Technical Paper

Application of Solvent-Impregnated Resins for Production Of High-Purity Nickel and Cobalt Liquors

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Application of Solvent-Impregnated Resins for Production Of High-Purity Nickel and Cobalt Liquors

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Abstract

The growth of the electric vehicle industry has resulted in an increased demand for metals used in the production of batteries, most notably nickel, cobalt and lithium. The mandate from battery producers is for metal salts of high purity, with the majority of impurities required to be at levels of less than 5 mg/kg. Conventional precipitation and solvent-extraction methods are not always able to produce liquors of the desired purity, while ion-exchange resins are highly suitable for the task.

Although the current available ranges of ion-exchange resins lack the appropriate selectivity for certain target impurities in a background of highly concentrated nickel or cobalt sulphate, suitable solvents do exist. The use of solvent-impregnated resins combines the best of both worlds, i.e., the selectivity of the solvents with the ease of engineering of ion-exchange resins.

This paper discusses the application of two new solvent-impregnated resins for the removal of specific impurities from nickel and cobalt sulphate liquors.

Keywords: solvent-impregnated resins, ion exchange, nickel, cobalt

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Contents

Introduction

The projected growth of the electric vehicle market over the next two decades has resulted in a simultaneous predicted increase in the need for the major metals used in the batteries used to power these vehicles, namely lithium, manganese, nickel and cobalt. Battery producers require feedstock of a very high purity. This, in turn, requires suppliers to devise innovative treatment methods, to adhere to the strict demands.

Precipitation methods for the removal of impurities typically form part of most flowsheets, but it is difficult to achieve removal of the impurities to suitably low levels without any co-precipitation of the valuable metal. To restrict losses of the valuable metal, precipitation is usually only done for partial removal of impurities. Additional impurity removal is done by more sophisticated methods, such as ion exchange or solvent extraction.

Background

Both metals and salts may be used as feedstocks in the production of batteries for electric vehicles. The nature of the feed material and the specifications are agreed upon between the supplier and end-user, hence some variation exists. In all instances, the specifications for impurities are very strict, as set out in Table 1. The majority of impurities must be removed to less than 5 mg/L in the liquor prior to product recovery by crystallization or electrowinning.

TABLE 1 Nickel and Cobalt: Specifications for Battery-Grade Sulphate Salt and Metal

Element	Unit	Salt Specification ($NiSO_4 \cdot 6H_2O$)[a]	Nickel Metal [b]	Salt Specification ($CoSO_4 \cdot 7H_2O$)[a]	Cobalt Metal [c]
Nickel	%/g/t	22.3%	99.8%	–	100–1700
Cobalt	%/g/t	10	≤ 1500	20.5%	99.95%
Copper	g/t	2	≤ 200	≤ 10	2–100
Iron	g/t	5	≤ 200	≤ 10	8–100
Cadmium	g/t	2	–	≤ 5	1–50
Zinc	g/t	2	≤ 50	≤ 10	10–70
Lead	g/t	2	≤ 50	≤ 10	8–100
Aluminium	g/t	5	–	–	10–30
Calcium	g/t	5	–	50–100	10–50
Magnesium	g/t	5	–	50–100	10–50
Manganese	g/t	5	≤ 50	≤ 5	8–100
Carbon	g/t	–	≤ 300	–	50–200
Sulphur	g/t	–	≤ 100	–	10–100
Phosphorus	g/t	–	≤ 50	–	5–10
Silicon	g/t	–	≤ 50	–	10–30
Arsenic	g/t	–	≤ 50	–	2–7
Antimony	g/t	–	≤ 50	–	3–6
Bismuth	g/t	–	≤ 50	–	3–5
Tin	g/t	–	≤ 50	–	3–5
Potassium	g/t	–	–	50–100	–
Sodium	g/t	–	–	50–100	–

a — As Per Umicore and AML (Alpha Fine Chemicals)(9)
b — London Metal Exchange (LME)(2)
c — London Metal Exchange(3)

