



Recovery of nickel, cobalt, copper and zinc in sulphate and chloride solutions using synergistic solvent extraction



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ABSTRACT

A number of synergistic solvent extraction (SSX) systems have been developed to recover nickel, cobalt, zinc and copper from sulphuric and chloride leach solutions by the solvent extraction team of CSIRO, Australia. These include (1) Versatic 10/CLX50 system for the separation of Ni from Ca in sulphate solutions, (2) Versatic 10/4PC system for the separation of Ni and Co from Mn/Mg/Ca in sulphate solutions, (3) Cyanex 471X/HRJ-4277 system for the separation of Zn from Cd in sulphate solutions, (4) Versatic 10/LIX63 system for the separation of Co from Mn/Mg/Ca in sulphate solutions, (5) Versatic 10/LIX63/TBP system for separation of Ni and Co from Mn/Mg/Ca in sulphate solutions, (6) Versatic 10/LIX63 system for the separation of cobalt from nickel in sulphate solutions by difference in kinetics, (7) Cyanex 272/LIX84 system for the separation of Cu/Fe/Zn from Ni/Co in sulphate solutions, (8) Versatic 10/LIX63/TBP system to recover Cu/Ni from strong chloride solutions, and (9) Versatic 10/LIX63 system to separate Cu from Fe in strong chloride solutions.

The synergistic effect on metal separation and efficiency is presented and possible industrial applications are demonstrated. The chemical stability of selected SSX systems is also reported.

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1. Introduction

Currently, no commercial solvent extraction (SX) extractant is highly selective for metals such as nickel and cobalt. The development and commercialisation of new, highly selective extractants are very expensive. As a consequence, development of new commercial extractants to fulfil this specific role is unlikely. Therefore, the use of synergists, preferably commercially available reagents, to improve the selectivity of the existing extractants is an attractive alternative. Many synergistic SX (SSX) systems have been developed and tested in the past three decades [1]. The SSX systems developed by the CSIRO SX team are described in detail below.

1.1. Separation of nickel from calcium by SSX with Versatic 10 and CLX50 (tested for Bulong Nickel, Australia)

Gypsum formation was a severe problem in Australia Bulong's nickel solvent extraction (SX) circuit (Fig. 1). Versatic 10 was used to extract nickel, however, calcium was co-extracted due to their close pH isotherms [2–5].

The pH isotherm of nickel with Versatic 10 was significantly affected by the addition of Acorga 5443A or CLX50, a 3,5-pyridine ester (Fig. 2). The pH_{50} value of nickel was reduced by 0.60 and 0.93 pH units

by adding 5% and 10% CLX50 to the organic solution, respectively (Table 1). The pH isotherm of calcium was not affected by the addition of CLX50. As a result, the $\Delta\text{pH}_{50(\text{Ca-Ni})}$ (the selectivity of Ni over Ca) increased from 0.77 without CLX50 to 1.37 and 1.70 with the addition of 5% and 10% CLX50, respectively (Table 1) while the separation factors of Ni over Ca increased from 47 to 258 and 1216, respectively, the extractions of Ni at pH 6.4 increased from 63.3% to 89.5% and 97.4%, respectively (Table 2) while the extraction of Ca slightly decreased from 3.5% to 3.2% and 3.0%, respectively, indicating very strong synergistic effect. Due to the largely increased separation factor of Ni over Ca, the formation of gypsum should be eliminated if 5%–10% CLX50 is added.

1.2. Separation of nickel and cobalt from manganese, magnesium and calcium by SSX with Versatic 10 and 4PC (tested for BHP Billiton, Australia)

High pressure acid leaching (HPAL) of nickel laterite ores results in solutions containing Ni, Co, Mn, Mg and Ca. The separation of Ni and Co from Mn, Ca and Mg has been achieved using mixed sulphide precipitation (MSP) and mixed hydroxide precipitation (MHP) followed by re-leach and further separation using SX. Direct solvent extraction (DSX) processes have been developed to directly recover Ni and Co from the neutralised leach solution without MSP and MHP and subsequent re-leach processes to save operating costs. The DSX processes are seen as having the greatest potential in the future, provided a highly selective, stable and inexpensive extractant or extraction system is available.

