Resin Freeze Desalination Process for Acid Recovery

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Abstract Acid streams rich in sulphate and metals such as acid mine drainage are normally neutralized with limestone or lime to produce gypsum and metal hydroxides or oxides as waste products. An innovative resin freeze desalination (RFD) process is described where metals are first removed with a cat ion exchange resin (Lewatit MonoPlus S108), followed by up-concentration of the acid using freeze desalination. It was found that complete iron removal was obtained with water containing (i) 0.7 g/L H_2SO_4 and 390 mg/L Fe^{2+} and (ii) 1.4 g/L H_2SO_4 and 1 056 mg/L Fe^{3+}. Both iron species were eluted from the resin using 3 % H_2SO_4. The iron-free, resin treated water was concentrated up from 30 to 42 g/L H_2SO_4 using freeze desalination.

Keywords AMD, cat ion-exchange, freeze desalination, HybridICE, Lewatit monoPlus S108.

Introduction

Effluents from the chemical and mining industries require treatment to reclaim the water for reuse or for discharge into the environment (Adler and Rasher 2007). A general treatment method is to use limestone or lime for neutralization to produce neutral water and, if the water contains sulphate, gypsum sludge which is normally stockpiled (Maree & Van Tonder 2000). Neutralized water can be further treated through desalination using reverse osmosis (RO), electro-dialysis (ED; Amjad 1993; Schoeman and Steyn 2002) or ion-exchange. The brine or regenerant streams produced in these processes requires further treatment before discharge into the environment to meet environmental regulations. The following methods are currently used for brine disposal or treatment: Evaporation ponds, Distillation, Direct contact membrane distillation, Vacuum membrane distillation and Membrane distillation (Younos 2005; Lawson and Lloyd 1997). As these methods are either environmentally unacceptable or costly, the HybridICE technology was developed (Mtombeni *et al.* 2011).

The main objective of this study was the testing of the novel resin freeze desalination (RFD) process to recover sulphuric acid from acidic and metal rich streams. The RFD process is a combination of, freeze desalination with ion-exchange. It consists of the following steps: (i) Metal removal with an ion-exchange resin, (ii) Concentration of the dilute acid stream after the ion-exchange resin stage through freeze desalination, (iii) regeneration of the resin with the concentrated acid recovered through freeze desalination and, (iv) the remaining acid, which is concentrated further, being recycled to be used elsewhere without neutralization. The benefits of this approach are: (i) Resins are used for the selective removal of metals, (ii) acid is not destroyed through neutralization, but recovered (iii) low energy cost as the energy required to freeze water is seven times less than to evaporate the same volume of water (2500 kJ/kg for evaporation versus 333 kJ/kg for freezing (Shone 1987), (iv) no pre-treatment is required, and (v) reduced brine volume for disposal.

Methods

Synthetic acid mine drainage water was prepared, similar to a typical mine water. Water A contained 0.7 g/L H_2SO_4 and 400 mg/L of Fe (II) and Water B, 1.4 g/L H_2SO_4 and 1085mg/L of Fe (III). Lewatit MonoPlus S108 cat ion resin was used for iron removal from acid solutions. A laboratory scale, HybridICE™ freeze desalination unit was used for freeze desalination.

The following procedures were followed:

- The resin bed of Lewatit MonoPlus S108, in a glass column (15mm diameter) was prepared in such a way that all air bubbles were eliminated.
- The resin bed was activated by passing three bed-volumes (BV) of 3 % sulphuric acid followed by three BVs of deionised water
- The acid water was fed into the cat ion-exchange column at a flow-rate of 5 mL/min.
- As the acid water passed through the column the metal ions were adsorbed onto the resin (H-R + MSO_4 → M-R + H_2SO_4; M = Fe^{+2}, Fe^{+3})
- The adsorption capacity of the resin was calculated.
- Upon saturation, the resin was regenerated by elution using 3 % H_2SO_4.
- Dilute H_2SO_4 was concentrated through freeze desalination using the HybridICE plant.
- The resin was regenerated with 3 % H_2SO_4.

Samples of eluate were collected regularly and filtered (Whatman No 1 glass fibre filter).

Acidity and pH determinations were carried out according to described procedures (APHA et al. 1985) and Fe (II) as described in Vogel (Vogel 1989). Total iron was assayed using atomic absorption spectrophotometry.