Ion-exchange (IX) resins are widely used to remove impurities to very low levels, typically < 2 mg/L, but as low as parts per trillion are required in some industries. There are several advantages of using IX resins instead of solvent extraction (SX) or precipitation, including:

- Ease of use and well-known engineering;
- Small footprint;
- Can be fully automated, requiring minimal operator intervention;
- Health and safety — reduced risk of fire compared with SX;
- Relative to precipitation, IX is more efficient in decreasing impurity levels to very low concentrations, whilst minimizing co-extraction of valuable metal and the subsequent need for large recycle streams;
- Low reagent loss compared with SX.

Existing commercial IX resins are limited in their ability to target some impurities from concentrated cobalt and nickel streams. Organic solvents exist that can fill that gap. Combining the functionality of an appropriate organic solvent with the engineering advantages of an IX resin provides industry with an attractive option.

A summary of typical reagents used to target specific impurities is given in Table 2.

TABLE 2 Impurity Removal by Available Ion Exchange and Solvent Extraction Reagents

	Ion Exchange Resins		**Organic Solvents**	
	Functional Group	Commercial Products	Functional Group	Commercial Products
Cu and Zn from Co/Ni	Aminomethyl Phosphonic	Purolite MTS9500, Lewatit TP260	D2EHPA (Di(2-ethylhexyl) phosphoric Acid)	Ionquest 220
	Iminodiacetic Acid	Purolite MTS9300, Lewatit TP207	None	–
Ni from Co	Bispicolyl Amine	Dow Ambersep M4195, Lewatit TP220, Purolite MTS9600	Carboxylic Acid	Versatic 10
	Hydroxypropylpicolyl Amine	Dow XUS43605, Purolite MTS9590	None	–
Co from Ni	–	None	Di(2,4,4-trimethylpentyl) phosphinic Acid	Cyanex 272, Ionquest 290

Zinc and Copper

The concentrations of copper and zinc in a cobalt advance electrolyte can vary between 50 and 200 mg/L, while the cobalt concentration can vary between 15 and 50 g/L, depending on the design of the electrowinning circuit. The cobalt concentration is thus orders of magnitude higher than those of the zinc and copper.

The efficiency of an amino-methyl phosphonic (AMP) acid for the removal of zinc and copper from concentrated cobalt streams has been demonstrated. The selectivity range of this type of resin is as follows:

$H^{+} > Fe^{3+} > Pb^{2+} > Cu^{2+} > Zn^{2+} > Al^{3+} > Mg^{2+} > Ca^{2+} > Cd^{2+} > Ni^{2+} > Co^{2+} > Na^{+}$

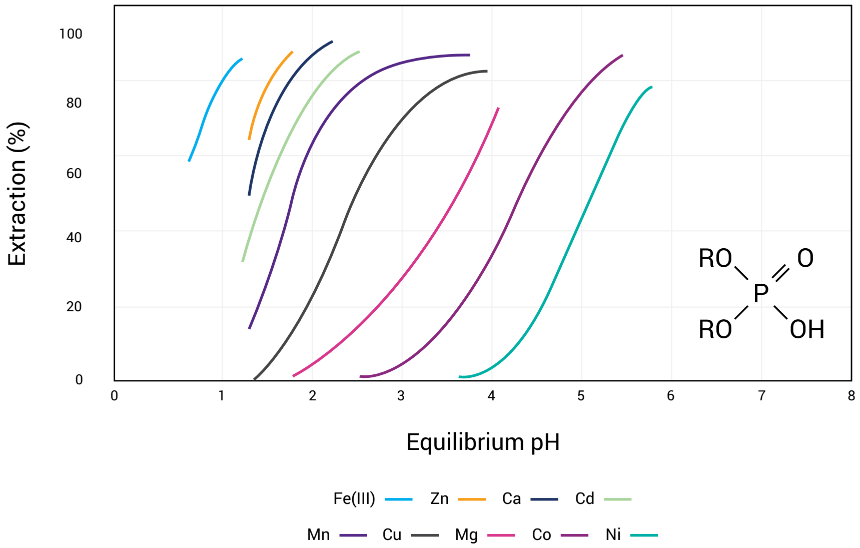
It was used by Bulong Nickel (now closed) on their cobalt refinery in Kalgoorlie, Western Australia(4). This functionality was also tested by Mintek for the treatment of the Kakanda Tailings dump(8). The feed to the IX unit operation contained 370 mg/L copper, 5 mg/L zinc and 65 g/L cobalt, at a pH of 4 to 5. Copper and zinc could be effectively and continuously removed to below 2 mg/L.

