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Urban Mining: the application of ion exchange resins

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ABSTRACT

Urban mining is defined as the process of recovering and re-using the waste produced by a city. Metals recovered from electronics and electric vehicle batteries will form a critical raw material in future production.

The superior selectivity of ion exchange resins ensure that they form a critical part of any hydrometallurgical processing route to produce high-purity metal products from recycled components.

INTRODUCTION

Modern cities generate vast quantities of waste that can be re-used or recycled. Such material can include the following:

- paper, plastic, glass
- electronic waste, such as cellphones, computers, televisions sets
- construction waste
- spent batteries

Of particular interest currently is the need to develop economically viable methods to recycle spent electric vehicle (EV) batteries. The use of electric vehicles is forecast to increase exponentially in the coming decades. The main reason for changing from the internal combustion engine to electric vehicles is to decrease the negative effect of human activities on the environment. It is thus critical to ensure that this change does not bring about even greater harm by producing large waste heaps of spent batteries.

EV batteries are considered unsuitable for use in a vehicle when the available capacity reaches 75% of the original capacity. This is estimated to be after approximately 10 years of use. The life of the battery can be extended by repurposing it for stationary energy storage, where space and mass is less important. Nevertheless, not all EV batteries will find a second life in this manner and the large majority of batteries will have to be recycled. Legislation in some parts of the world is already dictating that future batteries should contain a certain minimum portion of recycled metal to minimize the effect on the limited global resources of cobalt, nickel, lithium and other components.

RECYCLING ELECTRIC VEHICLE BATTERIES

While commonly referred to as lithium batteries, the lithium only makes up around 5% of the EV battery. It also contains graphite for the anode, aluminium or steel casing, plastic, copper wire and the metals used in the cathode. The name of the battery refers to the major components in the cathode, as shown in Table 1 (Verbaan, 2023).

Table 1

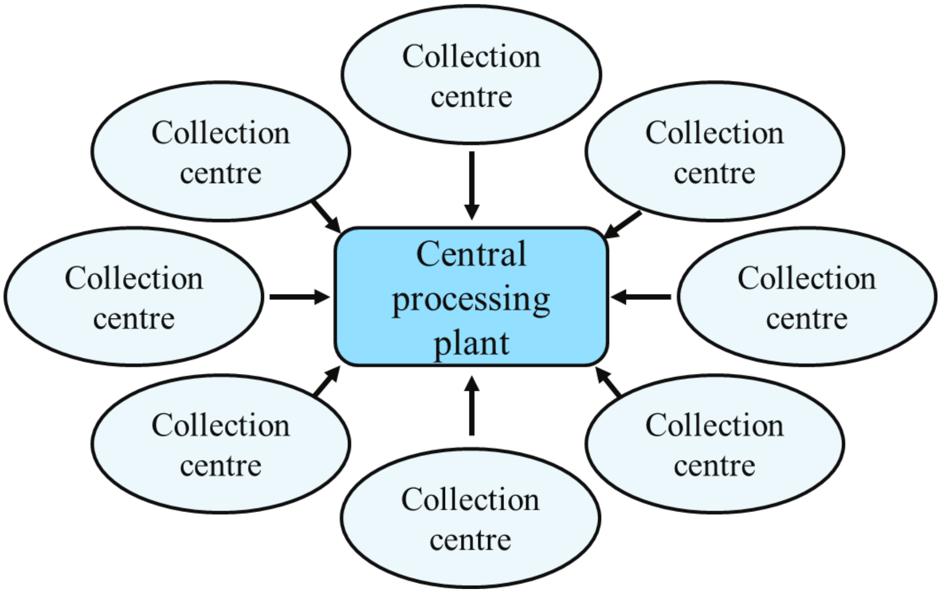
Composition of EV batteries

Battery	Composition of the cathode
LCO	Lithium cobalt oxide
NMC (622, 111, 811, 532)	Lithium nickel manganese cobalt oxide
NCA	Lithium nickel cobalt aluminium oxide
LMO	Lithium manganese oxide
LFP	Lithium iron (Fe) phosphate
NiOOH	Nickel oxy hydroxide

Recyclers of spent batteries use a hub-and-spoke type of system. The batteries are collected at multiple depots spread throughout a region. At these depots, physical dismantling of the batteries can be done. This involves the separation of the plastic and aluminium casing from the internals of the battery. The black mass, which is the portion that contains the valuable metals, is transported to a central processing facility, where it is separated into individual metal components of high purity. The logistical process is described in Figure 1.

