



Graver Technologies

Innovative Resin Technologies for World Class PWR Chemistry Operations

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Introduction

Graver Technologies' principal customer is the power utility. We are focused on the business and support for those utility customers. As such our Sales, Customer Service, Technical, Development, and Manufacturing groups are organized to effectively address this unique business and the special applications that are vital to the industry.

Graver Technologies is the original provider of bead & powdered resins and filters, along with being a part of the original company that supplied much of the capital equipment for worldwide condensate polishing. As the acknowledged leader in the innovation of product applications & development for utility resin and filter systems, Graver counts more than 30 patents in the utility field.

Graver has initiated over 30 unique products & systems that directly affect the utility business, particularly in the area of condensate polishing. These include the invention of the Powdex[®] resins and Ecodex precoat products, the introduction of pre-aminated cations for blowdown systems, the introduction of the new ultra-low chloride anion to allow operation of the cation past the amine break at high pH, and many others as well as new innovations under development.

New products and new applications are vital to the continued improvement in utility operating systems. We continue to focus our abilities to provide the latest in resin technological advancements to our customers and are pleased to discuss some of these innovations.

Ultra Low Chloride Anion Resin

Low chloride anion exchange resins have been available for many years. These anion resins are commonly classified as Nuclear Grade and many nuclear plant specifications invoke this requirement. Products meeting this low chloride level are generally available from most reputable ion exchange suppliers and manufacturers. As condensate polishing operating requirements become more stringent, lower chloride levels are desired. Graver Technologies recognized the need and worked closely with a US PWR plant to develop a new anion exchange resin product that fulfilled this need and has led to significant operational improvements.

Gravex GR 1-9 US Ultra, sets the standard with a new state-of-the-art level in ultra low chloride performance. Improvements are experienced with PWR condensate polisher operation. With nearly an order of magnitude lower chloride level than the nuclear grade resins, the unique GR 1-9 product is performing as no anion exchange resin has previously. The ultra low chloride anion allows the cation resin to be operated in the amine form. The new ultra low chloride anion resin also offers improved operation in other high purity applications including steam generator blowdown, fuel pool, and CVCS demineralizers.

Condensate Application

Graver Technologies worked jointly with Dominion Nuclear Connecticut at the Millstone site in Waterford, Connecticut. Both operating plants are seawater-cooled, pressurized water reactor (PWR) units. At Millstone, Unit 2 is an 895 MWe Babcock & Wilcox PWR and Unit 3 is an 1154 MWe Westinghouse PWR. Both PWR's operate as non-molar ratio plants.

Millstone's goal was to reduce corrosion product (especially iron) transport to the steam generators by increasing the amine concentration. Problems that ensue from such transport include internal surface fouling, reduced heat transfer, decreased steam pressure, and ultimately increased localized corrosion, commonly called Inter Granular Stress Corrosion Cracking (IGSCC). Conversely, minimizing iron transport extends steam generator life which is crucial since the cost of replacing a steam generator can run more than \$300 million.

Like many others in the industry, Millstone utilizes ethanalamine (ETA) to elevate pH of the secondary side condensate chemistry which minimizes feedwater corrosion transport. Millstone reported on a number of initiatives undertaken to address the iron transport problem through pH-related operational changes including higher efficiency regenerations, higher capacity strongly acidic cation resins, air injection into the condensate, and amine form operation of the condensate polishers. None of the efforts achieved the goal of acceptable operation at higher amine concentrations.