A synergistic system consisting of extractant Versatic 10 acid and a synergist decyl-4-pyridinecarboxylate (4PC) was developed to directly

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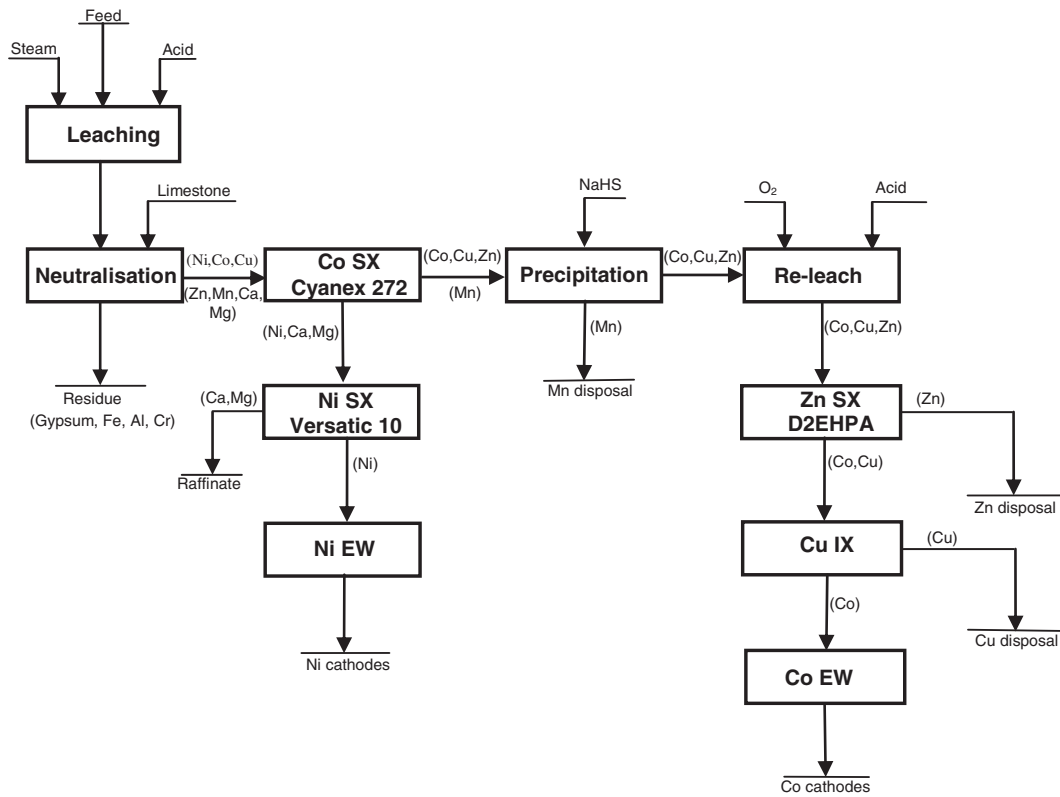


Fig. 1. A conceptual flowsheet of the Bulong process for the recovery of nickel and cobalt from leach solution of nickel laterites.

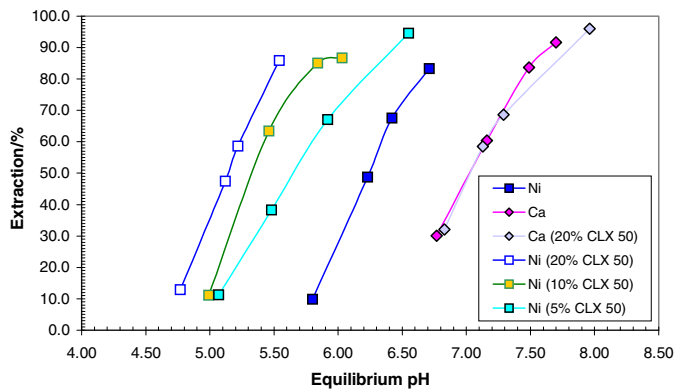


Fig. 2. The effect of synergist CLX50 on the pH isotherms of nickel and calcium with $0.5 \text{ mol}\cdot\text{L}^{-1}$ Versatic 10 acid at an aqueous to organic phase ratio (A/O) of 1:1 and 23°C .

