IDA resins: Versatile specialists

Dr Stefan Neumann of **Lanxess** looks at a selective ion exchanger for handling heavy metals

Transition - or heavy - metals play a key role in many technical processes, but they are often found only in very low concentrations that make processing difficult, for example in wastewater, as catalyst residue in a product or in the mining of low concentrate ores.

Transition metals such as lead, cadmium, cobalt, copper and nickel are valuable and rapidly diminishing raw materials. The decreasing availability and rising prices of raw materials are forcing industry to search for efficient methods of finding new sources, minimising losses and increasing purity.

Conversely, these metals possess toxic properties that adversely affect both human health and the environment, and these therefore need to be removed from wastewater, groundwater and drinking water. The use of special ion exchangers that can selectively bind and concentrate these offers interesting potential in both ways. Not all ion exchangers are suitable, however.

Selectivity the key

'Normal' ion exchange resins that are primarily used to soften water via the adsorption of Ca^{2+} and Mg^{2+} ions are usually unsuitable for the adsorption of heavy metals because the functional groups responsible for adsorption are normally sulphonic acids or salts that bind metal ions mainly via electrostatic interactions and therefore exhibit only limited selectivity. Therefore, traces of nickel ions would be adsorbed onto these resins, but would then be displaced quickly by other ions present in the matrix at a much higher concentration.

Nevertheless, some resins can offer very high selectivity for transition metals. These have been around since the 1960s but have previously been hugely overshadowed because 70% of all ion exchange resins are used to soften water. Such resins, like Lanxess's Lewatit TP 207 and 208, are highly selective, due to their chelating anchor groups.

The functional groups responsible for binding metal ions to these resins are immobilised iminodiacetic acids (IDAs). These have three binding points per anchor group via three interlinked ligands - the two acid groups and the free electron pair of the imino nitrogen (Figure 1).

This causes a strong entropic effect. Once bound, the metal has to break away simultaneously from three binding points before it can be desorbed. Furthermore, the bond is created by complex chemical mechanisms as well as by electrostatic forces. For example, nitrogen can interact with the d-orbital transition metal ions via its free electron pair.

Because of this, IDA resins show an extremely selective adsorption effect on all metal ions with suitable electron structures - in particular, heavy and transition metals. In complete contrast to conditions found with 'conventional' ion exchangers, the binding of alkali metals, such as sodium or potassium, that do not have 'docking points' for this lone pair is much poorer

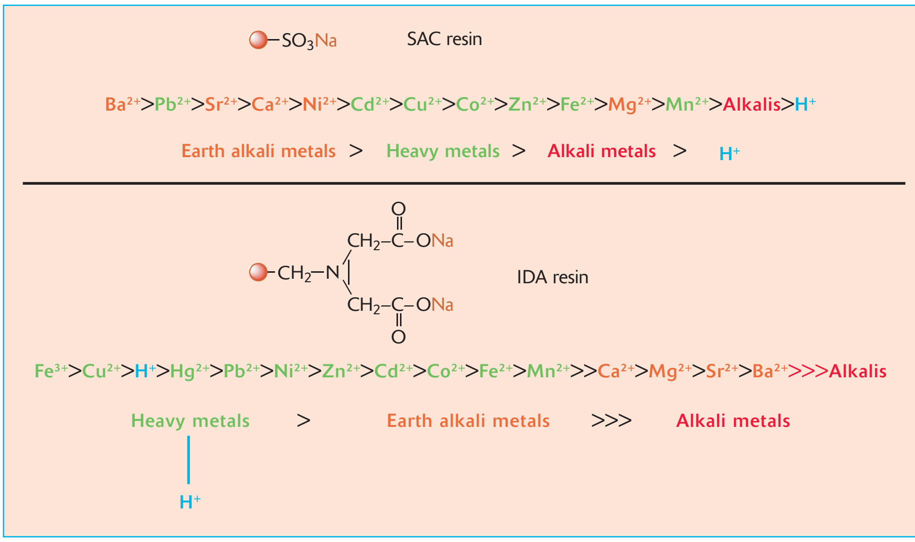


Figure 2 - Selectivity of resins: Non-selective, strongly acidic cation exchanger (SAC, above**) v heavy metal-selective resin (IDA,** below**)**

Chelating IDA acids bind metal ions much better than classic ion exchangers like monodentate sulphonic acids, which can only achieve this with difficulty, if at all. Earth alkali metals, such as calcium and magnesium, are bound by IDA groups via a complex chemical interaction. Although these bonds are significantly stronger than for alkali metals, they are still weaker than the bonds for heavy metal ions.