In the summer of 2002, Millstone conducted bench scale testing of a strongly acidic cation resin fully converted to the ETA form. This test utilized a mixed bed of the ETA form cation and a hydroxide form anion to determine impurity removal efficiency during a simulated seawater in-leakage to the condenser. Successful results in this bench test convinced Millstone personnel to evaluate the performance of an ETA/OH⁻ mixed bed in one condensate polishing vessel of Unit 2 in the spring of

2004. During the 42 hour test of the mixed bed with the amine form cation, chlorides in the steam generator rose steadily from 0.59 ppb to 3.50 ppb before the test polisher was removed from service. Even low part-per-trillion (ppt) concentrations of chloride in the effluent from the polisher can result in part-per-billion (ppb) levels in the steam generator due to the concentration factor (300 -350) at Millstone. Administrative limits on chloride as well as sodium, sulfate, iron, and copper in the steam generator are based on the INPO condensate polisher index (CPI). Typically, steam generator limits for chloride ion are set at low or even sub-ppb levels.

The elevated hydroxide concentration in the liquid phase in the ETA/OH⁻ polisher eluted chloride from the anion resin. It became important to reduce the residual chloride levels on the anion to previously unattainable levels. Millstone was unable to achieve the necessary chloride level with the techniques and highest quality regenerant chemicals available. At this point, Millstone personnel asked Graver Technologies to help provide a solution.

Graver Technologies knew and understood well the need and how to accomplish the desired results. Chloride specification for typical condensate grade anion is 0.5% of the ion exchange sites and 0.1% for a nuclear grade anion. Details of the extensive processing and test methodology needed were developed and implemented over a period of eighteen months, working closely with Millstone to learn the effects of special regeneration process steps. The result was the introduction of Gravex GR 1-9 US Ultra. Typical nuclear grade anion resins can leach > 100ppt at the vessel outlet. The very first Gravex lot achieved < 30ppt. Subsequent lots have exhibited 20ppt, 14ppt, and < 10ppt when processing the higher ETA content, high pH condensate streams. Steam generator chlorides have remained within acceptable limits. Thus superior protection of the steam generators and associated piping has been the result in addition to significant savings in chemical regenerant and amine chemical addition costs.

The Gravex product is now in regular use at Millstone and is installed in half of the beds in each unit. Plans are to install the anion in additional beds as resin is replaced. The longest service life Gravex bed is now four years old and on the way to five years of service without regeneration, processing in excess of six billion gallons. This specialty anion has now been installed in a second PWR with expectations to replace condensate anion in other plants interested in improving performance and reducing costs.

Benefits

- Improved corrosion product transport to steam generators
 - Lower iron levels and significantly reduces sludge buildup
 - Extends life of steam generators
- Lowest chloride ingress to steam generators
- Reduced attack on metallurgy throughout the condensate system
- Condensate polisher operation without regenerating the resins
 - Current experience is four years and expect to achieve five years without regeneration of either the anion or cation components – Normal practice for standard products is to regenerate anion resin several times per year and cation resin as often as weekly

- Chemical regenerant cost savings – No need for chemicals for five years or more per bed providing significant cost savings
- Reduction in the amount of amine that is added to the condensate cycle to small dosages for fine pH adjustments
 - Significant annual cost savings
- Reduced manpower requirements normally needed to perform condensate polisher regenerations and monitor large amine doses
- Ultimate low chloride level in other critical plant applications such as CVCS, blowdown demineralizers, and fuel pools

Low Sulfate Leakage Cation Resin

A low sulfate leakage cation exchange resin may be the perfect complement to the ultra low chloride anion. As steam generator and reactor contaminant limits continue to become tighter, the need for superior quality ion exchange resins has never been more important. Many requirements for the resins and their contaminants have also been tightened and good quality cations are available. Good quality however is no longer sufficient and superior quality will be needed by most operating nuclear plants. One of the major areas to address is sulfates from cation resins.

Strongly acidic cation exchange resins are sulfonated copolymers so the potential for sulfate leakage is inherent in the resins. During synthesis of the cation resins, loose polystyrene sulfonate oligomers oftentimes remain within the bead internal structure. These oligomers diffuse out of the bead over time and when rinsed through a condensate polisher bed will break down to sulfates in steam generators or reactors. Small bead particles that pass through the polishers would also contribute to sulfate measurements. In addition, the base polymer degradation/desulfonation can occur over time and is accelerated by temperature and an oxidizing environment.