While the resin has good selectivity for both copper and zinc over nickel and cobalt, a drawback is its high affinity for ferric. Ferric ions are not eluted during the standard elution with sulphuric acid and iron will gradually build up on the resin, thereby decreasing the available capacity. The use of this resin thus requires very efficient removal of iron prior to the IX.

The removal of zinc from a concentrated nickel stream at Rustenburg Base Metal Refiners in South Africa was successfully implemented after extensive testing(6). During the upfront laboratory test programme, the Purolite MTS9500 AMP resin was directly compared with the Lewatit OC1026, D2EHPA-impregnated resin. The latter product has a selectivity range as a function of increasing pH as illustrated in Figure 1(5).

FIGURE 1

Order of Selectivity of Extraction of Base Metal Cations by Di(2-ethylhexyl)phosphoric Acid (D2EHPA)



The D2EHPA-impregnated product was chosen for this application over the AMP resin due to:

- Higher zinc loading capacity at appropriate pH conditions;
- Reduced co-loading of iron, copper and lead;
- Higher selectivity for zinc over the main elements present (iron, copper, lead, nickel).

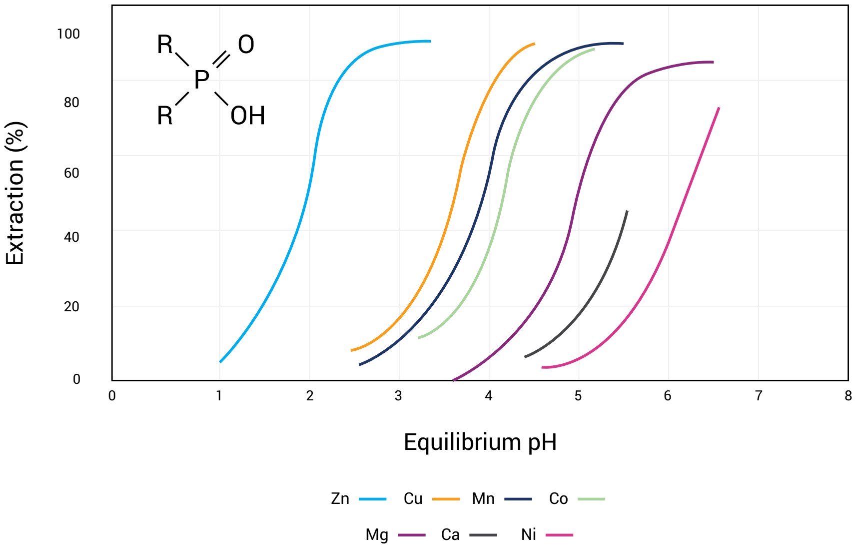
Cobalt from Nickel

Cobalt and nickel frequently occur together in nature, with 55% of the world's cobalt associated with nickel in laterite ores and 43% associated with copper in the central African Copper Belt. These two elements appear next to each other on the Periodic Table, with cobalt having an atomic number of 27 and nickel having an atomic number of 28. Thanks to this, they have very similar characteristics, making it difficult to separate the two.

