

Development of Ion Exchange Resins with Ultra-Low Residuals for Condensate Polishing Applications

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ABSTRACT

Graver Technologies developed and commercialized an ultra-low chloride strongly basic anion resin for condensate polishing applications. Multiple lots of this new resin were installed in a nuclear plant in the United States. The ultra-low chloride resin allowed this plant to increase their amine concentration and consequently to reduce iron transport.

Work is underway to develop a corresponding ultra-low sulfate strongly acidic cation resin for condensate polishing applications. The development study involves post-treatment of a number of commercially available strongly acidic cation resins under comparable, strictly controlled conditions. Sulfate leachables and total oxidizable carbon (TOC) measurements during and after the post-treatment operations serve as metrics for this project.

INTRODUCTION

Ultra-Low Chloride Anion Resin

Nuclear power plants need to minimize corrosion and corresponding deposition throughout steam/water circuits. Condensate polishers containing mixed beds of ion exchange resins play a vital role in reduction of impurities in water circulated through these polishers. However, residual impurities on regenerated form resins (strongly basic anion in the OH^- form and strongly acidic cation in the H^+ form) limit the ultimately achievable water quality. For strongly basic anion resins the most critical contaminants are chlorides and sulfates.

Typical specifications for nuclear or condensate grade hydroxide form anion resins allow a maximum of 0.1 to 0.5 % of sites in the chloride form and 0.1 to 1.0 % of sites in the sulfate form. Until recently, it was extremely difficult to obtain strongly basic anion resins with chloride and/or sulfate residuals below the 0.1 % of sites level.

The Dominion Millstone Nuclear Power Station in Waterford, Connecticut (U.S.A.) consists of two operating units. Unit 2 (895 MW) and Unit 3 (1 154 MW) are operating pressurized water reactors (PWRs) with Babcock & Wilcox and Westinghouse steam generators, respectively. The Millstone plant uses seawater from Long Island Sound for cooling. Both units utilize full flow condensate polishing and employ ethanolamine (ETA)/hydrazine chemistry operating on non-molar ratio.

Unit 2 at Millstone has seven condensate polisher vessels and eight mixed bed resin charges. At full power, six of the polishers are in service, one in standby, and one resin charge being regenerated. Similarly, Unit 3 has eight condensate polisher vessels and nine mixed bed resin charges. At full power, seven of the polishers are in service, one in standby, and one being regenerated. Each polishing vessel contains 5.7 m³ of resin with a 3:2 ratio of anion to cation components. Traditionally these mixed beds contained hydrogen form (H^+) Dow Monosphere 650C cation and hydroxide form (OH^-) Dow Monosphere 550A anion resins.

Millstone views reduction of corrosion product transport as a top priority [1]. Previous efforts to address this issue included increased efficiency regenerations, evaluation of higher capacity cation resins, and air injection into the condensate feedwater. Starting in the summer of 2002, Millstone began converting hydrogen form strongly acidic cation resin into the ethanolamine (ETA) form prior to placing it in service in mixed bed condensate polishers. The initial trial was terminated prematurely due to elevated chloride levels in the steam generator. Ultimately, the caustic (NaOH) used to regenerate the strongly basic anion resin was identified as the chloride source. This problem initiated a search for ultra-low chloride caustic and an ultra-low chloride anion resin for this application [2].

Ultra-Low Sulfate Cation Resin

All hydrogen form strongly acidic cation resins contain sulfonic acid sites. During the manufacturing process the copolymer (typically styrene/divinylbenzene) is functionalized using concentrated sulfuric acid. Consequently, sulfonic acid groups are bound to the benzene rings (typically one per ring). This attachment occurs regardless of whether the ring is attached to a crosslinked polymer or an uncrosslinked polymer. Despite the best efforts of the resin manufacturers, relatively short chain oligomers remain unbound to the resin matrix. Some of these oligomers will be trapped within the matrix rather than independent of it. The benzene rings in the oligomers will be functionalized just like the sites on the matrix itself. The functionalized oligomers are termed organic sulfonates. When the cation resin is put in service the organic sulfonates can leach out over time [34].

In recent years, the resin manufacturers have tried to address the leachable organic sulfonate problem by increasing the crosslinking used to make strongly acidic cation resins [5], especially for high purity applications such as condensate polishing in power plants and ultrapure water production in microelectronics plants. This approach, indeed, reduces the quantity of organic sulfonates residual to the resin.

