

Zinc removal from a base metal solution by ion exchange: process design to full-scale operation

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Changes to the process flow sheet and increasing zinc content of the feed materials to the Anglo American Platinum Rustenburg Base Metals Refinery circuit resulted in increasing deportment of zinc to the nickel product and necessitated a dedicated zinc-removal circuit to ensure continued consistent quality of the nickel cathode.

The development of an ion-exchange process for the removal of 0.03 g/L Zn from a stream containing 70 g/L Ni, 0.2 g/L Co, using the di(2-ethylhexyl)phosphoric acid-impregnated resin, Lewatit VP OC 1026, is described. Batch test work identified the most suitable resin for this application with respect to loading capacity and selectivity; continuous column test work allowed determination of the mass transfer zone length, on which the full-scale plant design was based.

A 15 m³/h plant was installed for removal of zinc from the selected process stream. Zinc contamination of the nickel cathode was reduced by 40% following commissioning of this ion exchange plant, allowing the target product specification to be consistently met.

Introduction

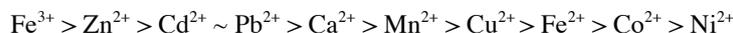
Zinc contamination of the nickel cathode at Anglo American Platinum's Rustenburg Base Metal Refinery (RBMR) has been a recurring intermittent problem since the commissioning of the refinery in 1981. Commissioning of the upstream Anglo Platinum Converting Process in 2003 resulted in greater zinc deportment to the RBMR feed, as a consequence of improved off-gas capture. A change to mining a greater proportion of Platreef ore, which contains significantly more zinc than Merensky and UG2 ores, also increased the zinc in the feed to the refinery. More recently, the decision to expand platinum production necessitated a corresponding RBMR expansion to accommodate the associated increase in the production of base metals (Cu, Ni, and Co). The new circuit and process changes exacerbated the risk of zinc contamination of the nickel cathode: mass balance analysis of the circuit indicated that a dedicated zinc removal section was required to reduce the zinc inventory in the circuit and to ensure the consistent production of nickel cathode conforming to the London Metal Exchange (LME) specification of <50 ppm Zn.

A project was initiated to provide a cost-effective, efficient, and environmentally safe process to bleed zinc from a base metal solution containing a high concentration of nickel in the RBMR circuit. The process stream identified as most appropriate from which to bleed zinc from this circuit contained approximately 70 g/L Ni, 0.2 g/L Co, and 0.03 g/L Zn, in a sulphate matrix, with relatively low acidity and low concentrations of other impurities.

Ion exchange was the technology considered for this application as it plays an increasingly important role in the hydrometallurgical industry for the purification, separation, recovery, and scavenging of metal ions, and is often the preferred separation method to use when the concentration of the metal to be removed is between 1 mg/L and 500 mg/L (Sole, 2008). Primary limitations of ion exchange for hydrometallurgical applications include its relatively low capacity for adsorption, relatively low selectivity of metal ions, poor mechanical stability of the resins, fouling, and the wash water requirements when used for high-grade applications. Unlike most competing solvent extraction processes, however, ion exchange does not require pH adjustment during the process and complete automation of the process is possible. It also uses benign reagents and does not contribute to carbon emissions or environmental damage.

Due to the relatively low concentration of zinc in the process stream, compared to nickel and cobalt, a resin that was highly selective for zinc was required. Selectivity over trace amounts of copper and iron(III) was also preferred. Inexpensive iminodiacetic acid resins complex nickel more strongly than zinc, and so were not considered. Several prior internal RBMR studies had shown that the di(2-ethylhexyl)phosphoric acid (D₂EHPA)-impregnated resin, Lewatit VP OC 1026, was suitable for the removal of zinc from various other nickel-containing streams. D₂EHPA is well known in solvent extraction applications for both the bulk recovery of zinc and its removal, particularly from cobalt and

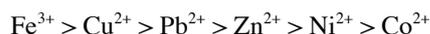
nickel sulphate liquors, as an impurity species (Cole and Sole, 2003). It exhibits a selectivity order as a function of increasing pH (Cole and Sole, 2003; Lanxess, 2011):



In an investigation of the removal of zinc from industrial waste liquors, Simpson and Laurie (1999) found that Lewatit VP OC 1026 showed the greatest selectivity for zinc, compared to resins with sulphonate (Purolite C100H and C160) and iminodiacetic acid (Purolite S930) functional groups. The waste liquor fortunately had low levels of iron(III) which would otherwise be extracted in preference (Juang and Chen, 1997). Their observed selectivity for zinc mirrors other work using D₂EHPA-containing resins (Cortina *et al.*, 1994; 1995). Lewatit VP OC 1026 has been successfully operating since the 1980s at Vale's Port Colbourne (Canada) refinery for the removal of zinc from a nickel electrolyte prior to electrowinning (Agnew *et al.*, 1988) and is also used in several nickel plating bath systems for the removal of ferric iron and zinc (Kotze, 2012).

Although solvent loss has often been considered a disadvantage of solvent-impregnated resins (Simpson and Laurie, 1999; Kotze, 2012), this risk is minimized if the acidity of the aqueous streams (adsorption, elution, and wash liquors) is maintained below pH 4 (Lanxess, 2011; Kotze, 2012). Recent improvements in the manufacturing process have also largely mitigated this risk. A major advantage of this system is the relatively low co-loading of cobalt at the pH of effective zinc removal (Kotze, 2012).

