Organic Fouling of Anion Exchange Resins

All surface waters (rivers, lakes, streams) contain "organic" materials. The term is a catch-all for a large class of carbon-based, naturally occurring compounds. The term *organic* is in contrast to inorganic, which refers to mineral salts, metals, silicates, etc. Organic indicates the origin of the materials in the water was at one time alive, that is, carbon-based.

As leaves, pine needles cones drop into waterways, a natural process of break-up and decay is started. The larger items are broken up by water cascading over rocks and waterfalls. Smaller pieces are then reacted upon by bacteria and algae present in the water as they scavenge for food. Natural enzymatic reactions break the small pieces down into molecular fragments, which are excreted by the micro-organisms.

The breakdown fragments then undergo a re-assembly chemistry, prompted by the presence of oxygen. Fragments are combined in a huge variety of ways into the class of materials we call "organics." These materials impart the yellow or yellow/brown color which most surface water exhibit.

Chemically, the individual organics are complicated, but they share certain characteristics:

- Variable molecular weight: some medium (25,000 daltons), some very large (over a million daltons)
- Complex carbon structures: benzene rings, nitrogen-containing rings (alicyclics), aliphatic (straight run hydrocarbon) sections, etc. (It is these complicated structures which impart the color to the water.)
- Abundance of –COOH groups, carboxylic acid
- Minor presence of hardness, iron, and even silicates

The COOH groups give organics an overall negative charge, so they only react with anion exchange resins. The organics worm their way into the complex polymeric structure of the resin and, literally, get trapped in that structure. Very little is removed by conventional regeneration with caustic.

The organics trapped inside the resin beads cause trouble:

- They take up active sites that otherwise would be used purifying water. This results in shortened runs, increasing regeneration frequency, and raising the cost of operating the water plant.
- They can bleed sodium ions into the anion effluent, prolonging the final rinse step of the anion regeneration. This uses up cation capacity and time.
- The sodium bleed can continue into the service cycle, interfering with coordinated pH/phosphate chemistry in high pressure boilers. This can require higher chemical feed rates and/or increase blowdown requirements, increasing the cost of steam production.

- Left untreated, they shorten the life span of the resin and greatly elevate the risk to the whole steam plant.

It is ironic that anion resins are very effective in removing dangerous organics from direct intrusion into the steam cycle. But the removal is by fouling.

In terms of root cause analysis, the ultimate origin of organic fouling is the natural reactions in the raw surface water as described earlier. Organics are part of nature. Other than changing water sources, this is not controllable. Surface waters are also subject to extremes of draught and rainfall, as recent history in the Gulf area has demonstrated. Draught seems to increase the production of organics in fallow water sources. The organics are then flushed out into the main tributaries during heavy rainfall.

Most plants use clarifiers and filter sets to handle the silt present in surface waters. The clarifier can also significantly reduce – but not eliminate – the organics getting through to the demineralizers.

Some plants use activated carbon, which is quite good in removing a large fraction – but not all – of the organics in a clarifier effluent. Unfortunately, the carbon loses its ability to absorb organics in under a year and most plants are unwilling to budget for carbon replacement at the optimal frequency. Older carbon can also serve as a source of microbial contamination of downstream tanks and equipment, including demineralizers.

Cation resins are also prone to fouling, but not with organics. Cation resins often get contaminated with high levels of hardness (calcium and magnesium) precipitates, and silt from upstream equipment.

The optimal program for addressing fouling of either resin type includes the following elements:

(1) Ensure the clarifiers, sand or multimedia filters are in good working condition
(2) periodically sample the cation and anion resins to determine the level of organic fouling
(3) have the resins professionally cleaned on a plant-specific schedule to reduce water plant operating costs (acid and caustic), and limit the damage organics can do to the boilers

For RTI,

William E. Bornak
VP Technology

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May we never forget.