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Properties of Lewatit® TP272, a commercial solvent impregnated cation exchange resin for cobalt recovery

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ABSTRACT

The typical hydrometallurgical processing of nickel and cobalt ores involves the precipitation of a mixed nickel–cobalt intermediate product. Alternatively, cobalt could be separated from nickel while in the aqueous phase using solvent extraction. However, solvent extraction has some problems including the need for considerable area for the separators, management of fire hazard, and operational issues such as contamination with organic cross-over with sequential solvent extraction unit operations. The use of an ion exchange resin can mitigate some of these issues; however, conventional cation exchange resins are not sufficiently selective for cobalt over nickel. Solvent impregnated resin offers the engineering advantages of ion exchange resin and the chemical selectivity of the solvent extraction process. This paper describes key properties of a new commercial solvent impregnated resin, Lewatit® TP272, including cobalt and nickel loading as a function of pH and cobalt loading isotherms at pH 5.5 and 5.0 which are identified as the ideal conditions to recover cobalt. The chemical degradation of this solvent impregnated resin was also determined by exposing the resin to greater than pH 6 solutions, which are conditions outside the recommended operating range for this resin. The capacity of the degraded resin was restored by reimpregnating the resin using a Cyanex® 272-ethanol–water mixture. Optical images of resin containing the blue cobalt complex reveal the porous structure.

1. Background

1.1. Processing of nickel–cobalt laterite ore

The majority of cobalt production is produced as a by-product of nickel or copper laterite mining operations. Nickel laterite ore composition typically varies widely with depth. Minerals rich in iron are found closer to the surface and magnesium rich minerals are below. The processing route is tailored to the mineralogy with lower grade iron rich nickel laterites tending to be processed by pressure acid leaching like the processing at Moa Bay, Cawse, Bulong, Murrin Murrin, Coral Bay, Ravensthorpe, Ramu, Goro and Ambatovy operations. Both cobalt and nickel are solubilised during pressure acid leaching and while cobalt is more valuable than nickel, the nickel:cobalt ratio in laterites tends to be greater than 10:1 making cobalt the most valuable constituent in the ore after nickel. Once in solution, separating aqueous divalent nickel from cobalt is not straightforward as both ions display similar properties and readily precipitate together as sulphides (Roy, 1961) or hydroxides (Harvey et al., 2011) as a mixed nickel–cobalt intermediate product.

1.2. Solvent extraction

Cobalt can be selectively extracted from nickel into an immiscible liquid organic phase using ‘solvent extraction’ (SX). The cobalt/nickel separation factor for three common extractants; DEHPA, PC88A and Cyanex® 272 (C272) are 14, 80, 7000 respectively. The organic loading selectivity order for C272 is Zn > Cu > Co > Mg > Ca > Ni (Rickelton et al., 1984). Aside from being the most selective of the three for cobalt, C272 has the additional advantage of being selective for cobalt over calcium which is important for laterite leach liquors which are saturated in calcium sulphate. Examples of refineries that have used C272 for cobalt–nickel separations are Bulong, Murrin Murrin, Ambatovy, Hartley Platinum, Kasese Cobalt, Knightsbridge and Tati-Nickel operations (Donegan, 2006; Cole et al., 2006). The SX process typically exhibits fast exchange reaction kinetics. However, the aqueous-organic phase separation stage of SX is relatively slow requiring large settling ponds at high capital cost. The solvent extraction process is also sensitive to many forms of contamination that can reduce SX plant capacity, inhibit phase separation and cause reagent loss

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due to the formation of scale, crud, immiscible phases, and emulsions. These issues cause ongoing challenges for SX operations and can have a deleterious effect in other parts of process (Ritcey, 1980; Miller, 2011).

1.3. Ion exchange resin

Ion Exchange (IX) is a liquid–solid extraction method whereby ions are loaded onto functionalised polymeric resin beads. IX resins have higher loading capacities, lower process costs, are less complicated and require a smaller plant footprint compared to solvent extraction. However, the synthesis of the resin is expensive relative to SX, in part due to the complexity and time required for functionalising the beads (Warshawsky et al., 2008). This cost has restricted the application of IX in hydrometallurgical processes. The features of IX resin lead to it being favoured for extracting minor solution constituents such as impurities and precious elements and SX is favoured for major components such as copper, nickel and zinc. As the resin functional groups are strongly bonded to the polymer structure, the extent of metal coordination complexes that can form are limited due to mobility constraints of the ligands compared with solvent extraction where ligands are fully mobile in the liquid organic phase. As such, there are no conventional cation exchange resins that offer a high degree of selectivity for cobalt over nickel, although resin functionalised with bis-picolylamine and iminodiacetate functional groups have shown to be selective for nickel over cobalt at low pH (Littlejohn and Vaughan, 2012). An IX resin process was also described whereby the cobalt could be selectively eluted from a loaded nickel and cobalt resin (Oxley and Barcza, 2013). However, such a process would be impractical as it would require considerable amount of the expensive bis picolylamine-type resin to load all the nickel and cobalt from the leach solution.

