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Reverse Osmosis Separation of Thiosalts from Mining Effluents

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Abstract

Cellulose acetate membranes were characterized in terms of pure water permeability constant, solute transport parameter, and mass transfer coefficient with a reference system of aqueous sodium chloride solution. Reverse osmosis separation behavior of sulfate, thiosulfate, dithionate, trithionate, and tetrathionate was studied. Plant effluents containing various thiosalts and metal ions were subjected to reverse osmosis at 300 psig, and product water of suitable quality for use in recycle operations was obtained.

INTRODUCTION

Tailings pond solutions containing thiosalts generate acid in the effluent receiving streams. The thiosalts, consisting of polythionates, $S_nO_6^{2-}$, $n = 3$ to 6, and thiosulfate, $S_2O_3^{2-}$, undergo eventual oxidation to sulfuric acid. (This degradation is sufficiently slow and incomplete in the tailings pond during the retention period that the total potential sulfuric acid cannot be neutralized before discharging the effluents into the nearby streams.) Subsequent oxidation of the residual thiosalts occurs in the streams and a significant amount of acid is thereby produced. This poses an environmental pollution problem.

This problem could be resolved by introducing possible modifications to the metallurgical process or by using a suitable method of treatment to reduce the amounts of thiosalts in the effluents to environmentally acceptable levels. Studies (*1*) on the generation of thiosalts showed that their formation increased with residence time, pH, and temperature, and that the generation of thiosalts could not be prevented using existing flotation technology. However, the rate of formation of thiosalts was found to be strongly dependent on the agitation rate. Thus there is the possibility of reducing thiosalt formation by reducing the agitation rate, but this is contingent upon maintaining satisfactory metallurgy. The following methods for the removal of thiosalts from mining effluents have been evaluated on a bench-scale: acid decomposition, ultraviolet decomposition, alkaline reduction, sulfide reduction, sulfite reduction, air oxidation, transition metal ion catalyzed oxidation, electrolytic oxidation, and adsorption. None of the above methods appeared wholly satisfactory for the removal of thiosalts from the effluents (*1*) at a low cost.

Reverse osmosis is a possible method for the removal of dissolved species from aqueous solutions that is characterized by a low expenditure of energy and simplicity of processing technology. Since high-pressure reverse osmosis requires higher capital investment and leads to membrane compaction problems, low-pressure reverse osmosis has been the subject of a number of studies (*2–8*) on the treatment of metal-bearing waste effluents in our laboratories. These show promise in the sense that both valuable metal ions and product water of reasonable quality could be recovered at the same time. Hence a detailed study was undertaken to determine the reverse osmosis separation characteristics of both individual thiosalt species present in the tailings pond solutions and composite solutions containing the various thiosalts in different concentrations. The results obtained from such studies are reported in this paper.

EXPERIMENTAL

The nonflow type experimental arrangement is the same as reported earlier (*5*). The static cell used has been described before (*6*). Cellulose acetate membranes obtained from Osmonics Inc. were used in the present studies.

All the reverse osmosis experiments were conducted at 23 to 25°C. The membranes were pressurized with pure water at 400 psig for about 2 hr before subsequent use in the experiments at operating pressures of

100 to 300 psig. The pure water permeability constant (PWP), the membrane permeated product rate (PR) for a given area of the membrane, and the solute separation (*f*) were determined at preset operating conditions. Solutions containing 1360 mg/L of sodium chloride were used to obtain membrane specification data and to specify the mass transfer coefficient (*k*) on the high pressure side of the membrane. The analysis of the feed and product solutions containing sodium chloride was carried out by conductance measurements. The feed and the membrane permeated product solutions containing the thiosalts were analyzed using the method developed by Rolia (*9*). Sulfate was determined gravimetrically as $BaSO_4$. The difference in sulfate obtained after oxidation of the solution with hydrogen peroxide and with potassium chlorate–nitric acid was used as an estimate of the amount of dithionate. Thiosulfate, trithionate, and tetrathionate were determined photometrically. The sulfite content of the solutions was determined iodometrically. Solutions containing metal ions Fe, Cu, Zn, Ca, Mg, Mn, and Pb were analyzed by atomic absorption spectrophotometry at wavelengths of 2483, 3248, 2139, 4227, 2852, 2795, and 2170 Å, respectively. Product rates were corrected with respect to viscosity and temperature (25°C). Because low concentrations were used in the reverse osmosis experiments, solute separation (*f*) was calculated using the relationship

$$f = \frac{\text{solute concentration in feed} - \text{solute concentration in product}}{\text{solute concentration in feed}}$$