Ion exchange using aminophosphonic acid resins has also been considered for the simultaneous removal of copper and zinc from cobalt electrolytes in several refineries. The order of selectivity of these resins, exemplified by Purolite's S940 and S950, Lanxess's TP 260, and Dow's Amberlite IRC747, amongst others, is given by (Purolite, 2008):



S950 was successfully piloted for the Kakanda project (Democratic Republic of Congo) flow sheet for the removal of trace amounts of copper (approx. 70 mg/L) and zinc (approx. 2 mg/L) from a cobalt advance electrolyte (50 g/L Co) prior to electrowinning using a lead-lag fixed bed ion exchange configuration (Dry *et al.*, 1998; Wyethe and Kotze, 2000). This resin was similarly employed in the development of the Kolwezi Mine Tailings (Democratic Republic of Congo) flow sheet (Alexander, 2001) (although the full-scale plant, renamed Roan Tailings Reclamation, will produce only copper and cobalt hydroxide products initially and does not include an ion exchange step). In assessing flow sheet options for the processing of Copperbelt ores, Swartz *et al.* (2009) also recommended the simultaneous removal of copper and zinc, using an aminophosphonic acid resin, as the basis for a zinc removal step in the purification of cobalt electrolytes. Bulong Nickel (now closed) successfully implemented this technology on their cobalt refinery in Kalgoorlie, Western Australia (Mayze, 1999).

Both the D₂EHPA-impregnated and aminophosphonic acid resins were considered for this application. The laboratory batch and continuous test work is described, based on which a full-scale ion exchange plant was designed. The successful performance of the commissioned plant is demonstrated.

Experimental

Feed composition

The stream from which to bleed zinc from the RBMR circuit was selected based on its relatively low flow rate, low concentrations of competing impurity cations (Fe(III), Fe(II), and Cu(II)) (Cortina *et al.*, 1994; Simpson and Laurie, 1999; Kotze, 2012), and suitable pH (pH 2.5 to 3.5) (Swami, 1993). The composition of the process stream is given in Table I.

Ion exchange resins

Lewatit VP OC 1026 (supplied by Lanxess) and S950 (supplied by Purolite) were evaluated. Lewatit VP OC 1026 is a macroporous cross-linked polystyrene resin with D₂EHPA as the active functional group (H⁺ form). S950 is a macroporous styrene divinylbenzene resin with aminophosphonic acid (Na⁺ form) functionality. The resins were used in the as-received ionic form, with no pretreatment. Dry-tapped resin masses and volumes are reported.

Table I. Composition of feed solutions to ion-exchange tests

Solution	Ni (g/L)	Cu (mg/L)	Co (mg/L)	Fe (mg/L)	Pb (mg/L)	Zn (mg/L)	pH
Typical plant	68	66	143	3	1	12	2.8
Range	55–70	50–100	100–300	2–15	1–10	10–50	2.0–3.5
Batch tests	56	98	246	11	7	180–200*	2.0–3.5
Column tests	65	100	300	15	8	45–200*	2.7

*Varied by spiking with $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (unspiked solution = 12 mg/L Zn)

Batch loading and elution tests

Batch shake-out tests were used to determine the adsorption isotherms at various pH and initial metal concentrations, to compare the exchange equilibria of the two resins. A known mass of resin (0.3 to 9.0 g) was placed in a 250 mL glass stoppered conical flask to which 150 mL of the pH-adjusted metal-containing solution was added. The flask was shaken for 24 hours at 25°C in a thermally controlled bath to ensure that equilibrium was reached. Following separation of the resin from solution, using a Buchner-type filter with a perforated glass disc, the filtrate was assayed for residual metal content and pH.

Batch elution tests were conducted in triplicate to establish the extent of zinc and iron removal from the resin. Initial loading of the resin was carried out from synthetic solutions made up to the required compositions using analytical-grade zinc sulphate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) and ferrous ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) or ferric ($\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$) sulphate. Fresh resin (5.1 g) was contacted with 150 mL of solution for 12 hours at 25°C in a thermally controlled shaker bath, after which the resin and solution were separated. Each loaded resin was placed into a new flask containing 150 mL of 100 g/L H_2SO_4 and shaken for a further 12 hours at 25°C. Assays of the initial and residual solutions were used to calculate the extents of extraction of zinc and iron from the feed and subsequent recovery of zinc and iron from the eluted resin.

Column loading tests

Column loading experiments were conducted using a glass column with an inner diameter of 22.2 mm. A perforated glass disc at the bottom of the column allowed containment of the resin, while a rubber stopper at the top of the column prevented floating of the resin (resin density, 0.97 g/mL, is less than that of the process solution). The resin bed (1 bed volume (BV) = 100 mL) comprised 97 g (258 mm bed height) of resin in the dry-tapped form. The feed solution was pumped, in downflow mode, through the column using a peristaltic pump with variable speed control. All experiments were conducted at ambient temperature (25°C). The zinc concentration of the feed was varied from 50 mg/L to 180 mg/L and the flow rate varied from 10 BV/h to 20 BV/h. Samples of the exiting solution were collected at intervals of 3 BV and assayed for residual metal content, from which breakthrough curves were plotted. The mass transfer zone length (MTZL) and resin capacity for zinc were calculated for each experiment.

Analysis

All solution samples were assayed for zinc, cobalt, nickel, iron, lead, and copper by inductively coupled plasma optical emission spectroscopy using mass spectrometric detection (ICP-MS). pH was measured using a calibrated glass electrode. Metal concentrations on the resins were calculated by difference.

Results and discussion

pH and temperature dependence of zinc loading

Figures 1 and 2 show the batch zinc loading curves for Lewatit VP OC 1026 and Purolite S950, respectively, under different conditions of pH, temperature, and contact time. For Lewatit VP OC 1026 (Figure 1), the loading capacity increases above pH 2.5. This corresponds well with the maximum loading reported between pH 2.5 and 3.5 by Swami (1993). The most favourable zinc loading was achieved at 50°C, which is attributed to better loading kinetics and higher initial pH of 3.5. Purolite S950 shows maximised zinc loading above pH 3.7 (Figure 2). It is evident that a 3 hour contact time at 25°C is inadequate for equilibrium to be achieved. Again, the use of elevated temperature (50°C) improved the loading kinetics and overall extraction. These resins are, however, stable only up to a maximum of 80°C

for Lewatit VP OC 1026 and 90°C for Purolite S950 (Lanxess, 2011; Purolite, 2008): at higher temperatures the resin bead structures are not stable and loss of the active functional groups will occur.