Systems utilizing strongly acidic cation resins at elevated feedwater temperatures suffer from a second source of sulfate leachables [6–9]. In this case, the leachable moiety is inorganic sulfate. The inorganic sulfate arises from desulfonation of the benzene ring. Unfortunately, sulfonation of the benzene ring is a reversible process. Moreover, the desulfonation process accelerates as the influent water temperature increases. Desulfonation also is more favorable when the sulfonated benzene ring has more than one point of attachment (e.g., divinylbenzene with two versus styrene with only one). Hence, increasing the amount of divinylbenzene in the polymer increases the amount of leachable inorganic sulfate. This latter statement is independent of the manufacturer or the porosity type (gellular vs. macroporous).

Although the quantity of sulfate leachable is generally quite low, these impurities are concentrated and confined in the steam generators. Both power plants and microelectronics plants have installed in-line ion chromatography equipment. This equipment, in turn, has allowed measurement of sulfate in the ppb or even ppt range. Consequently, the boiling water reactors (BWRs) now observe sulfate excursions of only a few $\mu\text{g} \cdot \text{kg}^{-1}$, such as those that occur on startup of new mixed beds.

In the case of the pressurized water reactors (PWRs) the sulfate issue is more complex. PWRs utilize amines to elevate pH (typically 9–10) to minimize corrosion/erosion problems. The most commonly used amine is ethanolamine (ETA), which is a very good solvent and has a history of problematic interaction with ion exchange resins. This

problem is generally more severe in PWR plants that have higher condensate temperatures (up to 65 °C). One apparent manifestation of this negative interaction is fouling of strongly basic anion resins with organic sulfonate leachables from the strongly acidic cation resin. The mass transfer kinetics test was developed by Harries [10] and McNulty [11] to quantify this fouling process in terms of sulfate leakage and the consequences with strongly basic anion resins.

Development work is underway in an effort to define post-processing techniques to generate an ultra-low sulfate strongly acidic cation resin. This work involves plant evaluations of a variety of strongly acidic cation resins, including resins with various crosslinking levels, from different manufacturers, and using various post-processing operating parameters. Results of these evaluations so far and progress toward establishing a viable, commercially available ultra-low sulfate resin are briefly discussed below.

EXPERIMENTAL

Ultra-Low Chloride Anion Resin

Initially, Graver Technologies post-treated commercial rayon grade caustic to further reduce the chloride contaminants. This upgraded caustic, in turn, formed the basis for development of an ultra-low chloride, hydroxide form strongly basic anion resin, Gravex GR 1-9 Ultra [12,13]. The key specification for the GR 1-9 Ultra was that < 0.030 % of the anion exchange sites on the resin were in the chloride form.

The first bed of GR 1-9 Ultra was installed in one condensate polisher in Unit 2 at the Millstone plant in September 2004. The mixed bed in this polisher also contained standard strongly acidic cation resin in the ETA form. After installation steam generator chlorides increased and stabilized at $1.4 \mu\text{g} \cdot \text{L}^{-1}$, which back-calculated to $28 \text{ ng} \cdot \text{L}^{-1}$ leakage from the condensate polisher. Three months later the ETA feedwater concentration was increased by 120 % to $2.75 \text{ mg} \cdot \text{L}^{-1}$. The increased ETA concentration, in turn, resulted in a steady drop in feedwater iron concentration from $\sim 3.0 \mu\text{g} \cdot \text{L}^{-1}$ to $\sim 2.0 \mu\text{g} \cdot \text{L}^{-1}$. The polisher with the GR 1-9 Ultra remained in service continually until April 2005 (217 days and > 3.3 billion liters of condensate). At that point, the mixed bed was removed from service, mechanically cleaned^a, and reinstalled in the vessel without regeneration of either component. As of September 1, 2008, this GR 1-9 Ultra resin has been in service for 1459 days (4 years) and has processed more than 83 billion liters (22 billion gallons) of condensate. The calculated chloride leakage from this polisher has fallen from $28 \text{ ng} \cdot \text{L}^{-1}$ at installation to $2 \text{ ng} \cdot \text{L}^{-1}$ presently.

^a Conventional air scrub/backwash techniques are used to clean resin mechanically.

As a result of this initial success, a second bed of GR 1-9 Ultra was installed in one condensate polisher in Unit 3 in April 2005. The success achieved with these two beds has led to the installation of a total of 15 beds spread between the two units. Table 1 summarizes the installation and service history for these beds as of September 1, 2008.