The separation of low values of nickel from more concentrated cobalt streams can be done using either bis-picolylamine or hydroxypropyl-picolylamine resins, as listed in Table 2; however, there is currently no commercial IX resin that can remove low levels of cobalt from concentrated nickel liquors. The best available option is the organic solvent di(2,4,4-trimethylpentyl) phosphinic acid. This reagent has a separation of roughly two pH units between cobalt and nickel, as illustrated in Figure 2(5).

FIGURE 2

Order of Selectivity of Extraction of Base Metal Cations by Di(2,4,4-trimethylpentyl) phosphinic Acid



Solvent-Impregnated Resins

The idea of combining a selective organic solvent with a styrene/divinylbenzene copolymer is not new, and these types of products have been around since the 1970s(1).

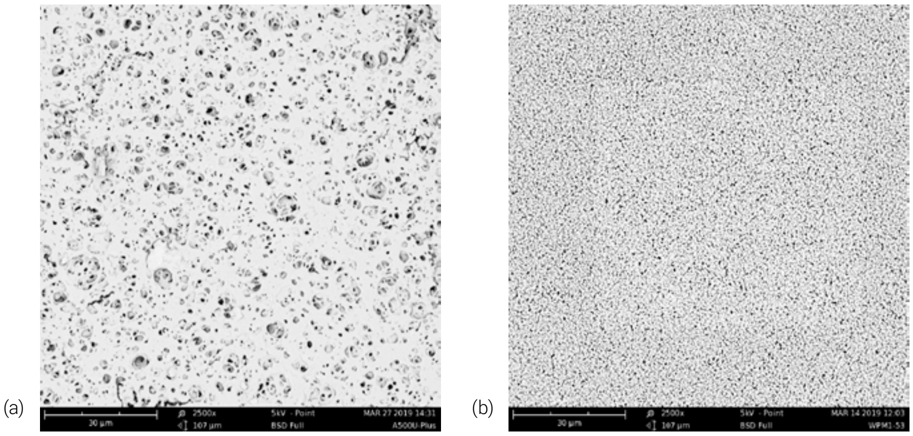
Production

Simply soaking a resin bead in a suitable solvent would result in a product in which the organic solvent adheres very loosely to the substrate. The solvent would easily wash out of the resin bead during use, resulting in rapid loss of capacity and the need for frequent replacement of the reagent.

For this reason, the solvent is incorporated at the start of the process, by adding it to the mixture of styrene and divinylbenzene. A porous spherical bead is formed, with the extractant strongly bound to the resin matrix. The structure of solvent-impregnated resins is very similar to that of standard macroporous IX resins, as shown in Figure 3 (2500 times magnification).

FIGURE 3

Pore Structures of (a) Macroporous (Purolite MTA5012) and (b) MTX7010 (D2EHPA-Impregnated) Ion-Exchange Resins



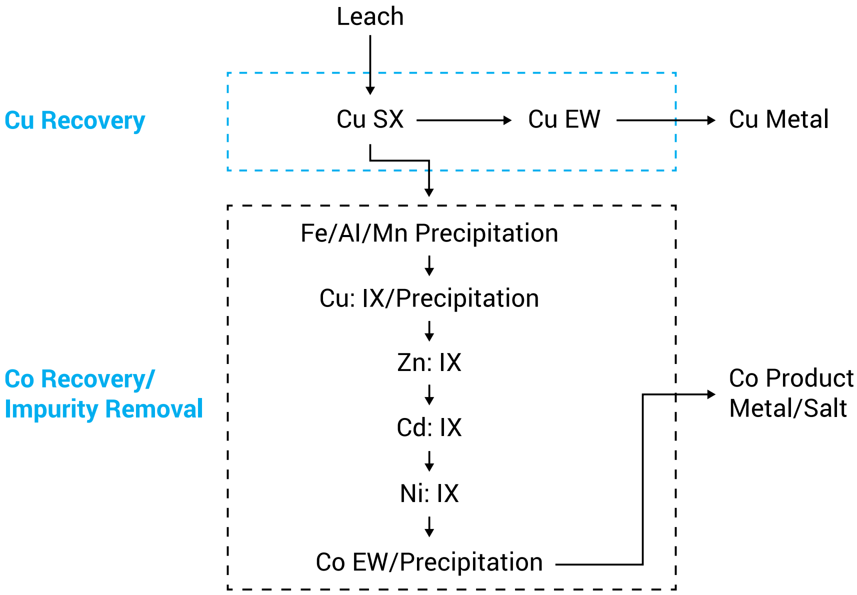
The solvent-impregnated resins are less dense than water and float on aqueous solutions. For this reason, the design of the reaction vessels should incorporate strainers at the top and bottom to retain the resin. A layer of inert material (typically polymer beads) can be added to protect the strainers.