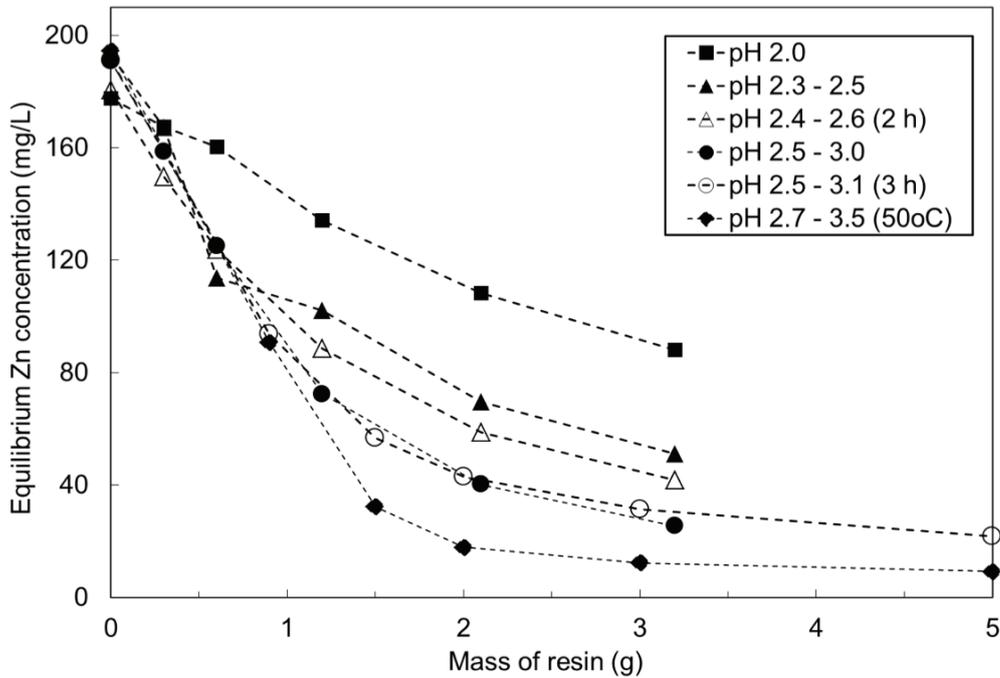


Figure 1. Effect of pH, contact time, and temperature on the batch loading of zinc onto Lewatit VP OC 1026. Experimental conditions: feed solution 190 mg/L Zn, pH as indicated; contact time 24 h; temperature 25°C (unless otherwise noted)

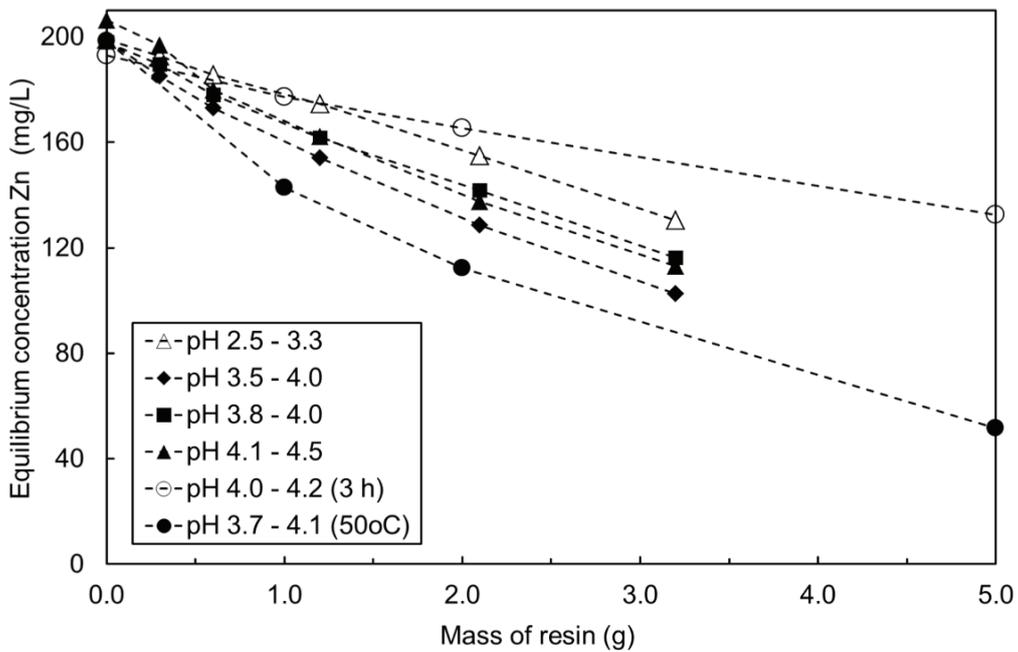


Figure 2. Effect of pH, contact time, and temperature on the batch loading of zinc onto Purolite S950. Experimental conditions: feed solution 190 mg/L Zn, pH as indicated; contact time 24 h; 25°C (unless otherwise noted)

Comparison of resin capacity for zinc

Figure 3 shows the loading capacities of the two resins for zinc, with their associated Langmuir isotherm plots. The batch tests were carried out in appropriate pH ranges for maximum adsorption by each resin.

The common two-parameter Langmuir equation is given by (Misak, 1995):

$$q_e = \frac{q_{sat} K_L C_e}{1 + K_L C_e} \tag{1}$$

where q_{sat} is the saturated amount of metal exchanged at a given solution condition (mol/kg) and K_L the Langmuir constant. The amount of metal exchanged at equilibrium, q_e (mol/kg), can be calculated by:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{2}$$

where C_0 and C_e (mol/m³) are the initial and equilibrium concentrations of metal ions in the aqueous phase, respectively, W is the mass of dry resin (kg), and V is the volume (m³) of solution. Plots of C_e/q_e against C_e were used to determine the Langmuir parameters (Figure 4). The parameter q_{sat} is obtained from the gradient (slope = $1/q_{sat}$). The calculated q_{sat} values, given in Table II, indicate that Lewatit VP OC 1026 loads more than double the mass of zinc per unit volume of resin than Purolite S950 at these solution concentrations. The coefficient of determination (R^2 in Figure 4) is approximately 0.99 for both resins, indicating that the Langmuir isotherm describes the observed adsorption behaviour well.