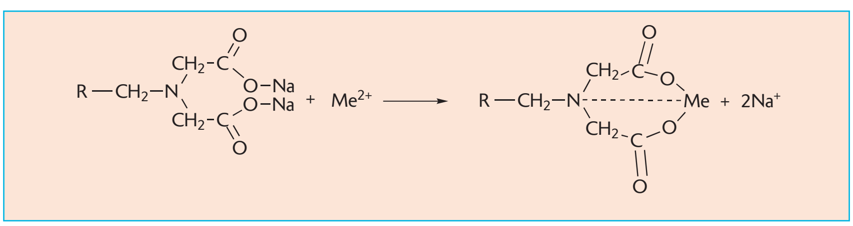
IDA resins are therefore able to extract even the smallest concentrations of, for example, copper, nickel or lead ions from 30% brine solutions. The bond established with these is so strong that they can no longer be displaced by sodium ions or others.

This capability makes IDA ion exchangers, also known as 'selective resins', attractive candidates for handling extremely low concentrations of heavy metals in a wide range of matrices. Residual concentrations of <10 μg/litre are technically viable.

These resins are also economical to use, due to their normally high uptake capacities and the long periods between regeneration cycles associated with this. For example, filters for separating nickel from drinking water can achieve a service life of up to 20,000 hours in continuous operation.

As heavy metals are involved in many areas of technology, IDA resins are suited to a wide range of applications throughout the entire value chain. For this reason, selective resins seem to represent - paradoxically and yet justifiably - a universally applicable product.

Figure 1 - Reaction scheme for binding a heavy metal ion to an IDA resin



Application areas

A key application is in the **extraction and cleaning of metals**. The demand for technically interesting metals is growing, while the amount of ores with high metal concentrations is declining rapidly. Consequently, mined ores often need to be concentrated before they can be isolated in a further process.

IDA resins are an ideal auxiliary product for this. Unlike conventional liquid extraction media, they can process solutions with low concentrations of metal and high suspended substance contents. IDA resins can be used to produce concentrations in ranges of up to several percentage points.

Their high affinity for copper, nickel, cobalt and other metals also makes it possible to extract them from the wastewater of mining plants, especially leachate from slag heaps and/or residue deposits. A reference project in one of the world's largest copper mines, in Bor, Serbia, recently provided compelling evidence of the cost-efficiency offered by this process.

Another area of application in the mining industry is the separation and cleaning of metals. For example, IDA resins can be used to remove troublesome traces of copper from nickel concentrates.

The broadest application area for IDA resins is in the **fine purification of educt and product streams**. Within this area, the most widely used process is is the softening of brine streams (30% NaCl) during chlorine production.

In this application, selective ion exchangers protect the sensitive membranes in the electrolytic cell against the blocking effects caused by calcium and magnesium. Any aluminium and nickel ions present in the brine's raw materials can also be removed reliably in this process.

Products in the food industry can also contain heavy metals, such as copper finding its way into wine via pesticides. According to the German Federal Environment Agency, levels of lead in redcurrant juice often exceed legal limits. Nickel has also been founds in process streams from the sugar industry.

The use of IDA resins in these areas has already been investigated in the laboratory and has also proven itself in a number of practical cases. In these applications, the ion exchanger only removes unwanted heavy metals, leaving the product otherwise unaffected.

IDA resins can also be used in **recycling product streams**. The electrolytes used for surface coating in galvanisation inevitably become contaminated during use. For example, corrosion processes cause iron ions to become concentrated in the zinc electrolyte used when coating sheet steel with zinc.