Application

The flowsheet in Figure 4 shows the typical impurity-removal steps required to produce a pure cobalt metal or mixed hydroxide, as used in the African Copper Belt. The presence of impurities varies between different operations and all steps might not be included in every flowsheet. The production of a cobalt sulphate salt is expected to require similar impurity-removal steps.

FIGURE 4

Typical Flowsheet Showing Impurity-Removal Steps for Cobalt Production on the African Copper Belt



At this stage, a generic flowsheet for the production of battery-grade nickel does not exist, because it depends on the origin of the material being used: for example, recycled batteries, mixed hydroxide, nickel sulphate streams, and others.

Based on the specifications in Table 1, it is clear that the same group of impurities will demand attention, regardless of the source of the raw material. These include iron, cobalt, nickel, copper, cadmium, lead, zinc, aluminium, calcium, and magnesium.

Zinc Removal from Cobalt Using MTX7010 (D2EHPA-Impregnated Resin)

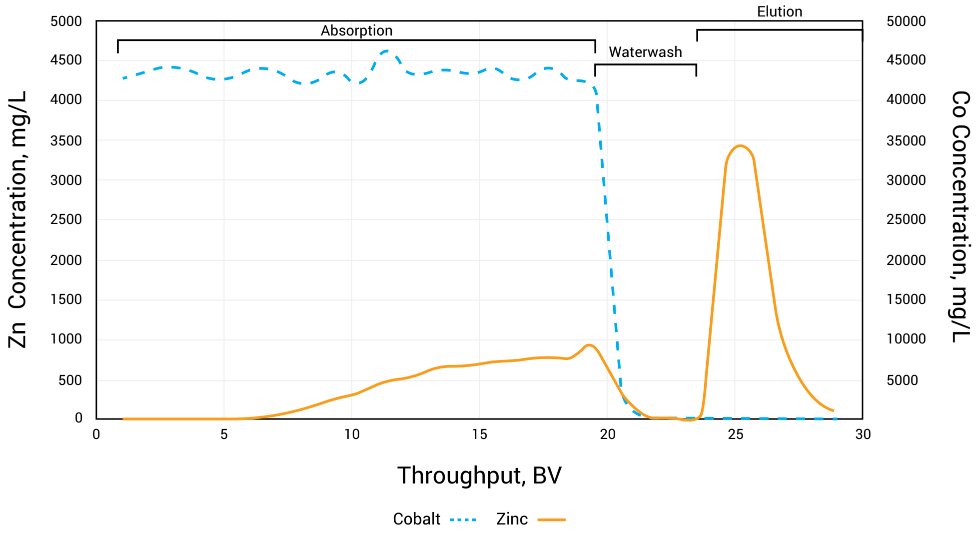
The ability of MTX7010 to remove zinc from cobalt was tested in a column set-up. The resin was loaded into a jacketed glass column and the resin bed pinned with glass wool. Synthetic liquor, simulating cobalt electrolyte, containing 50 g/L cobalt and 1 g/L zinc, was heated to 50 °C and the pH adjusted to 2. A total of 20 bedvolumes (BV) was passed downwards through the resin bed at a flowrate of 2 bedvolumes per hour (BV/h). One bedvolume is equal to the volume of resin used in the test. The temperature was maintained at 50 oC throughout the adsorption test. Barren samples were collected in 1 BV fractions and analysed for zinc.