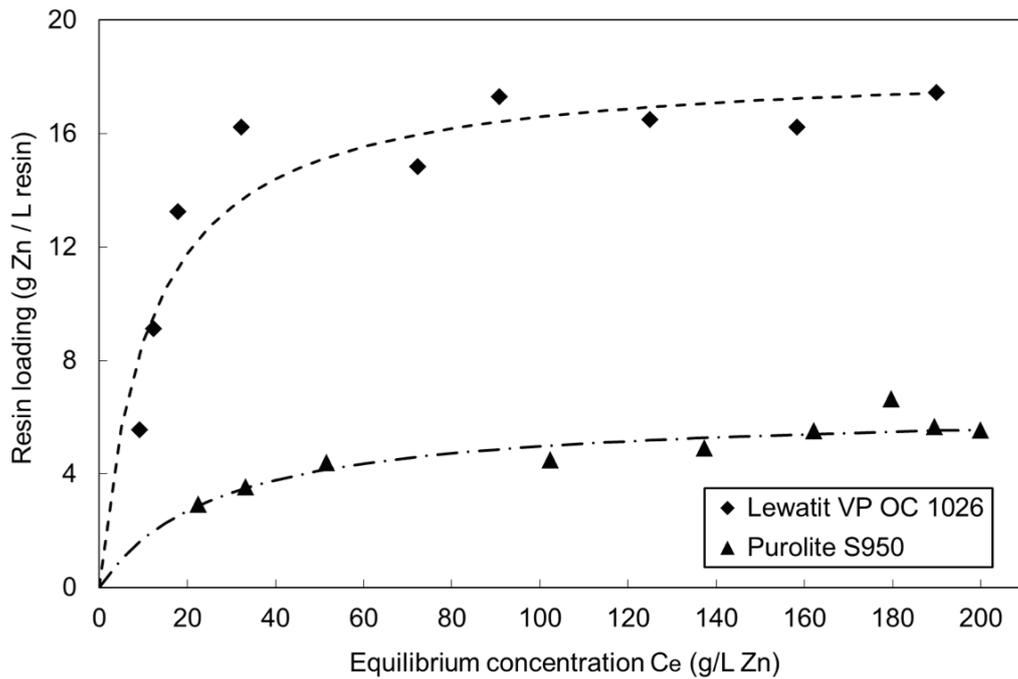


Figure 3. Zinc adsorption isotherms for Lewatit VP OC 1026 and Purolite S950, indicating maximum loading capacity of each resin and Langmuir isotherms. Experimental conditions: Lewatit VP OC 1026 feed solution: 190 mg/L Zn and pH 2.7 – 3.1; Purolite S950 feed solution: 200 mg/L Zn and pH 3.7 – 4.2. Agitated contact time of 24 h at 25°C

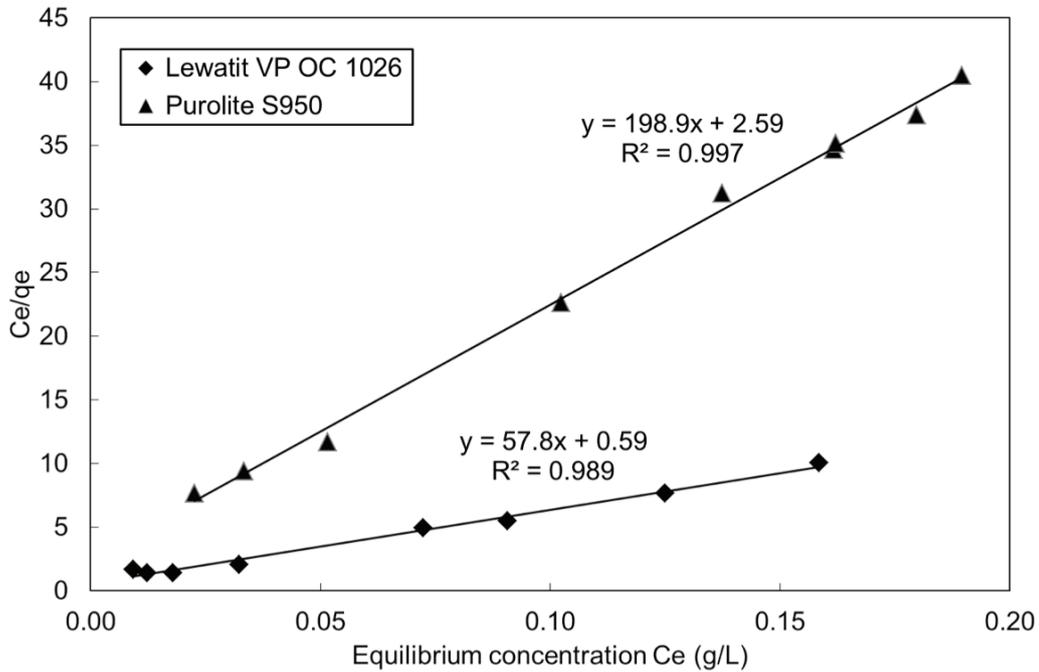


Figure 4. Determination of Langmuir parameters for the adsorption of zinc by Lewatit VP OC 1026 and Purolite S950

Table II. Resin loading capacities determined from Langmuir parameters

Resin	pH range	q_{sat} (g Zn/g resin)	q_{sat} (g Zn/L resin)
Lewatit VP OC 1026	2.7 – 3.1	0.017	16.8
Purolite S950	3.7 – 4.2	0.005	5.7

Favourable isotherms are characterized by higher resin loadings at lower solution concentrations, represented by a steep initial slope and levelling off at higher equilibrium concentrations; isotherms which start out flat are unfavourable, since such sorption systems only work well at high concentrations of the metal to be extracted (Naja and Volesky, 2006). Figure 3 suggests that the Purolite S950 isotherm is unfavourable by this definition compared to that of Lewatit VP OC 1026.