Leachable sulfate will also be the result of the degradation although it is often so slow and at such low levels that it may not be measurable, unless accelerated as described. Particulate leakage has been addressed by improved strainer designs and by the reduction of fine particles in the resins as well as strict particle size specification limits. Today, the particle issues are quite rare with a consistent good quality resin. Leachable sulfates however are a different matter. The residual oligomers are often present in all resins regardless of the original resin manufacturer. In addition to leaching into the condensate, the sulfate bearing materials can foul the anion portion of mixed beds leading to kinetic impairment and poor performance. It is essential that the levels are reduced during post manufacture processing. Graver Technologies is expert in high level processing of all resins and is in the process of developing superior quality and performing cation exchange resins.

Much of this experience comes from years of preparing high quality Powdex resins for condensate polishing in precoat filter demineralizers. Since grinding immediately exposes the bead internals, the diffusion time for any residual contaminants is practically nil. The bead resins for powdered production

must be of the very highest quality. The process techniques are being refined to apply to condensate and nuclear grade bead types.

Several manufacturers' condensate polishing resins, including the high cross linked cations, are being evaluated. All as-received resins show elevated leachable sulfate levels. Both Graver Technologies and nuclear plants would receive these same quality resins from base manufacturers. Preliminary results show significantly improved sulfate levels after applying special processing to the cations. Long term stability is also a part of the study to determine the optimum process techniques. Products to be commercialized as low sulfate Gravex cations complementary to the ultra low chloride Gravex anion.

Comments and Benefits

- As manufactured cations can leach contaminants that contribute sulfate to the condensate
- High crosslinked cations have been used to address sulfates
 - Condensate results are mixed – Some improvement but long term sulfate leakage is the same or sometimes not quite as good as standard crosslinked resins
 - Fuel pool results are improved as the resin better withstands peroxide contact
- Anion underlays have been used and reduce some leachable sulfates but do not address the source and the underlays are disrupted during resin movement for regeneration
- Cation resins should be fully processed to reduce leachable contaminants
- Cations fully processed for low leachable sulfate are high value products – Cannot be purchased on a low price basis
- Benefits of fully processed cations
 - Reduced sulfate bearing contaminants in the feedwater
 - Reduced fouling of anion component in mixed beds
 - Improved corrosion control reducing the likelihood of IGSCC
 - Extended anion life
 - Reduced need or elimination of anion underlays

High Performance Blowdown Demineralizer Mixed Beds

PWR plants are beginning to depend more on the steam generator blowdown demineralizers (SGBD) for control of cycle chemistry. As issues arose with anion kinetic impairment in some plants using ETA for condensate chemistry, several plants used the condensate polishers only for start ups, condenser leaks, or other anomalous situations. As customers were changing their mode of operation, the SGBD ion exchange mixed bed performance became even more important. Graver Technologies developed several specialty mixed beds specifically for this application.

The amine is removed from the cycle by the cation portion of the mixed bed. In some cases plants employ fully loaded cation beds preceding the mixed beds. Other plants prefer to use cation rich mixed beds. Two specialty mixed beds, Gravex GR 3-15 and GR 3-30, were developed for specific customer requirements and have performed well in the application – three cation to one anion by volume and by capacity. Other suppliers have been unable to prepare the specialty mixed beds while maintaining uniform mixing and product stability. Graver Technologies has the capabilities and the willingness to listen to and understand customers' needs and follow through with solutions that improve plant operations.

Benefits

- Made specifically for high performance PWRs
- High capacity for corrosion products and amines
- Special blending equipment and process to insure uniformity – much tighter cation to anion ratio tolerances than other manufacturers standard mixed beds
- Component selection and processing to insure maximum stability
- Longer bed life because of the high cation ratios
- Small primary to secondary leakage protection – reduction of radionuclides

Amine Form Cation Resins for Condensate Polishing Systems

Nuclear PWR condensates operate at elevated pH, often 9.0 to 9.3 or higher, to minimize corrosion transport. Various amines or combinations of amines may be used to maintain the elevated pH. These include ammonia, hydrazine, ethanolamine (ETA), and morpholine among others. As more amine is added, the higher the resulting pH.

