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Use of mixed-metals isotherm and log–log McCabe Thiele's diagram in solvent extraction—A case study

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Abstract

Nickel and cobalt are invariably associated with other transition element impurities like copper, zinc, iron, etc. It is essential to remove these impurities in order to attain the high standards of purity required for specific applications. Solvent extraction is a well-tested route for this purpose. The present paper describes the application of two novel concepts, viz. mixed-metals isotherm and log–log McCabe Thiele's (MT) diagram in solvent extraction. Mixed-metals isotherms can be applied to a system in which two metal ions compete for a single extractant. If these two metal ions are required to be extracted as a group, mixed-metals isotherms can precisely predict their behavior. Log–log MT diagrams are useful in determining the requirement of the number of stages in counter current extraction, especially when the feed and raffinate concentrations differ by several orders of magnitude. The two concepts have been successfully applied to develop a process for the separation of high purity cobalt and nickel from ocean nodules leach liquor.

Keywords: Mixed-metals isotherm; Log–log McCabe Thiele's diagram; Ocean nodules; Copper; Zinc; Cobalt; Nickel; DEHPA; PC-88A; Solvent extraction

1. Introduction

Ocean nodules contain a large number of metals like nickel, cobalt, manganese, copper, zinc, iron, etc. Vast resources of these nodules are found at the ocean bed. In countries like India, where the land resources of some metals like cobalt and nickel are scarce, ocean nodules are expected to become an important source of these metals. The leaching of ocean nodules was effected through the reductive ammonia leaching route in which metals like nickel, cobalt, copper and zinc were solubilised as their amine complexes leaving iron and manganese in the residue (Jana et al., 1999). Major portion of copper was recovered by solvent extraction using LIX 84. The raffinate solution was then subjected to sulphide precipitation and the bulk sulphide precipitate on sulphuric acid leaching generated the leach liquor. This solution contained nickel and cobalt along with impurities such as copper, zinc, iron, manganese and aluminum. The removal of these impurities is essential prior to the separation of cobalt and nickel. The efficient removal of these impurities can be effected only by solvent extraction, since selective precipitation does not yield high purity products, without considerable losses.

A number of methods involving different types of extractants have been developed and applied for the recovery of base metals (Chapman, 1987; Cote, 2000; Murthy et al., 1986; Nicol et al., 1987). In spite of this,

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Table 1
Effect of equilibrium pH and A/O on the distribution ratios and separation factor

Eq. pH	A/O	D(Cu+Zn)	D(Co+Ni)	$\beta = D$ (Cu+Zn)/ D (Co+Ni)	Co % extracted	Ni % extracted	Cu conc. in the raff. (g/l)
3.0	1:1	4.412	0.074	59.89	13.1	6.19	0.483
	2:1	4.936	0.067	73.30	6.55	2.91	0.735
	3:1	4.639	0.053	88.13	3.69	1.51	1.000
	4:1	4.581	0.042	108.2	2.29	0.91	1.170
	6:1	5.106	0.032	157.1	1.19	0.47	1.345
	8:1	5.237	0.023	230.1	0.65	0.25	1.500
	10:1	6.003	0.020	301.6	0.48	0.17	1.558
3.5	1:1	14.82	0.163	91.02	23.9	13.0	0.160
	2:1	13.33	0.131	100.2	11.9	5.60	0.340
	3:1	12.41	0.080	154.4	6.60	2.20	0.500
	4:1	10.50	0.058	181.7	3.80	1.20	0.710
	6:1	7.640	0.032	237.3	1.60	0.40	1.120
	8:1	7.240	0.021	352.1	0.90	0.20	1.340
	10:1	7.180	0.012	622.7	0.40	0.10	1.470
4.0	1:1	22.64	0.620	36.74	42.4	37.8	0.109
	2:1	22.13	0.348	63.49	21.0	14.2	0.219
	3:1	22.02	0.268	82.31	15.5	7.45	0.323
	4:1	20.71	0.205	101.2	10.0	4.34	0.430
	6:1	18.00	0.112	160.9	4.50	1.56	0.671
	8:1	14.33	0.074	193.3	2.60	0.75	0.950
	10:1	12.58	0.056	224.4	1.70	0.45	1.170

the development of a solvent extraction process for a particular feed solution requires extensive study of the various parameters. The route chosen is greatly influenced by the type, concentration of the associated ions and the specifications of the final product required. In the present process, the prime objective was to recover nickel and cobalt. For this purpose, the removal of copper and zinc was attempted in a single SX circuit. Hence, a novel approach of generating mixed-metals isotherms for (Cu+Zn) and (Ni+Co) systems was employed. This data provided more realistic estimates than that obtained from the study of individual isotherms. Another objective of the process was to obtain a high degree of purity and recovery for cobalt and nickel. This required minimum losses (<0.001 μg/ml) in the various streams. The requirement of the number of stages to achieve this criterion could not be deduced from the conventional MT diagrams. Hence, it was proposed to use the log–log MT diagrams for this purpose. The results were compared with those obtained from Kremser's equation as well as the actual trial runs.

2. Experimental

Typical process streams contained 0.9–1.8 g/l Cu, 0.6–0.8 g/l Zn, 0.15–0.18 g/l Fe, 1.66–1.92 g/l Co and 17.5–

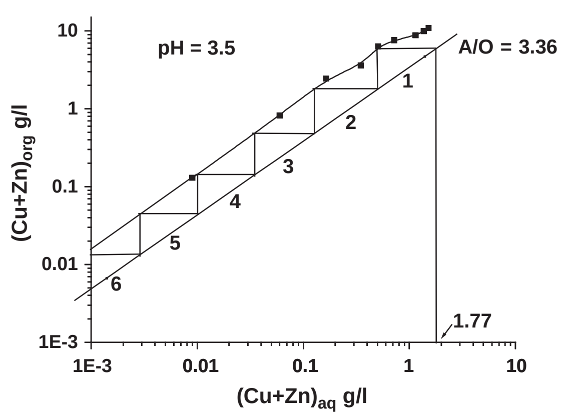

Fig. 1. McCabe Thiele's diagram for (Cu+Zn) extraction at pH_{eq} 3.5.

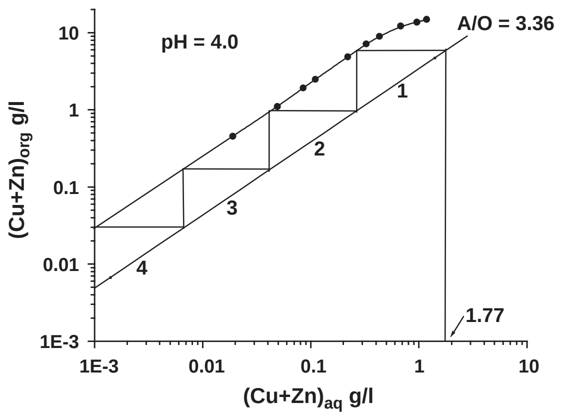

Fig. 2. McCabe Thiele's diagram for (Cu+Zn) extraction at pH_{eq} 4.0.