Resin selectivity and co-loading of other cations

Selectivity of the resin influences which other elements are co-loaded with the zinc and ultimately take up capacity on the resin. Co-extracted valuable metals, such as cobalt and nickel, could be lost through this process or require a complicated elution procedure to recover them, while more strongly complexed impurity elements may decrease resin capacity for zinc and ultimately foul the resin. The selectivity of a target ion adsorbed onto a resin from a multi-component solution is measured using the concepts of distribution ratio and separation factors, which can be calculated for each element using batch equilibrium data (Chaitanya *et al.*, 2011). The distribution ratio, D , is given by:

$$D = \frac{q_e}{C_e} \quad [3]$$

where q_e is the amount of metal exchanged at equilibrium and C_e is the solution equilibrium concentration. The separation factor K is then calculated by:

$$K_{Mt/Mi} = \frac{D_{Mt}}{D_{Mi}} \quad [4]$$

where the subscript Mt denotes the target metal to be extracted and Mi is any other metal in the solution that is co-loaded onto the resin. The higher the separation factor, the better the selectivity of the resin for the target species.

Table III shows the separation factors with respect to zinc increasing with increasing resin mass for Ni, Cu, Co, and Pb. For Lewatit VP OC 1026, the separation factor for Fe is between 0 and 1, indicating no selectivity between Fe and Zn. The observed selectivity order for Lewatit VP OC 1026 confirms that expected (Lanxess, 2011), and indicates that the iron in solution is present as the ferric species. Using Purolite S950, there is no selectivity in separation between zinc and copper or iron. The separation factors for Ni, Co, and Pb are orders of magnitude lower than those of the Lewatit VP OC 1026 resin but are in agreement with the expected selectivity order (Purolite, 2008). It is significant that the zinc distribution ratios for Purolite S950 (0.036 to 0.044) are an order of magnitude lower than those for the Lewatit VP OC 1026 resin (0.10 to 0.30). The distribution ratios and separation factors explain why the loading capacity of Purolite S950 is so much lower than that of Lewatit VP OC 1026 (Figure 3): co-loading of copper (approx. 80 mg/L in feed) and Fe (approx. ~8 mg/L) significantly reduce the capacity available for the loading of zinc on Purolite S950.

Since these batch results demonstrated higher zinc loading and higher selectivity for zinc over important valuable and impurity metals by Lewatit VP OC 1026, this resin was used for further column testing.

Table III. Separation factors measured for Lewatit VP OC 1026 and Purolite S950 batch experiments

Resin	Resin mass (g)	Separation factors				
		Zn/Ni	Zn/Cu	Zn/Co	Zn/Fe	Zn/Pb
Lewatit VP OC 1026	0.3	2	6	10	0	45
	0.6	9	23	80	0	160
	1.2	33	43	97	1	270
	2.1	35	151	1250	1	779
	3.2	95	185	1760	0	1190
Purolite S950	0.3	1	1	4	0	1
	0.6	2	1	5	0	1
	1.2	6	0	10	0	2
	2.1	5	0	13	0	2
	3.2	14	0	17	0	4

Column breakthrough curves

Figure 5 shows the breakthrough curves for Lewatit VP OC 1026 measured with the plant feed solution (Table I) spiked to different zinc concentrations and at different flow rates. These six experiments were considered for the calculation of the mass transfer zone length (MTZL). The MTZL is a critical sizing parameter in ion exchange systems, since this determines the size of resin vessel required for the application. These tests are run at a minimum of two different linear velocities to determine the relationship between fluid velocity and the length of the mass transfer zone. The MTZL has a nonlinear relationship with regard to velocity, *i.e.*, doubling the linear velocity will not necessarily double the MTZL (although doubling the MTZL will double the resin bed length). The MTZL is calculated from the resin bed length and the bed volumes of feed solution passed at breakthrough (when the exit concentration equal to 10% of the feed concentration for the species being adsorbed on the resin) and at saturation (90% of feed concentration) (Rossiter, 2009):

$$MTZL = l_i / L_i * \text{Column resin bed depth} \quad [5]$$

where l_i is the number of bed volumes to achieve breakthrough and L_i the number of bed volumes to achieve saturation.

The calculated MTZL values are summarized in Table IV. The MTZL for the experiments carried out at 180 mg/L Zn feed concentration could not be calculated as the experiments were not run to resin saturation. The shorter the MTZL, the less resin volume is required to achieve the same results for a specific condition. The results for 100 mg/L Zn in the feed solution indicate that it would be better to operate at a velocity of 5 m/h, since the MTZL is shorter, therefore requiring a smaller amount of resin to achieve the same results. This indicates that the loading kinetics are fairly fast and suggests that the mass transfer rate can be increased by increasing the flow rate. This is, however, not true for all solution concentrations: the MTZLs for the 50 mg/L Zn tests are similar, again indicating fast kinetics and that the column will achieve similar results at twice the linear velocity.

