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RECOVERY OF MANGANESE FROM MIXED METAL SOLUTIONS BY SOLVENT EXTRACTION WITH ORGANOPHOSPHORUS ACID EXTRACTANTS

The di(2-ethylhexyl) phosphoric acid (D2EHPA) and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272 by Cytec, USA) were used to extract manganese from sulfuric acid solutions containing Co, Mg, Ca and Na. Cyanex 272 was found to be slightly more selective for manganese than D2EHPA. Furthermore, it was found that a temperature increase has a negative effect on the Mn selectivity.

2-этилгексиловая ортофосфорная кислота (D2EHPA) и 2,4,4-триметилпентановая ортофосфорная кислота (Cyanex 272, компания «Cytec», США) использовались для извлечения марганца из растворов серной кислоты, содержащих Co, Mg, Ca и Na. Было выяснено, что Cyanex 272 обладает чуть большей способностью к выделению марганца, чем D2EHPA. Кроме того, было обнаружено, что увеличение температуры приводит к ухудшению селективности марганца.

Background.

The usage of manganese worldwide is increasing. Usually it is produced from Mn rich ores. The purpose of this investigation was to elucidate the possibilities to recover Mn from hydrometallurgical solutions containing low concentrations of Mn. The extractant for the experimental study was chosen among commercially easily available reagents. Two alternative organophosphorus acids were considered, namely the di (2-ethylhexyl) phosphoric acid (D2EHPA) and bis(2,4,4-trimethylpentyl) phosphinic acid which is the active compound in Cyanex 272.

The extraction isotherms reported in the REFERENCES have often been determined separately for different metals. In the current work the experiments have been carried out in multimetal mixtures in systems simulating real applications. On the other hand, it is known from the REFERENCES that the temperature can have a significant effect on the selectivity with organophosphorus acid type extractants. For example, the Co/Ni selectivity of D2EHPA increases with temperature which has been associated to the change from octahedral to tetrahedral cobalt complex [1]. Preston [2] and Cheng [3] has previously reported the effect of temperature on the selectivity with these extractants but not for this metal combination.

Experimental. Synthetic sulphuric acid solutions were prepared. Two multimetal solutions were made at different concentration levels; “Low” containing 0,58 g/L Mn, 0,25 g/L Mg, 0,26 g/L Ca and 0,22 Na (at pH = 2,8 and I = 0,1 M) and “High” containing 5,3 g/L Mn, 2,2 g/L Mg, 0,26 g/L Ca and 2,2 g/L Na (at pH 2,2 and I = 0,8 M). The bimetal solutions were made; one containing 3,7 g/L Mn and 0,58 g/L Co (at pH 4,0 and I = 0,3 M) and 5 3 g/L Mn and 5,6 g/L Co (at pH 4,1 and I = 0,8 M).