Figure 1

Hub-and-spoke collection and processing of EV batteries



This arrangement ensures collection depots are close to the source. It also allows discharging at the depot, thereby minimizing the risk of batteries catching fire during transport. A single central processing plant is preferable over a number of smaller satellite processing plants, due to the complexity and associated cost of the plant.

The processing of the black mass into its constituent metals can be done according to different routes. A pyrometallurgic route involves smelting at high temperatures. A hydrometallurgical route involves the dissolution of the metals in acid, to produce a metal-rich aqueous stream which undergoes further processing to separate it into the individual metal-salts. A combination of processing routes may also be used. Ion exchange resins can play a pivotal role in the recycling of EV batteries that is done via a hydrometallurgical route.

ION EXCHANGE

The composition of the leach liquor produced after acid leaching of the black mass varies, according to the nature of the batteries that were used as feed material to the leach. The technology is constantly evolving, and the composition of the batteries that are produced in the future is expected to differ from what is currently produced. To ensure flexibility in the production of future batteries, metal salts of very high purity have to be produced.

Typically, the concentrations of the main elements, such as lithium, nickel and cobalt, will be quite high in the pregnant leach liquor, in the region of several grams per litre. Impurities, such as copper, zinc and aluminium are expected to be lower, typically <300 ppm.

CHELATING RESINS: Ion exchange is not suitable to economically recover base metals from highly concentrated liquors, but it is very efficient in removing low concentrations of impurities to very low levels. A range of highly selective resins exist that can be used to target specific elements, as shown in Table 2.

Table 2

Matching the target impurity with the right resin

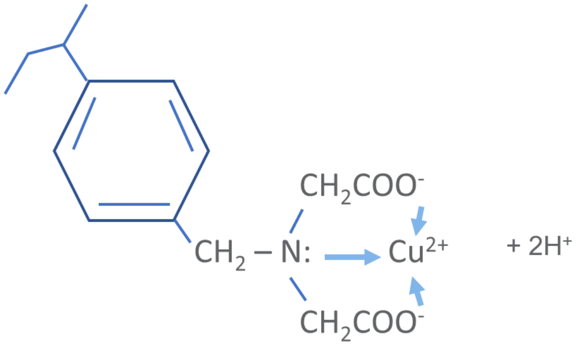
Target element	**Type of resin**	**Purolite product**
Copper, cobalt, nickel, zinc	Imino diacetic acid	MTS9300, S9320
Copper, zinc	Amino methyl phosphonic acid	MTS9500
Nickel from cobalt	Bis-picolylamine	MTS9600
Cobalt from nickel	Solvent impregnated: phosphinic acid	MTX8010
Calcium, zinc	Solvent impregnated: D2EHPA	MTX7010
Boron	n-methyl glucamine	S108

These chelating resins have a high selectivity for the specific target ions, due to the special nature of their functional groups. This is illustrated in

Figure 2, using the example of an imino-diacetic acid resin extracting copper. The two carboxylic groups each exchange a H^+ to extract the Cu^{2+} cation from the solution. At the same time, the nitrogen atom of the functional group shares a free electron pair with the copper. The combination of the two mechanisms, namely ion exchange and electron pair sharing, ensures superior selectivity for some metals over others.

Figure 2

Imino diacetic acid resin extracting copper



A typical selectivity range for this resin, operating under acidic conditions, looks as follows (Purolite, 2024):

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

The selectivity of the chelating resins is sensitive to pH and it is critical to operate at a pH that ensures maximum loading of the target element. For example, the imino diacetic acid resin is selective for base metals over the alkaline earth elements (calcium and magnesium) under acidic conditions. However, under alkaline conditions, the resin has good selectivity for the alkaline earths and can be used to selectively remove calcium and magnesium from the alkali metals, such as lithium, to produce high-purity lithium hydroxide.