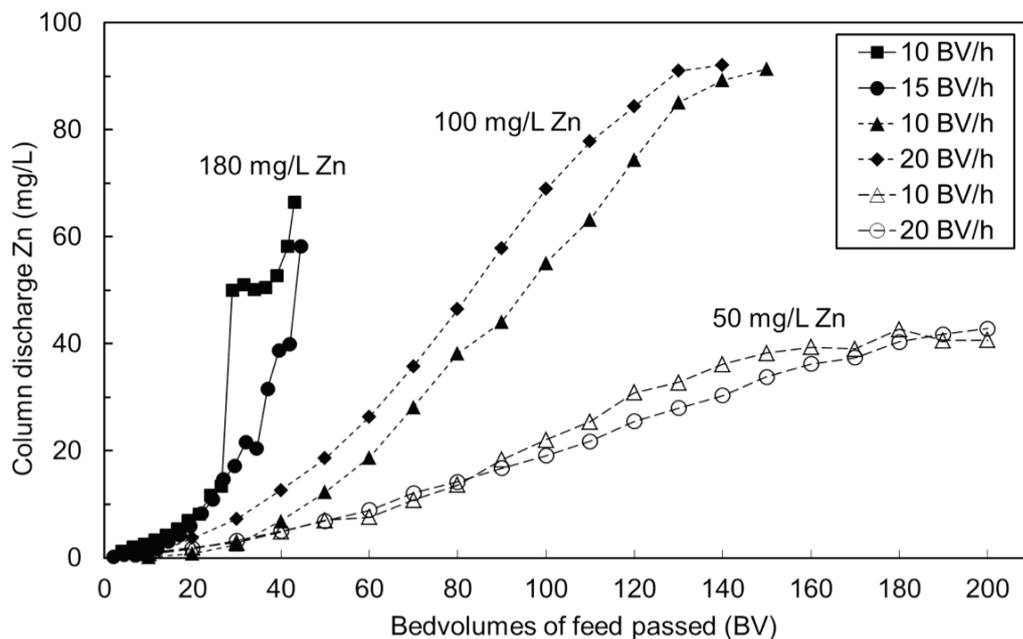


Figure 5. Breakthrough curves as a function of zinc concentration and flowrate. Experimental conditions: 100 mL BV Lewatit VP OC 1026; feed solution: 50, 100, and 180 mg/L Zn at pH 2.7; feed flow rates of 10, 15, and 20 BV/h

Table IV also gives the zinc loading capacity at saturation. The lower loading capacities observed for the 50 mg/L Zn experiments were not expected. An explanation is that the lower concentration gradient and constant iron loading ($q.v.$) may have reduced the effective capacity for available for zinc.

The MTZL calculations play an important part in sizing an ion exchange column, especially for a lead-lag system. These calculations were, however, only used to understand the behaviour of the resin in a column. The final column design was based on removing a fixed mass of zinc from the circuit; a single column was therefore installed.

Table IV. Determination of mass transfer zone length and loading capacity as a function of zinc concentration in the feed solution and flow rate.

Experimental conditions: 100 mL Lewatit VP OC 1026 resin; column diameter 22.2 mm; bed length 258 mm; feed pH 2.7

Feed Zn (mg/L)	Feed flow rate (BV/h)	Feed linear velocity (m/h)	Volume to breakthrough, I_i (BV)	Volume to saturation, L_i (BV)	MTZL (mm)	MTZL as proportion of bed length (%)	Loading capacity (g Zn/L resin)
200	10	2.5	28	-	-	-	> 7.5
183	15	3.9	30	-	-	-	> 7.5
97	20	5.0	35	125	72	28	7.2
93	10	2.5	45	128	91	35	7.7
48	19	4.9	40	200	52	20	5.3
45	10	2.5	35	170	53	21	4.3

Resin selectivity in continuous operation

The selectivity of Lewatit VP OC 1026 with regard to other metal cations was measured under column loading conditions. Figure 6 confirms that iron is the only other cation present in the feed solution that co-loads with zinc. The zinc and iron curves have similar shapes, as expected from the low separation factors of the batch tests. The nature of the iron loading was further examined using elution tests.

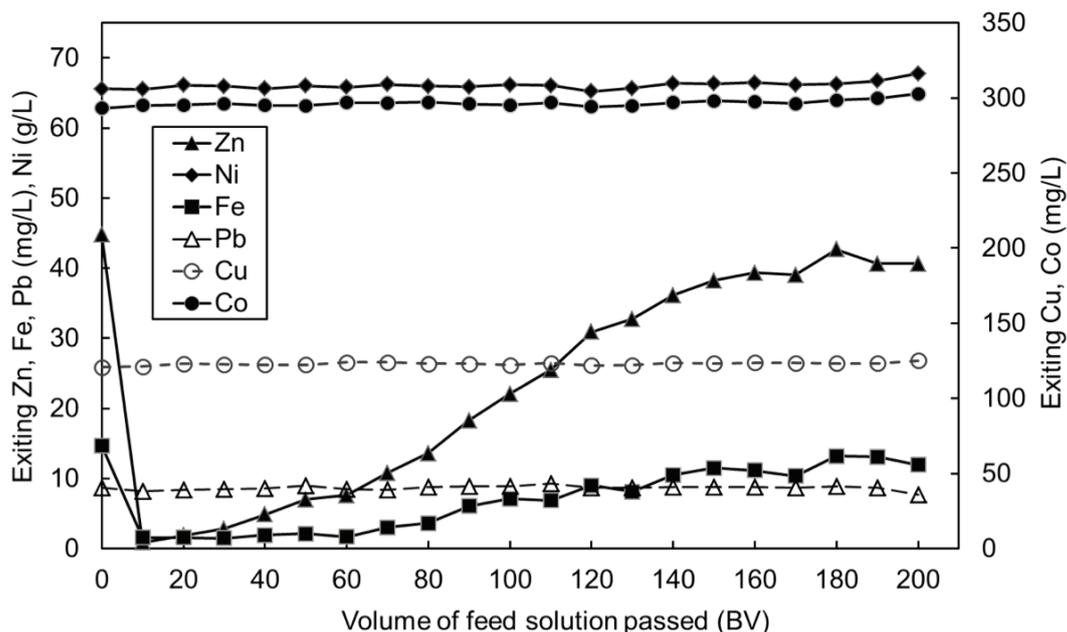


Figure 6. Resin loading curves showing selectivity of resin for zinc and iron. Experimental conditions: 100 mL BV Lewatit VP OC 1026; feed solution: 45 mg/L Zn, 15 mg/L Fe at pH 2.7; feed flow rate 10 BV/h

Batch elution of zinc and iron

Batch elution tests were carried out to evaluate how easily zinc and iron were stripped from the resin. The iron was of particular interest as it is not readily stripped from D₂EHPA with sulphuric acid: the common practice in D₂EHPA-based solvent extraction applications is to control residual iron levels on the organic phase by stripping with 6 M HCl (Akhlaghi *et al.*, 2010). The use of HCl in industrial metallurgical plants is usually not favoured as the materials of construction for mechanical equipment become very expensive.