Metal removal

Table 1 and Figs. 1 and 2 show the results when Fe^{2+} and Fe^{3+} rich waters were passed through a resin column filled with 50mL of Lewatit MonoPlus S108 resin. Both Fe^{2+} and Fe^{3+} were removed down to less than 10 mg/L until break-through occurred. The saturation index was calculated to be 3.52 equivalents Fe/L resin for Fe^{2+} (Fig. 1) and 3.21 equivalents Fe/L resin for Fe^{3+} (Fig. 2). This corresponded with the product sheet which claimed > 2 equivalents Fe/L resin (LanXESS 2011). Figs. 3 and 4 show that the saturated resins were completely regenerated with 3 % H_2SO_4,

Table 2 and Fig. 5 show the relationship between amount of resin and iron removal for different contact times as determined during batch studies. In the case of a low resin content of 2.38 mL resin/L water, the iron Fe^{2+}-absorption amounted to 2.52 equiv Fe/L resin at a contact time of 10 min, compared to 4.20 eq Fe/L resin at a contact time of 120 min. In a packed bed system during full-scale applications, 10 min contact time can be considered a realistic value. The design can be based on an adsorption capacity of 2.0 eq Fe/L resin, as recommended by the supplier. For counter current systems, where (i) the high metal concentration first encounters with the already loaded resin (to allow maximum utilization of

| Parameter	Figure			
	Loading		Regeneration	
	1	2	3	4
Iron species	Fe^{2+}	Fe^{3+}	Fe^{2+}	Fe^{3+}
Concentration (mg/L)	390	1056		
Feed rate (mL/min)	13.3	5		
Resin bed volume (mL)	50	50	50	50
H_2SO_4 (%)			3	3
Iron adsorbed (g)	4.92	2.71		
Iron desorbed (g)			2.99	1.54
Absorption capacity (equivalents Fe/mL resin)	3.52	3.21	1.94	1.65

Table 1. Experimental conditions and results of resin loading and regeneration results reported in Figs. 1 – 4.
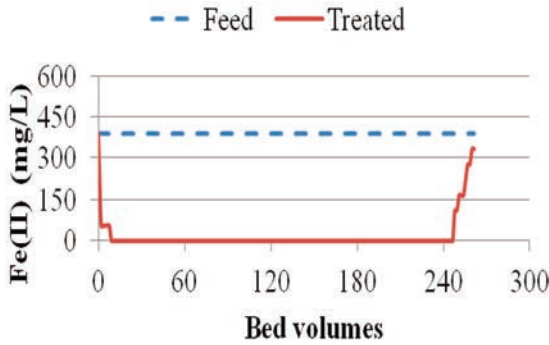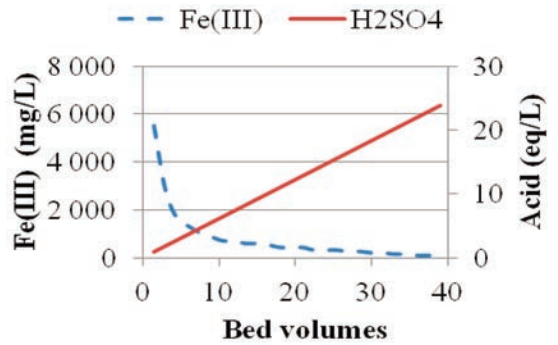
Fig. 1 *Iron (II) removal with resin (Bed volume = 50 mL; Fe(II)*$_{Feed}$ = *390 mg/L; Feed rate = 13.3 mL/min).*
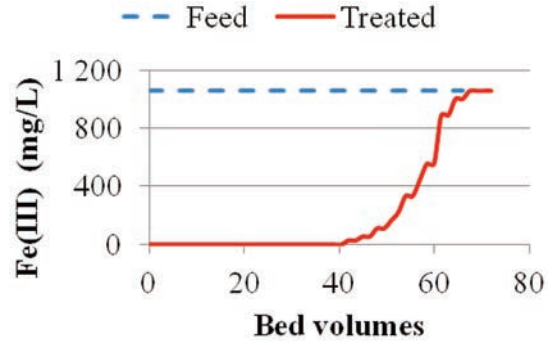
Fig. 2 *Iron (III) removal with resin (Bed volume = 50 mL; Fe(III)*$_{Feed}$ = *1 056 mg/L; Feed rate = 5.0 mL/min).*
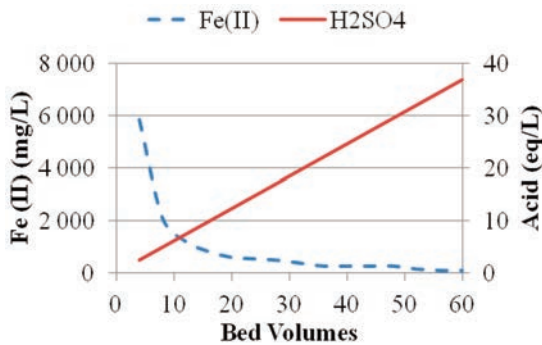
Fig. 3 *Regeneration of iron (II) loaded resin with H$_2$SO$_4$ (3 %).*

