the concentration of sodium sulphate was changed to 50 g/L. This was due to the fact that sodium sulphate started to crystallize at a higher temperature because of the presence of sodium chloride salt (see the black arrow on Fig. 2c). The implication of this was that if sodium sulphate was removed from the process before the ice formation point was reached, purity of the ice formed from the process would improve significantly. Ice formed from a solution containing sodium chloride and sodium sulphate could be contaminated by sodium chloride as a solution and sodium sulphate as a precipitate. This is in agreement with Olsson (1999) who explained that the basic salt-forming ions are found in the liquid phase in dissolved ionic form and as precipitated solid salt hydrates in brine inclusions in the ice. However, this contamination can only be on the crystal surface and not within the crystal lattice because according to Lorain et al. (2000), few compounds can be incorporated directly into the ice crystals; hence, any impurity entrapment would be due to trapped solutions or trapped salt crystals and not by direct incorporation into the crystal lattice. Figure 2f shows that the presence of sodium chloride in the solution caused a higher reduction in the heat of crystallization than the presence of sodium sulphate and this explained why ice is easily formed in the sodium chloride solution than in the sodium sulphate solution.

Ice formation behaviour in continuous process and seeded batch process

Results from the laboratory freeze desalination units showed that behaviour of 50 g/L NaCl solution and 33 g/L NaCl/17 g/LNa_2SO_4 solution was similar just as indicated by the experiment ran on the water bath. The proportion of sodium sulphate in the solution was not significant enough to cause major changes in the behaviour of the solution

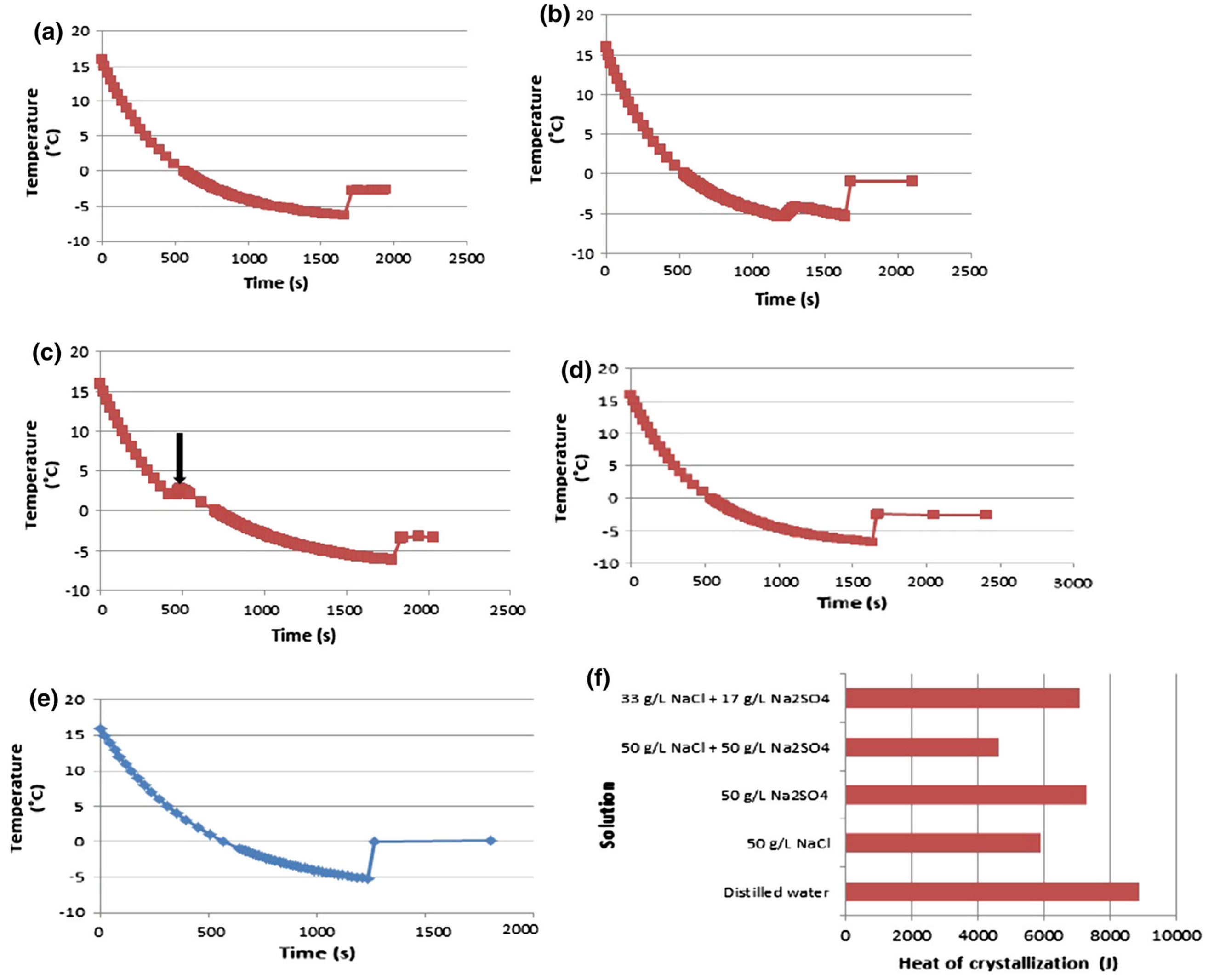

Fig. 2 **a** Temperature profiles of solution of 50 g/L NaCl. **b** Temperature profiles of solution of 50 g/L Na_2SO_4. **c** Temperature profiles of solution of 50 g/L NaCl + 50 g/L Na_2SO_4. **d** Temperature profiles of solution of 33 g/L NaCl + 17 g/L Na_2SO_4. **e** Temperature profiles of the distilled water. **f** Heat of crystallization of ice calculated for different solutions. The profiles are similar except that crystallization of Na_2SO_4 occurs at about −5.4 °C in a pure sodium sulphate solution, while it occurs at 2.7 °C in a solution containing sodium chloride and sodium sulphate at high concentrations. Heat of crystallization is highest with distilled water and lowest with the solution of higher concentration of sodium chloride and sodium sulphate. Temperature increase always occurs when crystallization has taken place due to the release of heat of crystallization