Figure 3 shows how Lewatit TP 207 ion exchange resins have been uses in this application. As IDA resins exhibit greater selectivity towards trivalent iron than zinc, they can extract iron ions from the zinc solutions galvanisation baths, feeding the reusable Zn^{2+} and Ni^{2+} back into the process. As a result, the electrolytes are continuously cleaned, enabling the quality of the zinc coating to be maintained constantly at a high level. Costly preparation and disposal procedures for used zinc solutions also become redundant.

A further example of cost-effective recycling in product streams is the recovery of cobalt from solutions produced during the manufacture of coatings containing it. The concentrate produced after the regeneration of the ion exchanger can be fed back into the process. This prevents the contamination of wastewater and minimises the loss of reusable materials.

Quality check on ion exchanger at Lanxess

IDA resins can be used in **purifying wastewater streams** containing heavy metals in detoxification plants. The central process involved here relies on chemical precipitation caused by adding lyes and/or sulphides.

However, it is sometimes difficult to ensure that heavy metal emission values are not exceeded when using this method. Challenges include the interactions between ions, the high levels of residual solubility for some metals and the formation of soluble hydroxy and other complexes if insufficient dosages of the precipitant are used.

Adherence to limits can be ensured when IDA resins are used after the precipitation stage. What are known as 'final exchangers' or 'police filters' also work, expecially if toxic sulphides are not used in the precipitation stage.

The process can be set so that environmentally friendly earth alkali and alkali metals are not retained and regeneration material from the ion exchanger can then be fed back into the precipitation stage. If wastewater contains only one heavy metal contaminant (as is the case in the PCB industry, with copper), the concentrate can be fed back into a galvanic recovery process as appropriate.

Processes used in the **purification of groundwater** include the 'pump-and-treat process'. This involves bringing polluted water to the surface, treating it and then pumping it back underground. IDA resins are ideal for treating water that is contaminated with, for example, traces of heavy metals such as nickel, cobalt, zinc, cadmium or lead.

Again, only the harmful substances are selected for adsorption, with the remaining components of the water and its pH value remaining unaffected. Results from an extended efficacy test, recently carried out under the supervision of the German Federal Environment Agency, show that nickel, for example, can also be removed efficiently and cost-effectively from drinking water using IDA resin without adversely affecting the quality of the water.

Development continues

This article can only provide a brief overview of the diverse range of applications for IDA resins that exist today. Others are sure to be added over the years ahead and product development work is ongoing.

Lanxess's own IDA resins are being developed in different grain-size grades to optimise them even further for various application areas. Further developments will include looking at modifying the internal structure of the resin by altering the polymer structure and degree of substitution so as to accelerate the kinetics of the exchange procedure or to enable selectivity to be set even more precisely. Working on customer-specific services will also increase.

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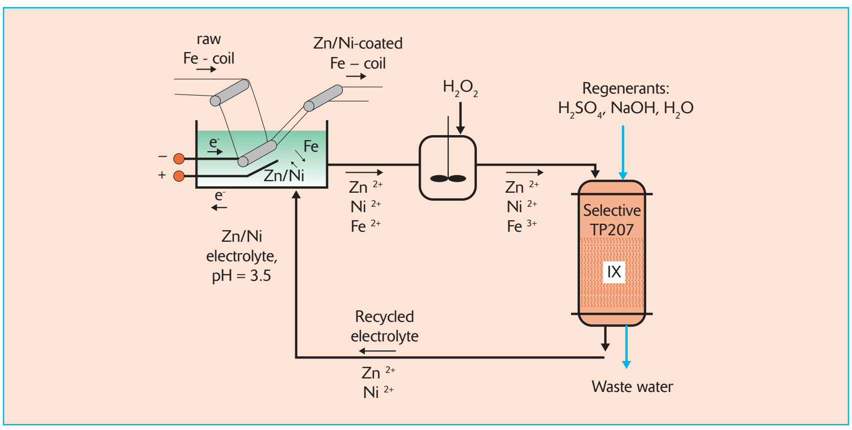

Figure 3 - Process flow of zinc-coating of sheet steel