Fig. 4 *Regeneration of iron (1II) loaded resin with H$_2$SO$_4$ (3 %).*

	Resin content (mL/L)				
	2.38	7.14	11.90	59.52	238.10
Time (min)	Iron(II) in solution (mg/l)				
0	390	390	390	390	390
10	222	111	223	56	56
30	167	56	56	28	28
120	111	28	56	28	28
Time (min)	Fe adsorbed (eq/L resin)				
10	2.52	1.40	0.50	0.20	0.05
30	3.35	1.68	1.00	0.22	0.05
120	4.20	1.81	1.00	0.22	0.05

Table 2 *Effect of resin concentration and contact time on metal removal.*

the resin absorption capacity), and (ii) where the final water is contacted at the end of the contact period with the fresh resin, the design can be based on higher values such as the 4.0 eq Fe/L resin as determined for the longer contact period. In cases where excess amounts of resin were contacted with the 400 mg/L Fe^{2+}

water, complete removal was achieved within 10 minutes.

Freeze crystallization
Figs. 6 and 7 show the acid concentrations in the brine and acid when cat ion-exchange resin treated water, containing 30 g/L H$_2$SO$_4$,
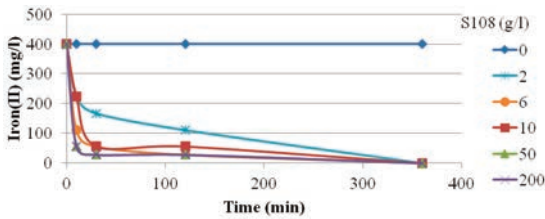
Fig. 5 *Effect of resin concentration on Fe²⁺ removal during batch reactions.*

was concentrated through removal of water via ice crystallization. Fig. 6 shows the behaviour of acidity versus time and CF_{Flow} (Concentration Factor$_{Flow}$). The term Concentration Factor$_{Flow}$ is defined as Concentration Factor$_{Flow}$ = Volume Fed/Volume of reactor. It was noted that as CF_{Flow} increased from 1 to 1.9 (corresponding with Time from 0 to 18 h), the Acidity of the brine increased from 30 to 42 g/L (as $CaCO_3$), while the Acidity in the Ice increased from 0 to 5.5 g/L. When spots of "dry" ice were harvested the Acidity was found to be < 0.5 g/L (as $CaCO_3$). When selected ice samples were analysed they were found to contain <0.5 g/L acid. By further improvement to the ice separation system, full acid recovery from the brine stream is expected to be achieved.

Fig. 7 shows $CF_{Acidity}$ and CF_{Flow} *versus* CF_{Flow}. $CF_{Acidity}$ was defined as Acidity of brine with change in or CF_{Flow} (or Time). It was noted that $CF_{Acidity}$ was below CF_{Flow}. This was due to a fraction of the acid remaining in the Ice. Further improvements in ice/brine separa-

ration efficiency will result in the values of $CF_{Acidity}$ becoming much closer to CF_{Flow} values.

Conclusions

1. Complete iron removal was obtained with waters containing (i) 0.7 g/L H_2SO_4 and 390 mg/L Fe^{2+} and (ii) 1.4 g/L H_2SO_4 and 1 056 mg/L Fe^{3+}.
2. Both iron species were eluted from the resin using 3 % H_2SO_4.
3. The iron-free, resin treated water was concentrated from 30 to 42 g/L H_2SO_4 using freeze desalination.

Acknowledgements

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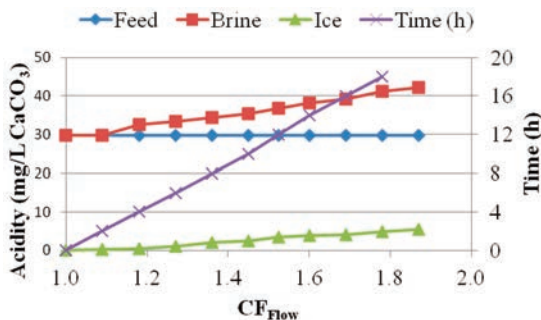
Amjad Z (1993) Reverse osmosis membrane technol-

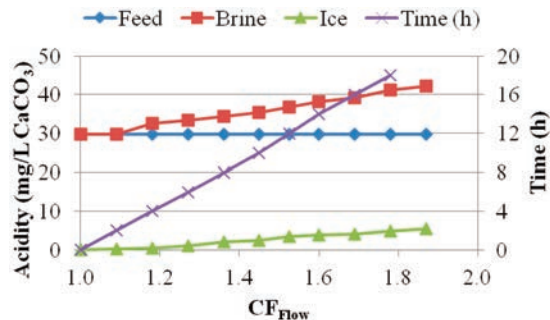**Fig. 6** *Behaviour of acidity of brine and ice during freeze desalination.*

Fig. 7 *Behaviour of up- concentration of acid during freeze desalination.*

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