RESULTS AND DISCUSSION

Membrane Specifications

Reverse osmosis membranes can be specified in terms of parameters such as the pure water permeability constant, A, and the solute transport parameter, D_{AM}/K_δ, at a particular value of operating pressure. These parameters were calculated by a computer program (*10*) using the experimental data on pure water permeation rate, solute separation, and product rate (flux) for the reference system of aqueous sodium chloride solution. The values of A and D_{AM}/K_δ for sodium chloride at 300 psig, presented in Table 1, specify the membranes used and also reflect the high productivity of the membranes.

Separation of Thiosalts

The reverse osmosis separation of individual salts such as sodium sulfate,

TABLE 1

Membrane Specification Data[a]

Film no.	$A \times 10^6$ (g mole H_2O cm^{-2} sec^{-1} atm^{-1})	D_{AM}/K_δ for NaCl (10^5 cm sec^{-1})	Feed concentration, 1360 mg/L NaCl, $k = 8.85 \times 10^{-4}$ cm sec^{-1}	
			Solute separation (%)	Productivity rate (g/hr)
1	2.62	11.8	73.6	29.9
1	2.67	11.6	73.6	30.5

[a] Membranes area 13.4 cm^2; pressure 300 psig.

TABLE 2

Separation of Thiosalts

Salt	Concentration (ppm)	Pressure (psig)	PWP (g/hr)	Productivity rate (g/hr)	Percent separation
Na_2SO_4	979	300	34.0	30.5	90.2
	979	200	22.3	20.0	89.2
	979	100	10.4	9.1	85.3
$Na_2S_2O_3$	990	300	34.3	30.9	90.6
	990	200	22.3	20.0	90.0
	990	100	11.1	9.4	87.8
$Na_2S_2O_6$	864	300	35.3	32.1	86.8
	864	200	22.7	19.6	85.5
	864	100	10.9	9.9	82.2
$K_2S_3O_6$	530	300	29.4	25.0	87.7
	530	200	19.0	15.9	87.7
	530	100	9.1	7.3	87.7
$K_2S_4O_6$	1532	300	27.9	20.4	92.2
	1532	200	18.4	12.9	92.9
	1532	100	8.4	6.5	91.6

thiosulfate, and dithionate as well as potassium trithionate and tetrathionate was studied as a function of pressure in the range of 100 to 300 psig. For every salt studied the percent separation reaches a maximum at nearly 300 psig (Table 2) and all further experiments were carried out at a pressure of 300 psig. From the data given in Table 2 it is clear that solute separation increases slightly in going from dithionate through trithionate, sulfate, thiosulfate, to tetrathionate. The product rates were found to increase in a linear fashion in going from a pressure of 100 to 300 psig (Table 2) for all the solutes.

In Tables 3 and 4 the data on the separation of various thiosalt species encountered in 12 different plant solutions are presented. The solutions

TABLE 3

Data on the Separation of Thiosalts[a]

	Effluent 1		Effluent 2		Effluent 3		Effluent 4		Effluent 5		Effluent 6	
Species	Feed	Product	Feed	Product	Feed	Product	Feed	Product	Feed	Product	Feed	Product
Free SO_4^{2-}	1085	124	1344	98.9	374	33	1450	99	317	16	653	54
Total thiosalts (as SO_4)	3379	144	3523	144	931	78	2592	103	854	45	2362	54
$S_2O_3^{2-}$	985	11	896	<1	202	<1	482	<1	39	<1	426	<1
$S_4O_6^{2-}$	233	25	179	13.4	112	7	67	5	123	9	314	9
$S_3O_6^{2-}$	403	<1	211	3.8	—	—	115	<1	—	—	192	<1
$S_2O_6^{2-}$	128	18	160	27.2	—	—	80	<1	—	—	160	<1
SO_3	32	<1	—	—	8	<1	—	—	—	—	88	<1

[a] All concentrations are in ppm; pressure 300 psig.