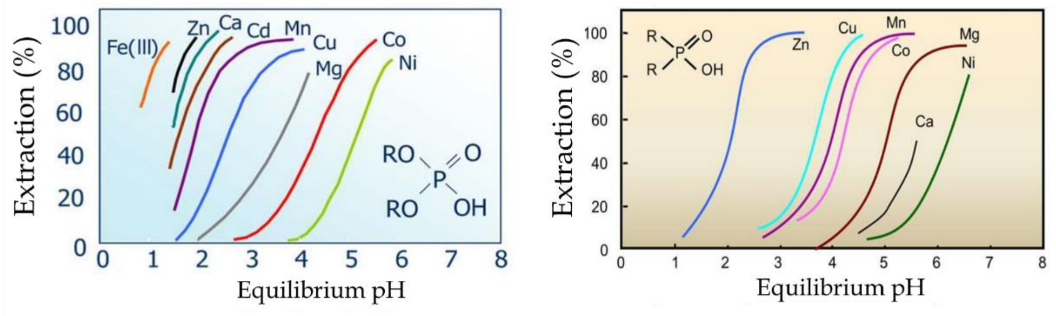
SOLVENT IMPREGNATED RESINS: While a wide range of IX resins exist that can be used for impurity removal, there remain some gaps in the portfolio. Organic solvents exist that can fill that gap. Combining the selectivity of metal-selective organic solvents with the engineering advantages of an IX resin provides the industry with additional impurity-removal options. Two ptions that are applicable to purification of base metal solutions are those impregnated with:

- D2EHPA (di-2-ethyl-hexyl-phosphoric acid);
- TMPPA bis(2,4,4-trimethylpentyl)phosphonic acid.

The pH vs. Extraction curves for the two solvents are shown in **Figure *3*** (Sole, 2018), with D2EHPA on the left and di(2,4,4-trimethylpentyl)phosphonic acid on the right. These curves clearly show the good separation that can be achieved between a number of typical impurities and cobalt (as well as nickel). For example, zinc and calcium is efficiently extracted by the D2EHPA-impregnated product at pH <2, whereas cobalt is only extracted at pH >4. By carefully controlling the pH of the liquor at pH 2, it is thus possible to selectively remove zinc and calcium from the liquor while allowing cobalt to pass through the resinbed without a change in concentration.

Figure 3

pH vs Extraction profiles for D2EHPA and TMPPA

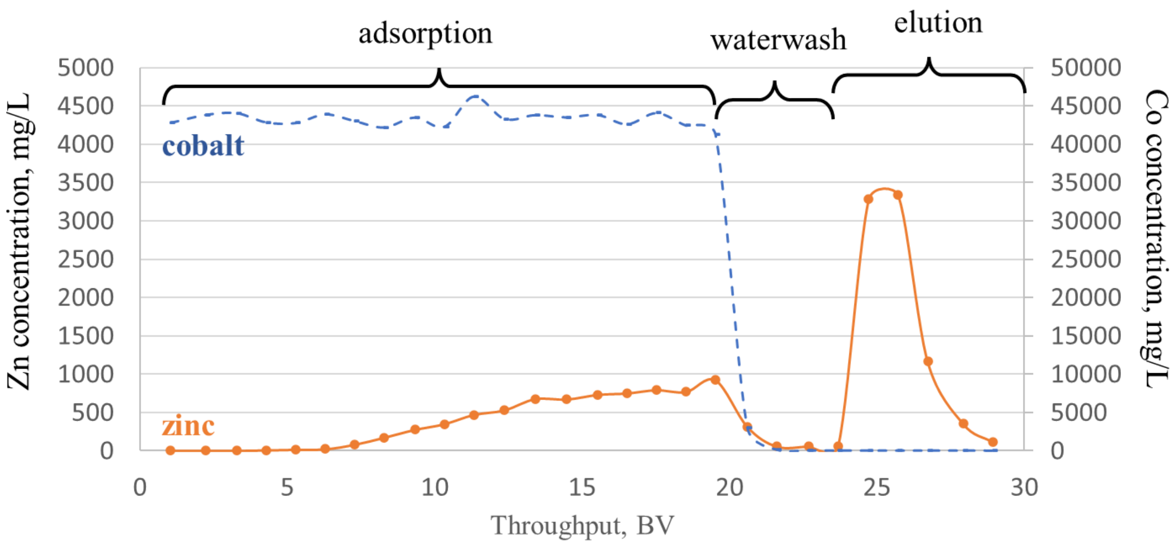


The ability of the MTX7010 D2EHPA-impregnated product to remove zinc from cobalt was tested using synthetic liquor with pH 2, containing 50 g/L cobalt and 1 g/L zinc (Van Deventer, 2019). The resin was loaded into a column and the liquor passed through it a flowrate of 2 bedvolumes per hour (BV/h), where a bedvolume is equal to the volume of resin used in the test. The barren samples exiting the column were collected and analysed for zinc and cobalt. After completion of the adsorption test, the entrained feed liquor was rinsed from the column by passing 5 bedvolumes of water through the resin bed. The resin was then eluted with 5 bedvolumes of 1 mol/l sulfuric acid. 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 4.