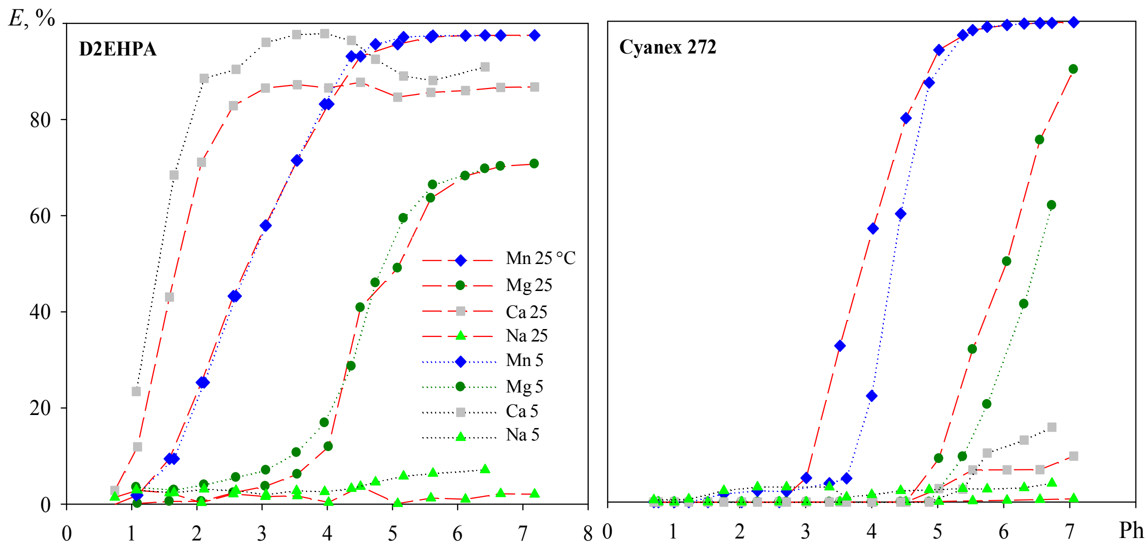
The extraction of manganese was studied by varying pH and temperature. The role of scrubbing of the loaded organic phase was also studied with the goal to produce pure manganese sulphate. The extraction, scrubbing and stripping were carried out in a stirred 1-littre glass reactor. Solution pH was adjusted with NH_3-gas. The analysis (from aqueous and organic phase) was done with ICP-OES so that the organic phase samples were first stripped with sulphuric acid which was then analyzed. The pH-extraction isotherms were determined simultaneously for each metal at 5 and 25 °C with the volume phase ratio (A/O) of 1,5 : 1. The isotherms with D2EHPA were also measured at 50 °C. Pure $MnSO_4$ solutions were made at the temperature of 25 °C by scrubbing with pure $MnSO_4$ solution (10 g/L) using the phase ratio of 1 : 3. The stripping of the organic phase was done with either 200 g/L H_2SO_4 or with a H_2SO_4 solution at pH of 2,7 using the phase ratio of 1 : 1.

Prior to extraction experiments the as-received reagents were first washed with sulphuric acid and then with deionized water. The total capacities of 25 vol- % D2EHPA and 25 vol- % Cyanex 272 were determined for the H-form extractants by titrating with 0,1 M NaOH. The capacities were 0,88 and 0,75 mol/g, respectively. A commercial aliphatic solvent was used as diluent.

Results. Both extractants are suitable for manganese separation. The extraction isotherms are shown in figure. The role of the extractant and conditions for manganese selectivity can be compared based on the pH_{50} values in Table.

pH_{50} values for the studied metals. The values are for I = 0,8 M (0,1 M in brackets if measured)

Metal	D2EHPA			Cyanex 272	
	5 °C	25 °C	50 °C	5 °C	25 °C
Mn	2,81 (–)	2,78 (2,31)	2,24 (2,18)	4,32	3,83
Co	1,85 (–)	4,52 (4,16)	4,24 (3,47)	n,d	n,d
Mg	4,87 (–)	5,00 (2,80)	4,39 (2,92)	6,12	5,94
Ca	1,29 (–)	1,71 (1,49)	1,67 (1,56)	>7	>7



Extraction isotherms for Mn, Mg, Ca and Na at 5 and 25 °C (I = 0,8 M)

The pH-extraction isotherms show that the separation of manganese is more effective from the more concentrated solutions than from the dilute ones. The selectivity for manganese against the other metals decreased with increasing temperature. The optimal pH to extract manganese and to scrub the impurity metals from the loaded organic reagent was between 2,7 and 3,0, when the extraction of Mn was 65 %. The solution produced by this method was nearly pure $MnSO_4$. Practically no Mg or Na and only small amounts of Ca were found (detection limit 1 ppm) in the solution after the extraction with D2EHPA. Cyanex 272 was an even slightly better reagent, because Ca was not extracted at pH < 5 and the final $MnSO_4$ solution had thus higher purity than obtained with D2EHPA.

REFERENCES

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