After completion of the breakthrough test, the resin was washed with 5 BV of water, at ambient temperature, to remove entrained feed liquor. The pH of the wash water was adjusted to 2 prior to use, to prevent loss or organic reagent. The resin was then eluted with 5 BV of 1 mol/L sulphuric acid, at ambient temperature. The eluate was collected in 1 BV fractions and analysed for zinc and cobalt.

The concentrations of cobalt and zinc in the barren liquor exiting the column during the different steps are shown in Figure 5.

FIGURE 5

Pore Structures of (a) Macroporous (Purolite MTA5012) and (b) MTX7010 (D2EHPA-impregnated) Ion-Exchange Resins



No cobalt loaded onto the resin, as shown by the fact that the cobalt concentration in the barren was equal to that in the feed throughout the loading cycle. Zinc was efficiently retained by the resin, with zinc in the barren only exceeding 2 mg/L after a throughput of 4 BV.

Efficient displacement of the feed was achieved within 2 BV during the waterwash after adsorption. The resulting liquor contained a high concentration of cobalt, with a similar relative composition to that of the feed liquor (albeit slightly diluted) and it could be returned to the circuit ahead of the IX unit operation.

The majority (94%) of the zinc was eluted with 3 BV of acid, allowing the removal of zinc from a large volume of feed liquor and transferring it to a small, concentrated volume. The small amount of cobalt that reported to this stream is likely to be due to entrained feed liquor, rather than extraction by the resin.

Cobalt Removal from Nickel Using MTX8010 (di(2,4,4-trimethylpentyl) phosphinic Acid Impregnated Resin)

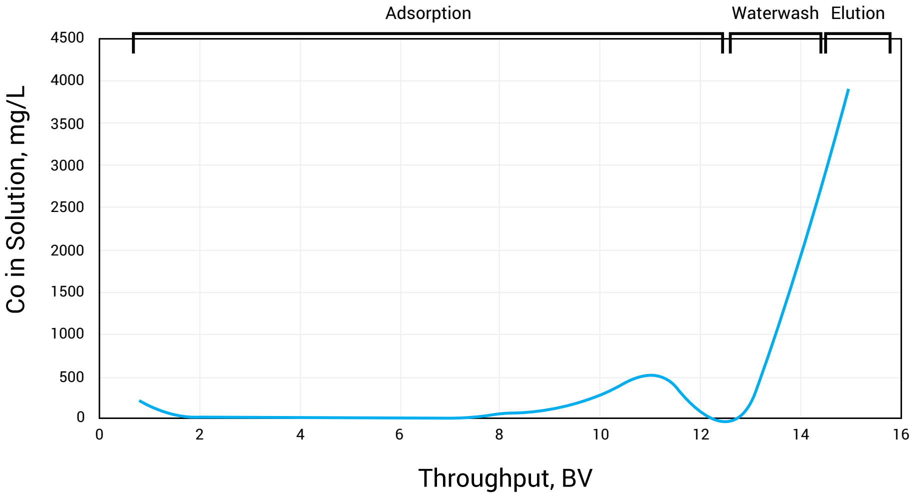
The ability of MTX8010 to remove cobalt from nickel was tested in a mini-column set-up. The resin was loaded into a jacketed glass column and the resin bed pinned with glass wool. Synthetic nickel electrolyte, containing 80 g/L nickel and 1 g/L cobalt, was heated to 50 °C and the pH adjusted to 5.5. A total of 12 BV was passed downwards through the resin bed at a flowrate of 2 BV/h. The temperature was maintained at 50 °C throughout the adsorption test. Barren samples were collected in 1 BV fractions and analysed for cobalt.

After completion of the breakthrough test, the resin was washed with 2 BV of water, at ambient temperature, to remove entrained electrolyte. The pH of the wash water was adjusted to 5.5 prior to use. The resin was then eluted with 2 BV of 0.5 mol/L sulphuric acid, at ambient temperature. The eluate was collected in a single fraction and analysed for cobalt.