Figure 4

Cobalt and zinc concentrations during adsorption, wash and elution steps



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

Efficient displacement of the feed liquor was achieved within 2 BV of waterwash. The barren liquor generated during this step has the same composition as that of the Feed liquor (albeit slightly diluted) and can be returned upstream of the ion exchange, thereby minimizing the loss of valuable cobalt. The majority (94%) of the zinc was eluted from the resin within 3 BV of acid. The small amount of cobalt that reported to this stream is likely due to entrained Feed liquor, rather than extraction onto the resin. This proves that it is possible to remove zinc from a relatively large volume of Feed liquor and transferring it to a small volume at much higher concentration.

The solvent is incorporated right at the start of production of the resin bead, by adding it to the mixture of styrene and divinylbenzene that forms the backbone of the resin (Kauczor, 1978). This ensures that the solvent is strongly bound to the resin matrix and does not leak during use. Loss of reagent can result in reduced capacity, as well as contamination of downstream processes (as experienced with entrained organics from conventional solvent extraction unit operations).

DESIGN: After choosing the best resin for a specific application, the next step is to ensure the optimum contactor design is selected. To achieve the stringent specifications set by the battery metals industry, a fixed bed configuration is used. During operation of a fixed bed system, a vertical concentration profile is established across the resin bed. The resin at the top of the column, that comes into contact with the Feed liquor, is loaded to maximum capacity. At the bottom of the column, where the barren liquor exits, sufficient resin capacity is available to ensure minimum impurity leakage. Continuous fixed bed systems use 20 to 30 columns in series. These systems have special distribution valves that allows any column to be at any time in either adsorption, desorption, or in the displacement rinse phase.

A simpler system, that also provides a reasonable amount of flexibility, consists of 3 columns in series, also referred to as a lead-lag-lag or merry-go-round configuration. Once the barren liquor exiting the first column reaches a pre-determined concentration (as determined during laboratory and pilot plant testwork), the column is taken off-line and eluted. The Feed liquor is immediately directed to the second column, which now becomes the lead column and operation is continued with 2 columns in series. Once elution has been completed, this column is returned to operation in the third position and operation continues with three columns in series. This configuration ensures that the last column acts as a final polisher to prevent impurity leakage to the treated liquor.

Typical operating conditions for the removal of impurities via ion exchange from solutions generated in hydrometallurgical processes are provided in Table 3. Note that flowrates are expressed in bed volumes per hour (BV/h). The use of such a relative number ensures easy comparison between units of different sizes, for example between laboratory scale, pilot scale and full-scale operations.

Table 3

Typical operating conditions

	Typical operating conditions	Comments
Configuration	Fixed bed, 3 columns in series, lead-lag-lag	Allows maximum resin utilization in the first column while preventing leakage from the last column
Service/sorption	4 to 8 BV/h	Relatively slow flowrate, due to slower kinetics of large chelating functional groups
Elution	2 BV/h	typical
Eluant	HCl or H_2SO_4	Chosen to fit in with the matrix, to prevent contamination
Conditioning	NaOH (typically) LiOH (if Na is undesirable)	The purpose is to displace the H^+ on the resin, to prevent the pH from dropping below the target value during sorption

CONCLUSIONS

An increase in EV sales will drive the demand for the metals used in these batteries, most notably lithium, nickel, cobalt, and manganese. Recycled spent batteries will be a critical source of raw material in the production of new batteries in the future.

A wide range of highly selective commercial ion exchange resins, both chelating and solvent-impregnated, are available that can be used in the hydrometallurgical recycling process to produce metal salts of high purity. The selectivity of these resins for certain elements over others are determined by the nature of the functional group. Additional selectivity is provided by careful control of the pH of the Feed liquor.

Selecting the right design further improves the separation and purification that can be achieved. The most efficient removal of impurities is achieved in a fixed bed configuration, where a vertical concentration profile is established across the resinbed. A fixed bed system, using 3 columns in series, in a lead-lag-lag configuration, provides flexibility. It also ensures maximum utilization of the resin in the first column, whilst adhering to strict impurity leakage conditions.

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