Chromium Removal Using Selective Ion Exchange Resins

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Chromate was used for years in cooling-water towers and loops as a very reliable means of corrosion protection and as a scale inhibitor. Increasing environmental pressures resulted in the discontinued use of chromate for these applications, and new corrosion inhibitors with potentially less impact to the environment are in use today.

Chrome is still used today in the plating of metal parts, but it is an inefficient process — about 15 percent of the chrome used is plated onto the work and 85 percent of the chrome is discharged into the rinse. Hexavalent chrome has poor draining properties, and much of the plating solution can end up in the rinse tank. Ion exchange is used to remove or recover that chromium. Any of the chrome that is not recovered must be treated before discharge.

The treatment of wastewater or groundwater that has been contaminated by the chromate ion can be accomplished by the use of anion resins. Success has been achieved by the use of strong or weak base anion resins, or selective anion resins.

Chromium exists primarily in trivalent (Cr(III)) or hexavalent (Cr(VI)) oxidation states. Cr(VI) is a problematic environmental pollutant because it is a strong oxidant and much more toxic than Cr(III). Cr(VI) exists as the chromate ion in basic solutions and as the dichromate ion in acidic solutions. Chromate discharge limits are becoming increasingly stringent; the maximum contaminant level (MCL) for chrome in drinking water is 100 ppb as set by the US Environmental Protection Agency.

The following are resins that can be used for chromium removal:

- **Strong-base anion resins.** Type 1 anion resin had been used in the past for the treatment of cooling-tower blowdown. The resin is regenerated with brine at 6 or 7 pounds per cubic foot of resin plus 2 pounds per cubic foot of sodium hydroxide. Exchange capacities of up to 3 to 4 pounds per cubic foot of sodium chromate can be attained, and the chromate eluted off the resin can be recovered and reused. It should be noted that chromate leakage following this process is fairly high by today's standards (several hundred ppb) and that the initial effluent following regeneration is likely to be greater than 100 to 200 ppb unless the resin is completely regenerated. Complete regeneration can be difficult using brine or brine/caustic.

  In a plating operation where recovery of the chromic acid is not important and it is only necessary to remove the chromate before discharge, a type 1 anion resin can be operated in either the hydroxide or chloride cycles to exchange for the chromate anion rinsed from chromium-plated pieces.

A Type 1 anion resin in the chloride form would collect the chromate anion on the exchanger, from which it could be stripped with NaCl in a concentrated form for disposal. Again, chromate leakage can be significant. The same resin, but regenerated with NaOH, would also collect the chromate anion on the bed during the service cycle, but would yield the bases of all the salts present. Passage of this effluent through a cation resin in the hydrogen form would yield deionized water.

A macroporous type 1 anion resin capacity for Cr+6 is somewhere between 0 and 3 pounds per cubic foot (average 1.5 pounds per cubic foot) depending on what else is in the water. The average of 1.5 pounds per cubic foot is based on 20 parts per million (ppm) influent chromate and 1 ppm effluent with less than 100 ppm sulfate present and a pH around 5. The maximum capacity of 3 pounds per cubic foot is achieved by operating at pH 4.5 with a primary and a polisher such that the primary leakage can go up to 50 percent of inlet level.

Some general guidelines for this application: service flow rate is 1 gpm per cubic foot; capacity is about 8,000 grains as $CaCO_3$ per cubic foot; throughput of a typical feed water with 100 ppm of total dissolved solids plus 15 ppm chromate anion would amount to about 1,300 gallons per cubic foot; regeneration can be done with 10 pounds per cubic foot of NaCl in a 10-percent solution (chloride cycle) or 8 to 12 pounds per cubic foot, or with NaOH in a 5-percent solution (hydroxide cycle) or 6 to 7 pounds per cubic foot of NaCl plus 2 pounds per cubic foot of NaOH (alkaline brine).

Some conditions can affect the capacity of an anion resin in this service. The optimum pH for chromium removal by anion resin is between 4 and 5.5. As pH increases, capacity decreases. As sulfate increases, capacity decreases. As effluent leakage or inlet chrome decreases, capacity decreases.

- **Weak-base anion resins.** Weak-base anion resins can exhibit high chromate capacities and low chromate leakages and are more resistant to oxidation. They are relatively unaffected by the presence of other anions such as sulfates and chlorides. They are economically regenerated with 3 to 5 bed volumes of 4 percent NaOH, but may require an acid conditioning step before resuming service. The complicated regeneration scheme and the handling and disposal of these regenerant streams must be taken into account when considering this resin.

The obvious drawback to using one of the above resins is the problem of how to dispose of the spent regenerant. Plating operations may have conventional wastewater treatment equipment available to precipitate the accumulated chrome from the regenerant wastewater. Groundwater treatment applications may prefer to regenerate offsite at a resource recovery facility, or use a higher capacity selective resin and simply dispose of the resin.

· **Chromate selective resin for groundwater.** A specialty resin has been developed with the capability to selectivity remove hexavalent chrome from polluted groundwaters, provided the pH is adjusted to below 6.5. If the pH is too high, the removal is not good. Capacities as high as 6 or 7 pounds of chromate per cubic foot of resin are possible with this resin. It is typically used as a non-regenerable media for groundwater remediation and trace chrome removal.

The resin uses a proprietary amine group converted to a target ionic form that enables it to achieve exhaustion capacities up to two to three times greater than the standard strong- or weak-base anion resins. The resin can be supplied at a buffered pH range so treated effluents will be near neutral to meet effluent pH guidelines. It is a coarse, granular material that gives low-pressure drop over long operational cycles.

The design flow through the resin bed should be 1 to 2 gallons per minute (gpm) per square foot, with a surface flow rate of 2 to 8 gpm per square foot. Two beds should be used in series so that the first bed can be loaded to the maximum. Removal is greater than 90 percent through the two beds in series.
When the primary column exhausts, the resin is replaced and the polisher becomes the primary with the fresh resin as the new polisher. Spent resin is then properly disposed of.

· **Chromate leakage.** For any of the above resins, the leakage of chromate is primarily due to a hydrolysis reaction and is strongly influenced by pH. Unfortunately, the same acidic conditions that favor high capacity also favor high leakage. It is relatively difficult to achieve less than 50 ppb of effluent chromate unless the operating pH is neutral to alkaline. This can result in the necessity to make compromises in the system design

For systems where the resin is regenerated and re-used, leakage also depends on how successfully the last traces of chromate are removed from the resin. It is quite difficult to achieve less than 10 ppb of chromate leakage from previously used resins.

Conclusion As effluent discharge regulations become more stringent, the ion exchange method of chromate removal using a selective, high-capacity, single-use resin becomes more attractive. Chromate pollution over the years from plating operations and corrosion control has contaminated many groundwater sources. A selective chromate resin is an economical remediation technique in many of these applications.

Application	Case 1 Groundwater Remediation	Case 2 Groundwater Remediation	Case 3 Cooling Tower Blowdown
Inlet TDS (ppm)	50	200	2000
Operating pH	4 to 5	7 to 8	5 to 6
Kinetic flow rate (gpm/cu.ft.)	2	2	2
Inlet chrome (ppm)	10 to 20	0.2	0.1
Primary capacity (lbs/cu.ft. as Cr)	7.2	0.2	0.1
Polisher leakage (ppm)	<0.05	<0.01	<0.05

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