TABLE 4

Data on the Separation of Thiosalts[a]

	Effluent 7		Effluent 8		Effluent 9		Effluent 10		Effluent 11		Effluent 12	
Species	Feed	Product	Feed	Product	Feed	Product	Feed	Product	Feed	Product	Feed	Product
Free SO_4^{2-}	1478	120	854	58	1344	44	1642	79	1325	81	1632	51
Total thiosalts (as SO_4)	3715	204	3005	132	4176	155	4378	135	3610	156	2918	161
$S_2O_3^{2-}$	616	26	750	12	336	9.6	750	18	750	27	370	3.8
$S_4O_6^{2-}$	1107	43	1344	35	2137	27	1250	16	1004	8.6	1001	10
$S_3O_6^{2-}$	902	9.6	499	1	1190	9.6	1056	5.8	749	5.8	461	3.8

[a] All concentrations are in ppm; pressure 300 psig.

were kept frozen before use. The feed and the product solutions were analyzed at the same time and thus any decomposition was the same in both samples. Reference to data in Table 3 shows that the concentration of thiosalt species which represents potential acid is reduced to less than 50 ppm for all six effuents. A similar reduction in the concentration of thiosalt species was also achieved by reverse osmosis treatment of the second set of plant solutions (Table 4). The product water obtained by the reverse osmosis treatment may be suitable for recycling to the plant with a minimum of disruption of the current circuit.

The product water obtained from the reverse osmosis treatment of the plant effluents was analyzed for metal ions such as copper, iron, zinc, manganese, lead, magnesium, calcium, and sodium. The data on the metal ion concentrations in the product water obtained from reverse osmosis treatment are given in Tables 5 and 6. The data presented in these tables show that the metal ion concentrations in the product water are quite low

TABLE 5

Metal Ion Concentrations in Effluents after Reverse Osmosis Treatment[a]

Metal	Effluent 1	Effluent 2	Effluent 3	Effluent 4	Effluent 5	Effluent 6
Cu	0.1	0.09	<0.02	0.04	<0.02	<0.02
Fe	0.6	0.6	0.02	<0.02	0.02	4.0
Zn	0.09	0.07	0.01	0.02	<0.01	1.0
Mn	0.02	0.03	<0.02	<0.02	<0.02	0.10
Pb	<0.2	<0.2	<0.2	<0.2	<0.20	<0.2
Mg	0.02	0.2	0.05	0.05	0.04	0.2
Na	32	37	13.0	77.0	11.0	8.0
Ca	2.0	1.0	0.6	1.0	0.6	2.0

[a] All concentrations are in ppm.

TABLE 6

Metal Ion Concentrations in Effluents after Reverse Osmosis Treatment[a]

Metal	Effluent 7	Effluent 8	Effluent 9	Effluent 10	Effluent 11	Effluent 12
Zn	<0.03	0.03	0.03	<0.03	0.03	0.80
Pb	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20
Fe	<0.10	0.5	0.30	<0.10	<0.10	0.40
Mn	<0.02	0.10	0.05	<0.02	<0.02	0.07
Mg	<0.10	0.20	0.20	0.10	<0.10	0.70
Cu	0.02	0.01	0.01	0.02	0.04	0.01
Ca	7.0	4.0	2.0	8.0	3.0	2.0

[a] All concentrations are in ppm.

and that the quality of the water is acceptable either for recycling within the plant or for discharge into nearby streams.

It can be concluded from these studies that the reverse osmosis treatment of the thiosalt and metal ion-bearing solutions is successful in the sense that product water of suitable quality can be obtained either for discharge into nearby streams or for reuse in the plant operations.

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