



# Application of Ion Exchange in Industrial Wastewaters

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Ion exchange is a naturally occurring chemical process by which one ion in solution (typically aqueous but not exclusively) is exchanged for another. A very common commercial application of this principle is found in many homes with a water softener. Within a water softener a bottle filled with a cation exchange resin replaces ions in well water often associated with hardness (e.g. calcium and magnesium) with sodium. Ca and Mg salts tend to be insoluble and are often associated with scaling as they "plate" out in tea pots, hot water heaters, faucets, etc. Sodium salts tend to be quite soluble and generally do not precipitate resulting in scale. Replacing the ions associated with hardness with sodium (softening) yields a higher quality water for most domestic and commercial applications.



Ion Exchange Bottle

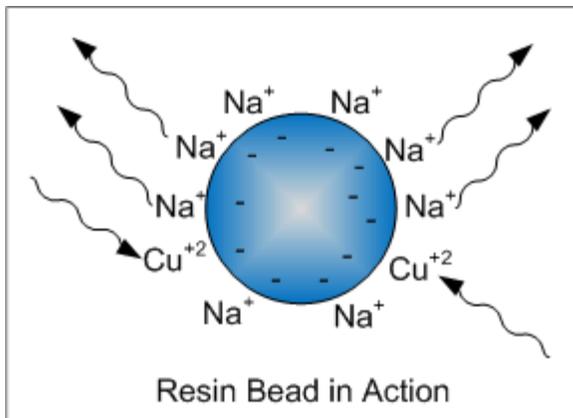


Resin Beads

In industrial applications such as de-ionized water systems used in the production of ultrapure water (UPW) free naturally occurring cations (Ca, Mg, Fe, etc.) are removed from water and replaced with H<sup>+</sup> and free anions (SO<sub>4</sub>, Cl, F, etc.) are replaced with OH<sup>-</sup>.

The capacity of a resin to take up target cations or anions is limited and when exhausted the resin must be regenerated. Ion exchange reactions are generally reversible and the regeneration process reverses the reactions freeing up the ion exchange sites previously "consumed" during the take up of the target species.

The reaction depicted below is a simplification of a cation resin regenerated in the sodium state (R<sub>Na</sub>) that, when in the presence of free copper in solution, will give up two sodium (Na<sup>+</sup>) ions in exchange for a single divalent copper ion (Cu<sup>+2</sup>).



As shown in the depiction to the left a single ion exchange bead will have many sites upon which is attached a loosely bound ion such as Na<sup>+</sup> in the case of a cation exchanger regenerated in a sodium form. When exposed to free ions for which the bead has a higher affinity, such as copper with a charge of +2 (Cu<sup>+2</sup>) the bead will liberate two Na<sup>+</sup> ions and tie up one Cu<sup>+2</sup> ion. One can observe the normally amber colored bead change to a deep blue color as the bead approaches saturation with the Cu<sup>+2</sup> ion.

Ion exchange reactions are normally reversible and this is displayed in the regeneration of exhausted resins. In time insufficient sites with free  $\text{Na}^+$  become available for the resin to be of use and the resin bed is considered to be exhausted. Fortunately the reactions described above are reversible and the bed can be regenerated. This typically involves a backwashing step with clean water to clean the bottle and resin of debris such as suspended solids, precipitated metals, etc. The resin is then exposed, over a period of time, to a low flow of diluted acid such as 10% HCl. The  $\text{Cu}^{+2}$  that was bound to the resin beads now "dissolves" back into solution as the bead gives up the  $\text{Cu}^{+2}$  in favor of  $\text{H}^+$  for which it has a higher affinity (under low pH conditions). The  $\text{Cu}^{+2}$  now exists in solution in a concentrated form in the spent regeneration acid and the resin beads now exist in a  $\text{H}^+$  regenerated form. In order to improve upon bed capacity the bed is now converted to  $\text{Na}^+$  form by exposure to a salt brine or, preferably, a dilute caustic (NaOH) solution.

**Bed Capacity vs. Influent Loading    Operating Cost based on Regeneration    Operating Cost base on Resin Replacement**

The major factors in the cost of operation are the cost of the regeneration chemicals and the cost to treat the spent regeneration chemicals that are now heavily laden with heavy metals.

The graph above provides a rough estimation of **Bed Capacity vs. Influent Metals Loading** as well as the **Cost of Operation / Liter of waste**. This is actual data from a  $\text{Cu}^{+2}$  reduction system for a one cubic foot resin bed of a heavy metal selective chelating cation resin. This resin has a very high capacity for divalent metals and low affinity for monovalent metals (i.e. Na, Mg, etc.).

The **Capacity** curve is not linear because there is competition from both monovalent and divalent ions in solution other than just copper. The impact of ions other than the target species increases as the concentration of the target species decreases in solution.