1.4. Solvent impregnated resin

A technology termed ‘solvent impregnated resin’ (SIR) combines the engineering advantages of IX resin with the enhanced chemical separation factors of SX. SIR’s were first developed around 1971 with proposed use in selective removal of metals from solutions (Warshawsky, 1971; Grinstead, 1971). An SIR is a macroporous polymeric bead with a solvent adsorbed on the surface and within the pores. The solvent can be impregnated by one of two ways; dry impregnation, better for hydrophobic extractants or; wet impregnation, best for hydrophilic extractants. The extractant can also be incorporated in the organic mixture during polymerisation giving the beads a relatively high extractant concentration (Kauczor and Meyer, 1978). These resins can be thought of as having “a liquid-complexing agent homogeneously dispersed in a solid polymeric medium” (Cortina et al., 1992). A review of methods to synthesise SIRs was published by Kabay et al. (2010). Solvent impregnated resin combines the IX engineering advantages of a relatively low capital cost, simple maintenance and control, with the enhanced selectivity offered by SX. One major disadvantage of solvent impregnated resin is the high sensitivity for degradation by solvation or leaking of the organic if exposed to aqueous solution at neutral or alkaline pH. This results in a more rapid loss in capacity than conventional cation exchange resin and can cause practical challenges around pH control in the system if the operating pH is near-neutral. Examples of industrial applications are the use of D2EHPA impregnated resin for separating zinc from chromium containing solutions in electroplating and zinc from cobalt or nickel solutions in electrowinning (Cortina et al., 1994; Strong and Henry, 1976; Vaughan et al., 2013). C272 impregnated resin has been trialled previously and assessed for cobalt and nickel selectivity in ammonium sulphate and nitrate solutions (Yoshizuka et al., 1990). This experimental research provides data regarding the loading properties of the new C272 impregnated resin developed by Lanxess named Lewatit® TP272 (TP272).

2. Materials and methods

2.1. Lewatit TP272 resin properties

The specified properties of the TP272 are summarised in Table 1. The resin beads are macroporous cross-linked polystyrene wet impregnated with the solvent C272 where the organic cation exchanger is bis(2,4,4-trimethylpentyl) phosphinate. Therefore the resin retains additional organic solvent and water. The extractant is integrated into the resin beads during the polymerisation process ensuring penetration into the small pores. The density of the beads is initially lower than water and will float in solution but when the resin is contacted with the leach solution, the resin density increases from the metal loading and sinks. The specified resin loading capacity of 12.5 g-Zn/L-resin is equivalent to 13.8 g-Co/L-resin assuming similar loading coordination.

The cation exchange reaction for acid and cobalt is described by the equation shown in Fig. 1 which occurs on the surface and within the pores of the resin bead. The reaction would be the same for other divalent metal cations.

2.2. General experimental

- Reagent grade metal sulphate salts were used to prepare solutions in deionised water and pH adjustment was carried with sulphuric acid or sodium hydroxide solutions. The liquid solvent C272 was provided by Cytec.
- Solution samples were initially filtered through a Nylon membrane filter (0.2 μm pore size) before being diluted and stabilised by acidification prior to assaying.
- The diluted solutions were assayed by atomic absorption spectrometry.
- Experiments (metal loading, equilibrium isotherm, degradation, regeneration) were undertaken at a temperature of 25 ± 2 °C.
- Resin masses refer to the as-received wet basis.

2.3. Experimental set-up

Experiments were conducted to establish the resin loading behaviour of nickel and cobalt as a function of time, pH, and resin concentration. The experimental apparatus consisted of a 1 L baffled glass reactor that was mixed with overhead agitation fitted with a low shear impeller. An agitation speed of 600 RPM was found to provide adequate mixing, which avoided pH hot spots with minimal physical damaging to the resin beads. The solution pH was continuously monitored with a probe calibrated at pH 4 and 7.

2.4. Resin stripping

Loaded resin from the equilibrium isotherm experiments were stripped to validate the amount of cobalt extracted during each test. Excess solution was filtered off the resin using a Buchner

Table 1
Physical and chemical properties specified for TP272 (Lanxess, 2011).

Bead size	0.3–1.6 mm
Bulk density	530 ± 5% g/L
Density	0.97 g/L
Water retention	28–35 wt.%
Zinc capacity	12.5 g/L min