during cooling. The concentration of the concentrated solution and the fluidized bed reactor (FBR) solution was almost the same. A significant amount of Na_2SO_4 was harvested from the fluidized bed reactor which justified the inclusion of the fluidized bed reactor in the process. Salts which crystallize before ice could be easily harvested from the process leading to a reduction in the concentration in the process water and consequently elimination of their intervention in the formation of ice in the process. The result of the treatment of 50 g/L sodium sulphate solution in a seeded batch process using the water bath showed that 45 % of Na_2SO_4 was recovered when the solution was seeded with Na_2SO_4, while 42 % water was recovered as ice after seeding with ice (Table 1). Results showed that when sodium sulphate crystals have been removed from the solution, then ice could easily be formed. Although Lewis et al. (2010) stated that Na_2SO_4 crystallizes out

Table 1 Values of different parameters after seeding 50 g/L Na_2SO_4 solution

Initial electrical conductivity of solution	48.6 mS/cm
Seeding temperature	−4.5 °C
Mass of salts after filtration	9.1 g
Electrical conductivity of solution after filtration	38.7 mS/cm
Mass of ice	166.5 g
Electrical conductivity of ice	32.8 mS/cm
Electrical conductivity of concentrate	44.1 mS/cm

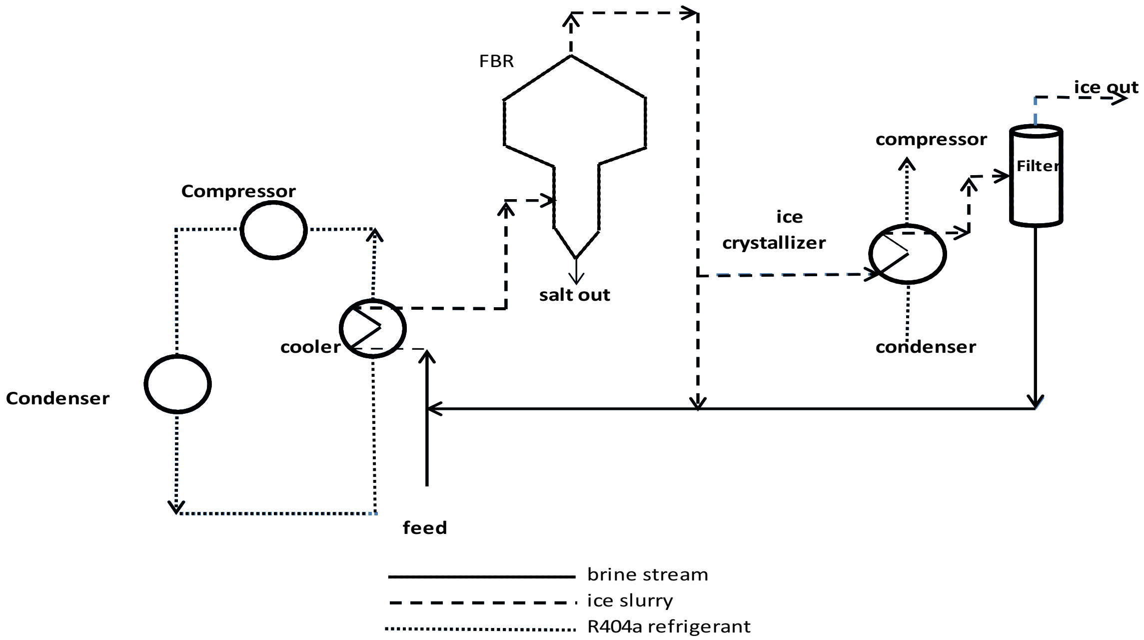

Fig. 3 New process flow diagram

between 3.5 and −23.25 °C while ice crystallizes out at −5.25 °C, both salt and ice were successfully crystallized out at about −4.5 °C by seeding. The result also indicated the necessity of separating the cooling heat exchange from the ice crystallizer. It was noted that nucleation and consequently ice formation took place immediately when the seed was added. Figure 3 shows the newly developed process flow diagram.

Conclusion

In conclusion, ice formation is favoured by more soluble salts than less soluble salts because the presence of more soluble salts reduces the heat of crystallization of ice significantly, and a new flow diagram for freeze desalination process is developed with a fluidized bed reactor and a separate heat exchanger for ice crystallization. Both findings would be necessary for the design of the new pilot plant for freeze desalination of mine wastewater. The proposed process (Fig. 3) in contrast to the existing one (Adeniyi et al. 2014) involves the removal of less soluble salts in the fluidized bed reactor based on solubility change with temperature and by introducing salt seeds. The process water will be recycled until the temperature of 0 °C is achieved before feeding it into the ice crystallizer. Crystals of salts will be removed in the fluidized bed reactor before the process water is fed into the ice crystallizer where it is seeded with ice to facilitate ice formation. Pure water is finally removed as ice through the filter. The new process enhances the recovery of salts and ice both by seeding and by temperature control.

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