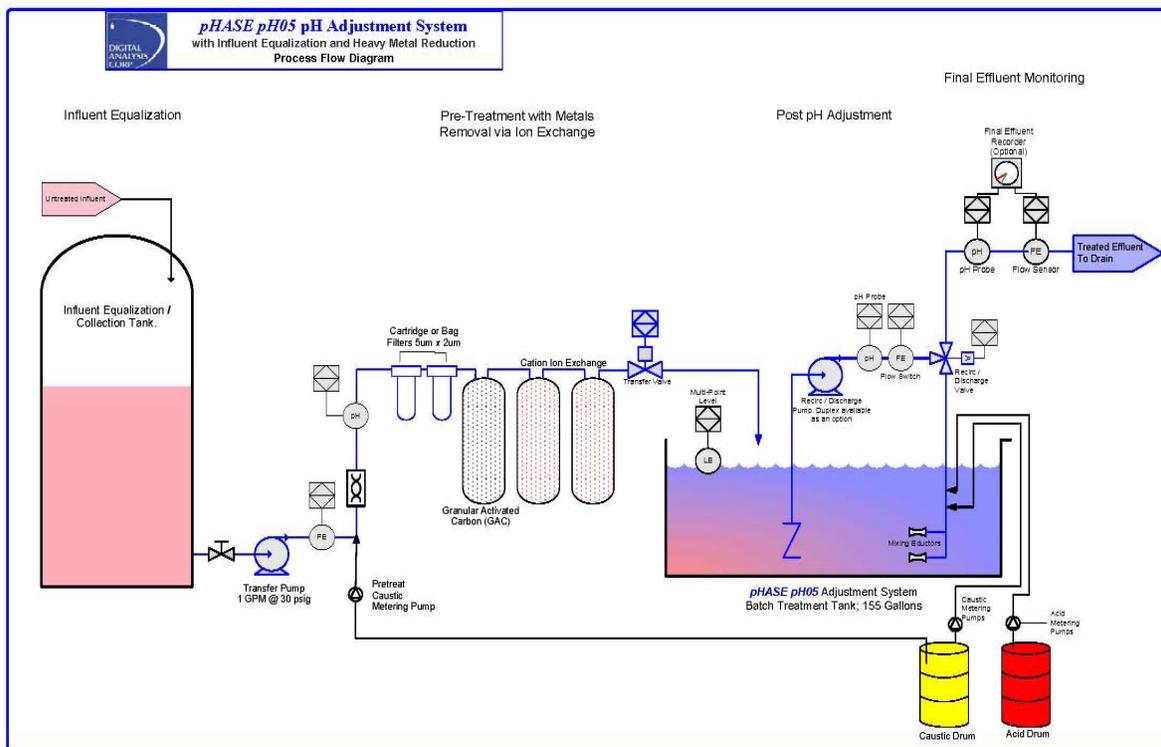
The **Cost** curve reflects the cost of operation resulting from the cost of the regeneration chemicals (acid, base, and water) as well as the cost to treat spent regeneration chemicals and to haul off the resulting hazardous sludge product. This cost is very highly variable and is a function of local conditions such as chemical costs, sludge disposal costs, and constituents of the waste stream (e.g. the presence of oil, even

in low amounts, will decrease bed capacity as the resin beads become coated thereby isolating ion exchange sites from the dissolved species in solution).

An alternate **Cost Curve** is shown that depicts cost of operation when local regeneration is not used and the resin is simply discarded as a hazardous waste. This is a very common option for low volume generators that cannot justify the capital cost and manpower for a local regeneration system.

### System Example:

In a typical application we will have an acidic wastewater stream from a plating, pickling, or stripping operation that will have some dissolved metals in solution. For example, a stainless steel electropolishing operation typically yields low levels of both Cr+3 and Ni in an acidic solution. Or a wire drawing operation will yield both Cu and Cd in an acidic solution. With metal levels less than 50 mg/L in the waste stream a system using ion exchange followed by pH adjustment will produce a treated waste stream with metals < 0.020 mg / L (if not significantly lower) and a pH in the range of  $6.0 < \text{pH} < 9.0$ .



The Process Flow Diagram (PFD) illustrated above shows our pHASE\_MX\_pH05 metal reduction system which is designed to handle 50 GPH of acidic influent flow laden with metals such as Cu and Cd. All wastes are collected within the influent equalization system from which batch transfer take place. If necessary we employ a simple pretreatment loop within which we pH adjust into an optimum range for metal reduction via ion exchange (e.g.  $3.0 < \text{pH} < 5.0$ ).

The effluent stream to be treated is pumped through a mechanical filtration step to reduce suspended solids, a carbon filter to reduce oxidizing agents and organics, and finally ion exchange columns to remove heavy metals. From the ion exchange columns the effluent is treated by the pH adjustment step into an acceptable discharge range (e.g.  $6.0 < \text{pH} < 9.0$ ) and then to drain via a final effluent monitoring system.

The ion exchange bottles can then be regenerated on site or they can simply be emptied into a hazardous waste drum and hauled off as such. This is a common option for very low volume generators.

Ion exchange can also be used as a final effluent polishing step to remove trace amounts of heavy metals at the end of a conventional metal hydroxide precipitation system. Since optimal precipitation occurs at different pH values for different metals it may not be possible to achieve permit compliance levels for all metals. Ion exchange is an excellent tool for targeting all metals that have broken through a precipitation step. Ion exchange may also be a good tool for targeting metals that are tied up with sequestering agents.

Advantages of Ion Exchange over other conventional treatment methods (e.g. precipitation):

- Capable of achieving very low levels of residual metals. Typically in the low ppb range.
- For low volume generators the capital cost can be quite low
- Has some ability to remove metals in the presence of chelating agents
- For binary solutions or streams low in TDS can be used for recycling purposes

Disadvantages:

- Cost of operation is higher
- For all but low volume generators the capital cost will be higher

Summary:

Among the best available technologies for heavy metal removal from industrial wastewater ion exchange must always be at or near the top of the list when considering available methodologies. For low flows or for applications where the influent metal loading is low this is often the best approach and sometimes the only answer when discharge limits are extremely low, as is happening more often than not. Careful application and pretreatment of the waste stream is an imperative as is a treatability study to confirm efficacy.

Digital Analysis can perform detailed effluent analysis and conduct a treatability study. If you have a potential application please feel free to give us a call or send an email.

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