The cobalt concentration in the solution exiting the column during the adsorption, wash and elution steps is shown in Figure 6. Unfortunately, the adsorption test was stopped before complete breakthrough was achieved. Nevertheless, the test confirmed that the resin has a good capacity for cobalt in the presence of nickel, as indicated by the fact that breakthrough only occurred after several bedvolumes had passed through the resin bed. Efficient displacement of the entrained feed liquor was achieved within less than 2 BV of wash water. This portion of liquid contained a high concentration of nickel and it is envisaged that it would be returned to the circuit ahead of the IX. Complete elution was achieved with 2 BV of acid, ensuring transfer of the cobalt from the feed to a small concentrated eluate stream.

FIGURE 6

MTX8010, Cobalt Concentration During Adsorption, Wash and Elution Steps



A batch test was also performed, to confirm the nickel and cobalt loading. The MTX8010 was contacted with synthetic liquor containing 120 g/L nickel and 1 g/L cobalt at a solution:resin ratio of 100. The temperature was maintained at 50 °C and the pH controlled at 5.8 throughout the contact period. After 24 hours, the resin and liquor were separated and a small volume of resin was eluted with 50 g/L sulphuric acid to determine the metal loadings. A total of 8 g/L cobalt and 1 g/L nickel loaded onto the resin. It should be possible to decrease the extent of nickel co-loading by operating at a slightly lower pH.

Reagent Stability

Loss of solvent from the resin matrix is a concern, because it would mean regular replacement of reagent to ensure that the performance of the circuit remained as per design. This risk is mitigated by incorporating the organic reagent during the manufacturing process.

In addition, the resins should not be exposed to alkaline conditions. Care must be taken to ensure that the feed, wash waters and eluate are acidified. In the case of the MTX7010, a maximum operating pH of 4 is recommended, while the MTX8010 should not be exposed to pH levels exceeding 6.

To confirm the stabilities of the solvents when exposed to liquors of varying acidity and metal concentration (as would be encountered on a full-scale plant), a special cycling test was developed, the steps of which are described in Table 4.

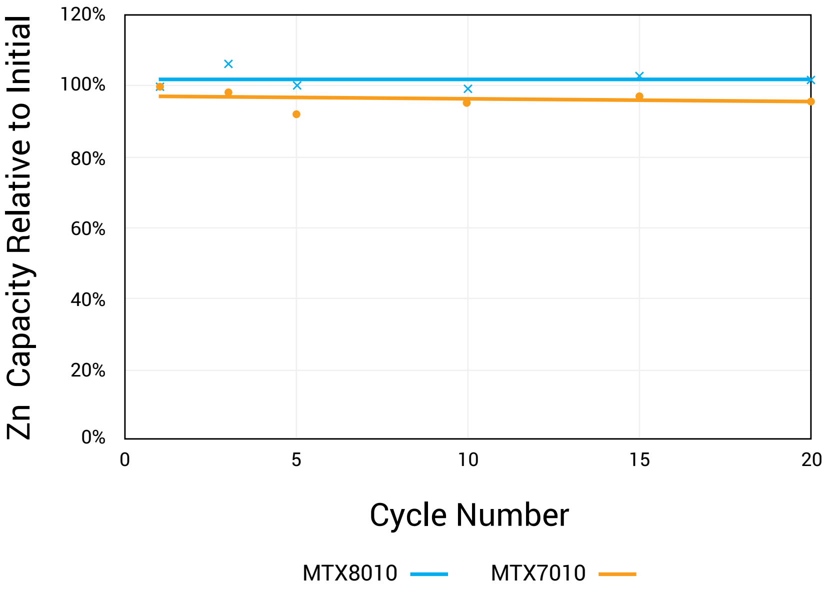
TABLE 3 Cycling Test Conditions

		Solution	Solution Volume, BV	Flowrate, BV/h
Step 1	Loading	Zn acetate, acidified to pH 5	10	5
Step 2	Water Wash	Demineralised water, acidified to pH 3	5	5
Step 3	Elution	5% sulphuric acid	5	5
Step 4	Water Wash	Demineralised water, acidified to pH 3	4	5