Lewatit VP OC 1026 was loaded using synthetic solutions containing 200 mg/L Zn and 50 mg/L Fe (in the ferrous and ferric forms). In both cases, zinc loading of 90% and iron loading of >95% were achieved. The resins were then eluted with 100 g/L sulphuric acid, achieving 100% recovery of the loaded zinc, but only 10% to 15% of the iron was removed, irrespective of whether iron had been introduced in the ferrous or ferric form, indicating that approximately 90% of the iron loaded remained on the resin. This suggests that any Fe(II) in solution rapidly converted to Fe(III) on exposure to air and that 100 g/L sulphuric acid is not adequate to remove Fe(III) from the resin.

Since the batch elution tests showed that zinc elutes easily and completely, column elution tests were not conducted. It was accepted that the resin would eventually foul with Fe(III) in the long run and would need to be eluted periodically with HCl. This was not considered to be a significant operational issue because the iron content of the RBMR feed liquor was expected to reduce on commissioning of the new refinery process.

Plant design, commissioning, and operation

Design procedure

Based on the successful outcomes of the laboratory testwork, a full-scale plant was designed to treat 15 m³/h of the process stream with composition given in Table I. The design calculation procedure, detailed in Table V, was adapted from Crittenden *et al.* (2005) to develop the full-scale design criteria. The following aspects were considered:

- Scale-up considerations
- Column design details, including volume of resin, surface area of columns, number of columns, sidewall height, pressure drop, and inlet and outlet arrangements
- Overall cycle time.

Plant commissioning and operation

The full-scale ion exchange plant was successfully commissioned over a period of three months during 2011. The plant consists of one 3 m³ ion exchange column, a media filter and two cartridge filters to ensure clarity of the feed (<10 mg/L total suspended solids), and three storage tanks, all constructed in 316L stainless steel. Operation of the plant is entirely automated.

Loading at 7.5 BV/h is carried out until the exiting stream reaches 80% of the zinc concentration of the feed stream, after which zinc is eluted using 100 g/L H₂SO₄ at 5 BV/h. The column is rinsed with acidified (pH 4) demineralized water before starting the following loading cycle. The zinc-barren process solution is returned to the main circuit, while the zinc-containing eluate reports to the effluent treatment plant for neutralization and then to the smelter for recovery of any residual valuable metals.

The plant operates to the design specifications and achieves the required efficiency of zinc removal. During the commissioning period, the feed concentration averaged 18 mg/L Zn, and the exiting solution averaged 9 mg/L Zn. Co-loading of elements other than Fe(III) was negligible.

Table V. Design criteria calculation procedure for the full-scale plant

Parameter	Symbol/formula	Comment
Design flow rate (m ³ /h)	Q	Maximum
Zn in feed (g/L)	Co	Feed average
Service flow rate (BV/h)	SFR	
Volume of resin (m ³)	$Vr = Q/SFR$	BV
Inert resin	Lewatit IN42	To avoid distributor plugging
Bed depth (m)	d	Industry range: 0.75-3 m
Inert resin depth (m)	di	
Required freeboard (%)		Manufacturer's data sheet
Freeboard (m)	df	
Side wall height (m)	$H = d + di + df$	
Resin bed cross-sectional area (m ²)	$A = Vr/d$	
Column diameter (m)	$= (4/\pi * A)^{0.5}$	
Superficial velocity (m/h)	$u = Q/A$	Industry range: 10-36 m/h
Empty bed contact time (min)	$EBCT = 60/SFR = d/u$	
Total column volume (m ³)	$Vc = A * H$	
Pressure drop (kPa)	$dP = dPs * Q / (d + di)$	max: 172 kPa
Specific pressure drop (kPa.h/m ²)	dPs	For water
Zn mass flow to column (kg/h)	$Q * Co$	
Total resin capacity (kg Zn)	$V * q$	
Time for full loading (h)	$tf = Vr * q / Q * Co$	Resin saturation
Elution frequency (BV)	$tf * SFR$	

Elution was carried out every 250 BV (approx. 33 h cycle time). Figure 7 shows typical elution profiles for zinc and iron: zinc spiked to a maximum of 6800 mg/L in the eluate and the iron to a maximum of 8.5 mg/L. A mass balance indicated that 93% of the total zinc fed to the column was loaded but only 12% of the iron, while 94% of the zinc on the resin was eluted and only 21% of the iron, confirming the batch elution test results. Only 2% of the iron present in the feed solution therefore reports to the eluate. While the incomplete elution of Fe(III) remains an issue, the overall co-loading of iron is lower than expected due to the high proportion of iron in the feed solution as Fe(II): only Fe(III) is co-loaded with zinc. Fe(III) accumulating on the resin with time requires periodic elution with HCl.

Verification of plant performance

Figure 8 shows the zinc content of nickel cathode in the five months before and after the installation of the zinc ion exchange plant. It is evident that a step-change improvement in zinc contamination resulted following the commissioning of the ion exchange process: the mass flows and zinc concentrations fed to the refinery for this entire period were essentially constant, but the average zinc concentration in the nickel cathode dropped from 32 ppm to 18 ppm. Based on these data, it was calculated that the zinc ion exchange plant can remove 80% of the total zinc that enters RBMR. This is more than adequate to ensure a nickel cathode product consistently containing < 50 ppm zinc.