Nine vessels containing seven different lots remain in service as of September 1, 2008. Effluent chloride levels from the ultra-low chloride polishers still in service range from 2 to 20 $\text{ng} \cdot \text{L}^{-1}$. Remarkably, four separate vessels (three separate lots) containing GR 1-9 Ultra resin are currently showing only 2 $\text{ng} \cdot \text{L}^{-1}$ of chloride leakage from the polisher. Lot GR-2579 installed on January 21, 2006 was removed after the anion resin was contaminated during vessel repair. Lots GR-2497 and GR-2668 (March 29, 2006 and March 30, 2006 installations) were returned to H^+/OH^- service after calculated effluent chloride levels exceeded 30 $\text{ng} \cdot \text{L}^{-1}$. Lot GR-2374, originally installed on April 7, 2005 and converted back to H^+/OH^- service after 202 days of operation, recently was regenerated at the Millstone plant with ultra-pure caustic and returned to service in a mixed bed with amine form cation resin.

Currently both units at Millstone operate with amine (ETA) form cation resin polishers. Unit 2 utilizes four of six polishers in the amine form while Unit 3 employs five of seven

polishers in the amine form. Feedwater ethanolamine is $\sim 2.75 \text{ } \mu\text{g} \cdot \text{L}^{-1}$ for Unit 2 and $\sim 3.5 \text{ } \mu\text{g} \cdot \text{L}^{-1}$ for Unit 3 at present.

Ultra-Low Sulfate Cation Resin

A series of strong acid resins are currently being subjected to post-treatment under controlled conditions in plant equipment to profile sulfate leachables. The resin candidates for these evaluations represent different manufacturers, Gaussian and uniform particle size resins, and varying crosslinking levels. These trials utilize 2.85 m^3 of cation resin in standard plant equipment. All water used in the trials can be characterized as high resistivity, low TOC deionized water made in the plant. Operating parameters such as flow rate and temperature are fixed for all trials. In addition, all resins undergo post-treatment for the same period of time with samples of resin taken periodically during post-treatment and at the end of the trial for laboratory analysis of sulfate extractables.

Resin samples taken during and after post-treatment are analyzed for sulfate leachables/extractables using a dynamic method. This method is a variant of an existing customer procedure. Once the extractables/leachables from these tests are generated, an ion chromatograph (IC) is used to measure sulfate. Sulfate measurements at the

Location	Lot number	Installation date	Length of service (days)	Total throughput [$\text{L} \times 10^9$]	Initial effluent chloride [$\mu\text{g} \cdot \text{L}^{-1}$]
Unit 2					
	GR-2164	09/02/04	1 459	22.7	28
	GR-2497	09/01/05	125	2.0	
	GR-2579	01/11/06	963	15.0	25
	GR-2579	01/21/06	114	1.8	25
	GR-2668	05/24/07	465	7.2	16
	GR-3100	08/09/07	388	6.0	19
Unit 3					
	GR-2374	04/07/05	482	7.9	33
	GR-2497	09/01/05	202	3.2	
	GR-2668	03/29/06	531	8.3	22
	GR-2668	03/30/06	171	2.7	27
	GR-2668	04/14/06	870	13.5	22
	GR-3100	12/07/07	255	4.0	20
	GR-3234	01/13/08	231	3.6	10
	GR-3234	03/31/08	153	2.4	8
	GR-2374	05/01/08	122	1.9	30

Table 1:
Installation and service history of GR 1-9 Ultra resin.

single digit $\mu\text{g} \cdot \text{L}^{-1}$ (ppb) level necessitate modification of standard IC parameters to insure a flat baseline and reasonable elution time.

RESULTS

Ultra-Low Chloride Anion

As of September 1, 2008, the ultra-low chloride anion resins have treated more than 102 billion liters of condensate and have achieved a cumulative service time of 6 531 days. For Unit 2 during the current Cycle 18, chloride concentrations have typically ranged between 1.2 and 1.4 $\mu\text{g} \cdot \text{L}^{-1}$ with some measurements of $\sim 0.8 \mu\text{g} \cdot \text{L}^{-1}$. These values comply with the maximum chloride concentration of 1.6 $\mu\text{g} \cdot \text{L}^{-1}$ imposed as part of the INPO^b Condensate Polisher Index (CPI).