Condensate polishing system mixed beds are typically loaded with strongly acidic cation resin in the hydrogen form and the strongly basic anion resin in the hydroxide form (H^+/OH^-). Most common cation to anion ratios used are either a 1:1 stoichiometric mix or a 2:1 volume mix. Combined volumes for a system range from 1,000 (> 28m³) to more than 2,000 (~ 57m³) cubic feet. In all cases there is a

significant amount of hydrogen form cation that will remove amines up to the resin's capacity. The amount of amine removed by the cation resin must be replenished by injection into the condensate after the condensate polishers. Annual amine costs may be several \$100,000 dollars per unit.

Graver Technologies began offering ammonium form powdered resin more than 40 years ago to maintain fossil plant condensate pH. Today 10,000s of cubic feet of hydrogen form cation are converted to the ammonium form at Graver's NJ site using a special proprietary process with high purity regenerant chemicals and rinses. The ammonium form cation is ground and used in several powdered resin products.

Graver Technologies had the knowledge, experience, and capability to manufacture the high-quality morpholine form cation products needed to improve the operating performance of a large, two-unit PWR plant. A morpholine form powdered cation along with hydroxide form powdered anion are used in the condensate system's precoat filter demineralizers. Extremely long runlengths are obtained and most of the cycle chemistry is controlled by the Steam Generator Blowdown Demineralizers (SGBD).

Specialty Gravex products utilizing morpholine form cation were developed for the SGBDs and have been used routinely for about 15 years. Cycle chemistry at this 2 x 1,200 MWe PWR is among the best in the world. Morpholine form cation (GR 2-5 SG (M)) is followed by a mixed bed also with the morpholine form cation component (GR 3-22 SG (M)). About 1,000 cubic feet (28 m³) total are used annually. The products are made with a special macroporous cation and blended with a high capacity gel anion for the mixed bed. The morpholine form macroporous cation is selective for sodium and helps maintain excellent chemistry parameters. Morpholine concentration and pH are maintained and injection of additional morpholine is reduced to a minimum, saving significant chemical costs.

Cation resin in the ethanolamine (ETA) form is a new offering. It can be used in the same manner as the morpholine form Gravex products with the cation followed by the mixed bed in the SGBD. Similar performance and advantages are expected. The ETA form cation may also be used in deep bed condensate systems. This is already being done as described in the Ultra Low Chloride Anion section. Combining several of these new process treatment concepts, the cation can be processed to achieve the lowest possible sulfate value, specially regenerated to the ETA form, and then used with the Ultra Low Chloride Anion to provide perhaps the ultimate condensate polishing system for PWRs.

Benefits

- Reduced consumption and cost of amine chemicals
- More stable amine concentration
- Simple pH maintenance
- Reduced corrosion product transport
- Multi-year runlengths with reduction of regenerant chemicals and costs

Summary

- *Gravex ultra low chloride anion resin has lowest residual chloride level and minimal leachable chloride in high pH environments – lowest steam generator chlorides*
- *Gravex ultra low chloride anion operates for 4 years (expect 5 years) without regeneration, saving considerable regenerant chemical and other costs*
- *As manufactured cation resins exhibit measurable leachable sulfate - Gravex low sulfate leakage cation is the perfect companion to the ultra low chloride anion for the ultimate purity condensate mixed bed*
- *Specialty Gravex SGBD mixed beds are uniformly mixed, stable products with high capacity for amines and corrosion products*
- *Amine form Gravex cations for use in SGBD and condensate polishers to maintain cycle pH and reduce operating costs*
- *Amine form cation used with ultra low chloride anion allows higher amine concentrations to reduce corrosion product transport to the steam generator reducing the resulting sludge buildup – steam generator life extended*