Table 1
 pH_{50} , ΔpH_{50} and separation factors with different CLX50 concentrations

	0% CLX 50	5% CLX 50	10% CLX 50
$\text{pH}_{50}(\text{Ni})$	6.25	5.65	5.32
$\Delta\text{pH}_{50}(\text{Ni})$	0	0.60	0.93
$\text{pH}_{50}(\text{Ca})$	7.02	7.02	7.02
$\Delta\text{pH}_{50}(\text{Ca-Ni})$	0.77	1.37	1.70
Separation factor (Ni/Mn)	47	258	1216

Table 2
Extraction of Ni and Ca at pH 6.4 with different CLX50 concentrations

Element	Extraction/%		
	0% CLX 50	5% CLX 50	10% CLX 50
Ni	63.26	89.45	97.39
Ca	3.52	3.18	2.98

recover nickel and cobalt from sulphate leach solutions without intermediate precipitation and re-leach as for the MSP and MHP processes [4,6–10]. It is impossible to separate Ni and Co from Mn, Mg and Ca (Fig. 3) with the 8% Versatic 10 alone due to small $\Delta\text{pH}_{50}(\text{Mn-Ni})$ of 0.3 pH units and $\Delta\text{pH}_{50}(\text{Mn-Co})$ of 0.2 pH units (Table 3). By adding 10% 4PC to the Versatic 10 system, separation of nickel, cobalt, zinc and copper from manganese, magnesium and calcium could be achieved (Fig. 4) with $\Delta\text{pH}_{50}(\text{Mn-Ni})$ of 1.9 pH units and $\Delta\text{pH}_{50}(\text{Mn-Co})$ of 1.1 pH units (Table 3). The separation factors of Ni and Co over Mn increased from 3.9 and 1.7 to 1993 and 126, respectively. A pilot plant leach solution from BHP Billiton was tested using this system in semi continuous tests. Trials using this synergistic SX system resulted in almost >99.9% Co and Ni extracted, leaving Mn, Mg, Ca and Cl in the raffinate (Table 4). Some 96% of the co-extracted Mn, 100% of the co-extracted

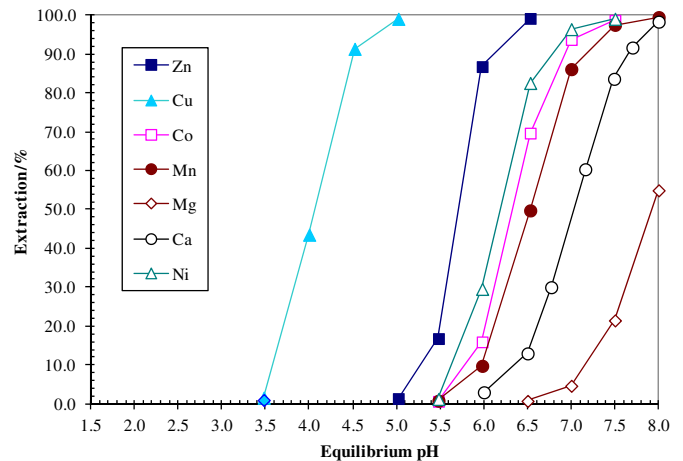


Fig. 3. Extraction pH isotherms of metals with the synthetic laterite leach solution and 8% or $0.5 \text{ mol}\cdot\text{L}^{-1}$ Versatic 10 in Shellsol 2046 at an A/O ratio of 1:1 and 40°C .

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