Figure 1 shows the effects on steam generator chemistry of the introduction of a mixed bed containing ultra-low chloride anion resin into the condensate polishers. As seen in this figure, during the first two weeks after installation chloride levels quickly stabilize around 1.5–1.8 $\mu\text{g} \cdot \text{L}^{-1}$ while sodium and sulfate levels remain below 0.5 $\mu\text{g} \cdot \text{L}^{-1}$. Conductivity rises toward an equilibrium value of $\sim 4.7 \mu\text{S} \cdot \text{cm}^{-1}$ in the first few days.

Since the introduction of ultra-low chloride anion resin and the corresponding increase in ethanolamine concentration, final feedwater iron levels have steadily decreased in both units at Millstone. Currently feedwater iron levels stand at historic lows.

^b INPO is the acronym used for the Institute for Nuclear Power Operations in the United States

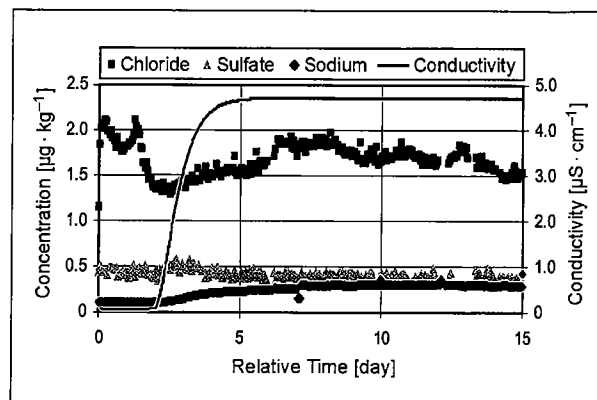


Figure 1:
Steam generator effects.

For Unit 2, feedwater iron levels during Cycle 15 (April 2002 through October 2003) ranged between 4.0 and 5.3 $\mu\text{g} \cdot \text{L}^{-1}$. During Cycle 16, the dissolved oxygen content in the condensate was increased to $\sim 12 \mu\text{g} \cdot \text{L}^{-1}$ using air injection. This elevated dissolved oxygen level resulted in almost a 40 % decrease in average feedwater iron. Once the first charge of ultra-low chloride anion resin was installed the feedwater iron continued to decline from $\sim 3.0 \mu\text{g} \cdot \text{L}^{-1}$ to $\sim 2.0 \mu\text{g} \cdot \text{L}^{-1}$ by the end of Cycle 16 (April 2005). As more ultra-low chloride anion resin was added to Unit 2 through Cycles 17 and 18, the feedwater iron declined further, averaging $\sim 1.8 \mu\text{g} \cdot \text{L}^{-1}$ in June 2007 and $\sim 1.6 \mu\text{g} \cdot \text{L}^{-1}$ in June 2008.

Feedwater iron levels are inherently higher for Unit 3 at Millstone since no air injection is employed in this unit. During Cycle 9 (January 2002 to May 2003) feedwater iron levels ranged between 2.0 and 5.0 $\mu\text{g} \cdot \text{L}^{-1}$. These levels

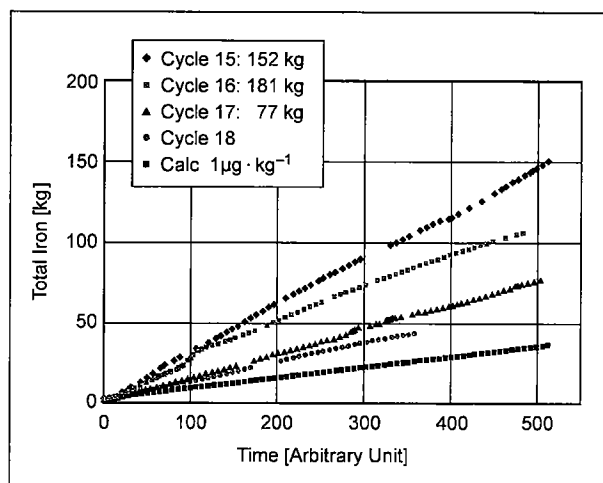


Figure 2:
Millstone Unit 2: corrosion product transport to the steam generator.