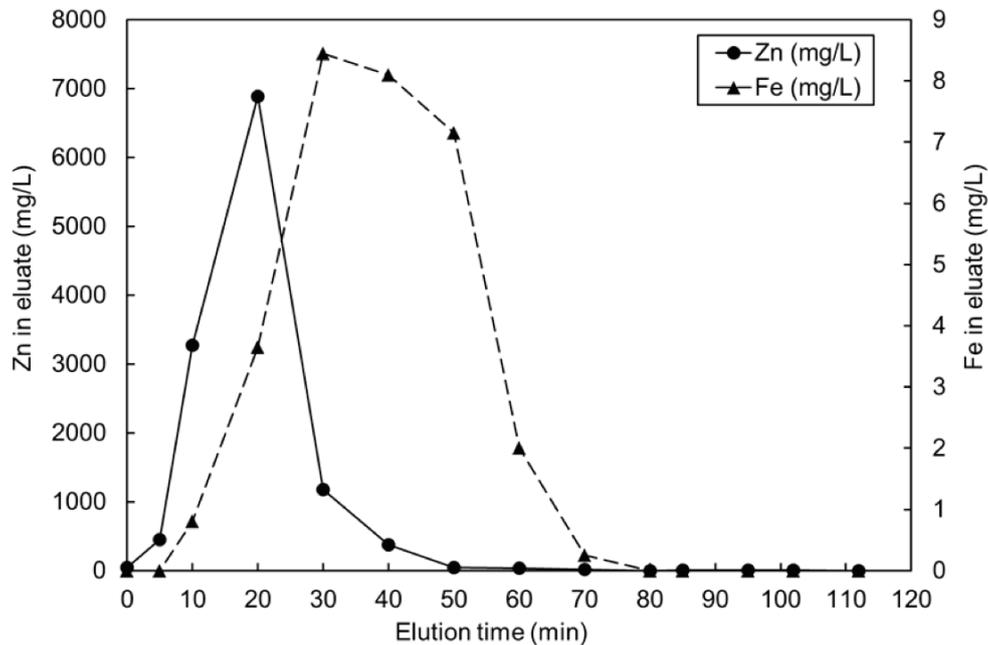


Figure 7. Typical elution profile of full-scale plant after 250 BV of loading. The elution cycle is a 40 min contact with 10 vol.% H_2SO_4 followed by a 40 min wash with acidified ($pH < 4$) demineralized wash water at flow rates of 5 BV/h

Conclusions

Ion exchange has proved an appropriate technology to remove trace quantities of zinc from a nickel- and cobalt-containing process stream from a base metal refinery. The D_2EHPA -impregnated resin, Lewatit VP OC 1026, was identified as having the most suitable functionality for this application, based on laboratory batch and column tests:

- Maximum zinc loading capacity for Lewatit VP OC 1026 is more than double that of Purolite S950 at appropriate pH conditions: co-loading of iron, copper, and lead reduce the loading capacity of Purolite S950
- Lewatit VP OC 1026 at $pH \sim 3$ was several orders of magnitude more selective for zinc compared to Purolite S950 with respect to measured separation factors for the main elements present in the feed liquor

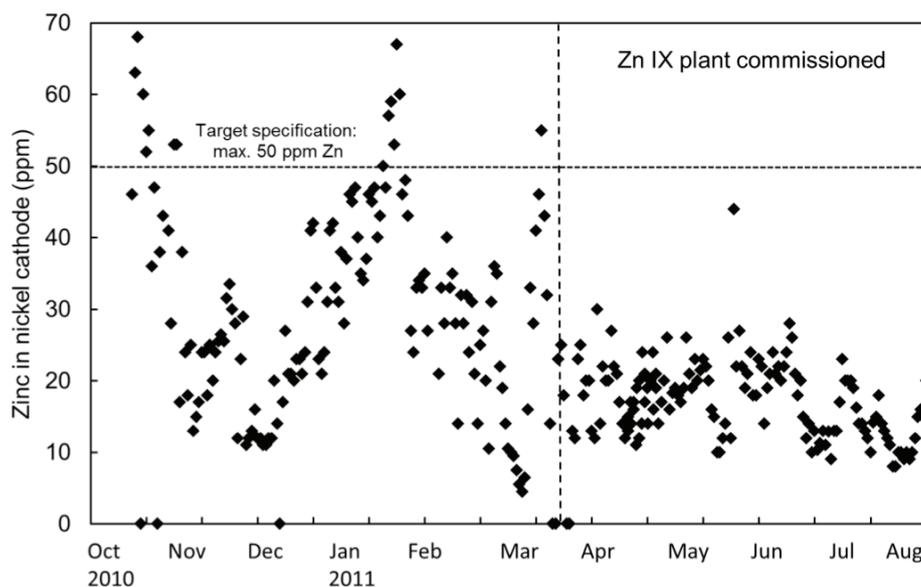


Figure 8. Zinc contamination of the nickel cathode before and after commissioning (mid-March 2011) of the RBMR zinc ion exchange plant

- The separation factors of zinc and iron(III) for both resins were between 0 and 1, demonstrating that iron(III) is very strongly co-loaded with zinc. Loading of iron remained constant for different Zn:Fe ratios and column feed rates
- Column tests showed that, for a feed containing 100 mg/L zinc, the loading capacity is higher when feeding at 5 m/h compared to 2.5 m/h. The shorter MTZL at the higher linear velocity means that less resin is required for the same mass of zinc removed.

This test work provided the design basis for a commercial ion exchange plant to treat 15 m³/h, the performance of which confirmed the laboratory results:

- The resin loaded only zinc, with negligible co-loading of other elements present in the process, besides Fe(III). The zinc concentration in the process stream was reduced by approximately 50% in a single column contact
- Plant elution data showed that less than 12% of the total iron fed to the column loaded onto the resin and that only approximately 20% of the loaded iron was eluted from the resin, indicating that most of the iron in the feed occurs as Fe(II) and does not load, whereas the small quantities of Fe(III) do load. The loaded Fe(III) will eventually foul the resin in the long term, reducing the zinc loading capacity, and requires elution with HCl to limit this effect
- The plant elution profile indicated that the zinc elution with 100 g/L sulphuric acid is rapid and that almost all the zinc is removed during an 80 minute elution cycle.

During the first six months of operation, the full-scale ion exchange plant effectively reduced the zinc inventory in the refinery circuit which, in turn, reduced the average zinc concentration in the nickel cathode from 32 ppm to 18 ppm.

Acknowledgements

Appreciation is extended to the management of Anglo American Platinum for permission to publish this work. The support of Barry Mc George (RBMR), the analytical services provided by Deborah Craig (Anglo American), and the hard work of the commissioning team at RBMR are gratefully acknowledged. Resin samples for the testwork were kindly supplied by Lanxess and Purolite.

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