Each resin was subjected to 20 cycles, where each cycle consisted of Loading, Washing, Elution, followed by a second Washing step. The eluates were analysed to determine the zinc capacity of the resin after cycle numbers 1, 3, 5, 10, 15 and 20. The data are plotted in Figure 7. No loss of capacity was measured after 20 cycles.

FIGURE 7

Cycling Tests, Zinc Capacity



Conclusions

Solvent-impregnated resins can be used with success to remove impurities from concentrated cobalt and nickel streams. Two different products were tested, namely:

- MTX7010, impregnated with di(2-ethylhexyl)phosphoric acid;
- MTX8010, impregnated with di(2,4,4-trimethylpentyl)phosphinic acid.

MTX7010 is recommended for the removal of low levels of zinc from concentrated cobalt liquor. MTX8010 has good affinity for cobalt and is recommended for the removal of low levels of cobalt from concentrated nickel liquors.

The stabilities of the reagents were tested by subjecting the impregnated resins to special cycling tests, during which the resins were sequentially subjected to liquors with varying acidity and metal concentration (to simulate fluctuations that the resins will be exposed to in a full-scale operation). A cycle consisted of loading, primary water wash, elution and a final water wash. No reagent losses were detected after 20 cycles, confirming stability of the reagents.

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References

1. Kauczor, H.W., Meyer, A. Structure and properties of Levextrel resins. Hydrometallurgy 1978, 3, 65–73.

2. London Metal Exchange (2018). Special contract rules for primary nickel quality: ASTM standard specification for nickel B39-79 (2013). https://www.lme.com/media/Files/Branding/Chemicalcomposition/Non-ferrous/chemical-composition/nickel.pdf

3. London Metal Exchange (2018). Chemical composition for each cobalt brand. https://www.lme.com/en-GB/Metals/Minor-metals/cobalt/Approved-brands

4. Mayze, R. An engineering comparison of the three treatment flow sheets in Western Australian nickel laterite projects, in Proceedings of the ALTA Nickel/Cobalt Pressure Leaching and Hydrometallurgy Forum, ALTA Metallurgical Services, Melbourne, 1999.

5. Sole, K.C. The evolution of cobalt-nickel separation and purification technologies: Fifty years of solvent extraction and ion exchange. In Proceedings of the First Global Conference on Extractive Metallurgy: Extraction 2018. The Minerals, Metals and Materials Society, Warrendale, PA, 2018, pp.1167–1191. https:doi.org/10.1007/978-3-319-95022-8_95.

6. Taute, J.J., Sole, K.C., Hardwick, E. Removal of zinc from a base-metal solution using ion exchange at Rustenburg Base Metal Refiners, Journal of Chemical Technology and Biotechnology, 2014, 89, 919–926.

7. Vaughan, J., Dieters, C., Fu, W., Byrne, K.l. Properties of Lewatit TP272, a commercial solvent impregnated cation exchange resin for cobalt recovery. Minerals Engineering (2015), http://dx.doi.org/jmineng.2015.07.005

8. Wyethe, J.P., Kotze, M.H. Impurity removal by fixed bed ion exchange from cobalt electrolyte derived from the Kakanda Tailings Dump. In Proceedings of ALTA SX/IX 2000; ALTA Metallurgical Services, Melbourne, 2000.

9. Yahorava, V., Bazhko, V., Leso, R.R., Solvent-impregnated resins for niche applications in metals processing. In Proceedings of Copper Cobalt Africa, incorporating the 9th Southern African Base Metals Conference, Southern African Institute of Mining and Metallurgy, Livingstone, Zambia, 10–12 July 2018, pp. 345–352.

Notes

Notes

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