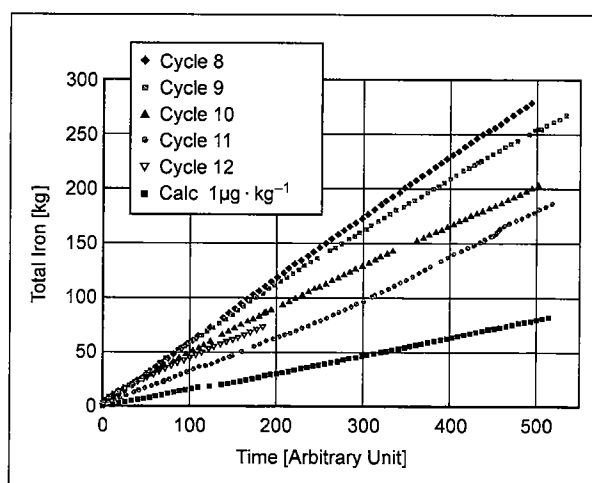


Figure 3:
Millstone Unit 3: corrosion product transport to the steam generator.

Location	Cycle number	Total iron [kg]
Unit 2		
	15	151.8
	16	106.8
	17	77.3
	18	?
Unit 3		
	9	243.7
	10	207.7
	11	184.1
	12	?

Table 2:
Corrosion product transport.

trended downward through Cycle 10, Cycle 11, and Cycle 12. The feedwater iron averaged $\sim 2.4 \mu\text{g} \cdot \text{L}^{-1}$ in June 2007 and $\sim 2.0 \mu\text{g} \cdot \text{L}^{-1}$ in June 2008.

Figures 2 and 3 show cumulative iron transport quantities to the steam generator for consecutive cycles (18-month duration) for each unit at the Millstone plant. Table 2 summarizes these data as a function of unit and cycle. Since the introduction of ultra-low chloride anion resin and the concomitant increase in ethanolamine, the reduction in total corrosion product transport has been quite dramatic (ca. 50 % in 3 cycles in Unit 2 and ca. 25 % in 3 cycles in Unit 3).

Ultra-Low Sulfate Cation Resin

Experimental post-treatment of various strongly acidic cation resins commenced in December 2007. Extensive data have been generated on three separate resins. These data indicate that post-treatment significantly reduces sulfate leachables/extractables, at least initially. Shelf-life studies with these post-treated resins are underway to determine whether the reduced sulfate leachables are temporary or permanent.

DISCUSSION

The introduction of an ultra-low chloride anion resin at the Millstone plant resulted in dramatically reduced chloride contamination in the steam generators, increased feedwater amine levels, and most importantly a significant and ongoing decrease in corrosion product transport. Moreover, Millstone utilizes amine form (ETA) cation resin in

combination with the ultra-low chloride anion resin in condensate polisher mixed beds. Amine form operation at Millstone results in accrued savings of roughly \$550 000 per year due to reduced regenerations. The amine cation resin still protects the steam generators from seawater ingress. Additional benefits include more flexibility in terms of staffing and maintenance to minimize chemistry excursions. Most importantly, the amine form operation elevates the operational pH and thereby reduces corrosion product transport. Indirect benefits of these operational changes include exceptionally long run lengths, elimination of mid-cycle anion regenerations, and reduced regeneration and disposal costs for cation resin due to in-line conversion to the ethanolamine form and continuous operation in the amine form.

The Millstone plant has converted more condensate polisher beds to ultra-low chloride anion resin and amine form cation resin during 2008 since the INPO CPI limits on chloride no longer apply.

The success of the ultra-low chloride anion resin encouraged Graver Technologies to attempt to develop a similar ultra-low sulfate cation resin. Since desulfonation is an inherent property related to the chemical structure of the strongly acidic cation resin, only the organic sulfonate leachables can be addressed by post-treatment of standard strongly acidic cation resins. The purpose of our study is to determine to what degree organic sulfonate leachables/extractables can be reduced and whether such reduction varies among resins with different crosslinking and from different manufacturers.

CONCLUSIONS

The ultra-low chloride anion resin, Gravex GR 1-9 Ultra, offers significantly fewer ($< 0.030 \%$) of the ion exchange sites in the chloride form. This reduction, in turn, yields significantly lower chloride leakage from the condensate polishers and consequently reduced cumulative chloride in the steam generators. This reduction of chloride in the condensate allows increased use of ethanolamine, which, in turn, reduces the iron transport. In addition to exceptionally long run lengths, indirect benefits from using the ultra-low chloride resin include the ability to increase ethanolamine concentration without generating excessive chloride in the steam generator, less iron transport, elimination of mid-cycle anion resin regenerations, and reduced regeneration and disposal costs for cation resin due to in-line conversion to the ethanolamine form and continuous operation in the amine form.

We are not prepared to draw conclusions from the post-treatment trials designed to generate an ultra-low cation resin yet. We hope to present results from these studies at next year's EPRI Condensate Polishing Conference.

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