NEW ION EXCHANGE RESIN DESIGNS AND REGENERATION PROCEDURES YIELD IMPROVED PERFORMANCE FOR VARIOUS CONDENSATE POLISHING APPLICATIONS

STEPHEN W. NAJMY, The Dow Chemical Company, Midland, MI

INTRODUCTION
Condensate polishing is an application that has seen a variety of developments over the past five years with respect to new ion exchange resin products and alternate procedures for installing, regenerating and re-mixing the mixed resin products. This paper describes experiences at several power stations that continue to benefit from the use of either a new resin product design or a modified resin handling procedure. These success stories come from
1) Two BWR nuclear power stations seeking to achieve improved feedwater iron and reactor water sulfate control, and
2) One PWR nuclear power station looking to extend service cycle run length and better manage steam generator chloride excursions due to salt water condenser inleakage

NEW LOW CROSS-LINKED CATION EXCHANGE RESIN FOR ENHANCED CRUD REMOVAL IN A BOILING WATER REACTOR (BWR) NUCLEAR POWER PLANT

In a BWR nuclear power plant, excessive feedwater iron can cause two major concerns:
- Heat transfer reduction – Iron buildup on the cladding of the nuclear fuel reduces heat transfer efficiency and can lead to nuclear fuel cladding failures.
- Shutdown dose rates – Non-optimal feedwater iron concentrations affect the transport of activated corrosion products, causing an increase in radiation dose rate on the reactor piping and increasing worker exposure.

While some BWR stations have the benefit of an upstream pre-filter system, other stations rely on their deep-bed condensate polishers for crud filtration. Such is the case at Niagara Mohawk’s Nine Mile Unit Two Nuclear Power Station – a BWR plant in central New York. In the mid-1990’s it became evident that new technology was necessary for this plant to meet stringent industry guidelines for feedwater iron. However, the problem was further compounded when this plant experienced an increase in condensate iron due to the loss of one of its moisture separator/reheaters (MSRs) at the end of one of its operating cycles in 1997.

An opportunity for low cross-linked cation exchange resins

In the early 1990’s several manufacturers were producing commercial quantities of cation exchange resins using styrene-divinylbenzene (DVB) copolymers with 6% cross-linking. Previous work in Japan suggested the potential for enhanced crud removal with these products. This spawned interest in the U.S. and soon afterwards a pilot-scale study began at the Public Service Electric & Gas Hope Creek Station along with full bed trials at several other BWR stations. It was during these full bed trials that stations reported increased reactor water sulfate levels due to the installation of these low cross-linked cation resin products. By 1994, all BWR plants, with the exception of Commonwealth Edison’s Dresden Station, removed the so-called 'crud' resin from their condensate polisher vessels. The explanation for the increased sulfate was simply the lower cross-linked cation resin having inadequate thermal stability compared to the conventional 10% cross-linked styrene-DVB cation resin. So, although feed water iron reduction was an important goal, it could not come at the expense of increased reactor water sulfate. An increased level of sulfate will accelerate corrosion in nuclear fuel rods and other internal components, which can greatly reduce power generation economics.

Challenge: Meeting feedwater iron guidelines without spiking sulfates

To meet guidelines set by the Institute of Nuclear Power Operations (INPO) and the Electric Power Research Institute (EPRI), the Nine Mile plant needed to reduce feedwater iron from 2-3 ppb with MSRs in service, or 5 ppb with MSRs out of service, to 1 ± 0.5 ppb. After researching the data from a previous EPRI collaboration project evaluating low cross-linked resin, Nine Mile concluded that a cation resin developed by researchers from
The Dow Chemical Company was a product worthy of study. The essence of the Company's invention\textsuperscript{6,7} was a proprietary new technology for stabilizing low cross-linked resin.

* Trademark of The Dow Chemical Company

That resin, Dowex\textsuperscript{®} Guardian\textsuperscript{®} CR-1 cation resin, has a low cross-linked copolymer backbone that offers enhanced particulate iron and copper removal compared to conventional cation exchange resins. However, it has differentiated performance versus other low cross-linked resins because:

- the resin is produced using a unique stabilization technology to reduce the release rate of organic sulfonates\textsuperscript{8}
- the resin combines a uniform particle size distribution with a small average bead diameter (approx. 550 microns) and a lower true hydrated density to minimize the separation of the cation/anion resin during transfer back to the service vessel.

To first qualify the new cation resin product engineers from Nine Mile devised a series of laboratory tests to assess the risk of sulfate leakage in the presence and absence of iron and copper impurities. This study\textsuperscript{9} included an assessment for the impact on the surface kinetic properties of the anion resin. The Company's conventional 10% cross-linked cation resin was used as the control system in these lab tests. Encouraged by the lab results and the evaluation of the previous testing of low cross-linked resin, Nine Mile engineers in collaboration with EPRI proceeded to a full-scale plant trial.

In January 1998 the plant converted one of its 10 conventional deep-bed condensate polishing resin beds to Guardian CR-1 resin, rounding out the mixed-bed system with Dowex Monosphere\textsuperscript{®} 550A Anion Exchange Resin. In July 1998, a second resin bed was converted to the Dowex Guardian CR-1/Monosphere 550A mixture.

Plant trial shows iron level reduction with stable sulfate levels

The plant's Chemistry Department sampled and analyzed the condensate demineralizer influent (CDI), polisher bed effluent, and final feedwater streams. The reactor water coolant was also monitored for sulfate levels. The plant completed six, 30- to 40-day service cycles (January 1998 to April 1999) with the low cross-linked beds, comparing their results to the performance of the control bed (a new charge of Dowex HGR-W2/Dowex SBR-C).

During the first two cycles (with MSRs out of service), effluent iron averaged about 4 ppb (an 85 percent removal rate) from the new resin bed versus about 8 ppb (a 60 percent removal rate) from the control bed. After the MSRs were returned to service (cycles 3–6), the effluent iron averaged about 1 ppb (a 97 percent removal rate) from the new resin bed, versus about 4.5 ppb (an 80 percent removal rate) from the control bed. These data are depicted in Figure 1.

The impact on reactor water sulfate is shown in Figure 2. This plot includes the seasonal variation in the hotwell condensate temperature. As shown in Figure 2, through the hot summer months sulfate levels in the reactor water stayed near 1.5 ppb. In addition, after ultrasonic cleaning, sulfate spikes were not observed when the cleaned new resin beds were placed back into service. The plant's full-scale trial confirmed that the new resin provided improved iron removal without increasing reactor water sulfates.

Successful trial leads to optimized-ratio of new resin and conventional cation resins

Based on the favorable iron and sulfate results, the Nine Mile plant converted two more condensate polishing beds to this new resin pair during the remainder of Operating Cycle #7, leaving the other six beds operating with the conventional 10%-XL gel cation resin. This allowed the plant to further reduce its iron level to about 1.0 ppb—well within the industry guidelines—and still maintain plant economics. To finalize the optimization, the original two low cross-linked resin beds were replaced (typically after about 13,000 hrs of service) with the new resin. Plus, an additional bed was converted during a refueling outage in the spring season of 2000. The plant also reduced its resin beds from ten to nine so that each bed has a dedicated vessel to prevent cross-contamination.

The plant reports\textsuperscript{9} that the early results (after about 30 days) of Operating Cycle #8 with five low cross-linked resin beds and four conventional resin beds have been exceptional with an integrated weekly iron average of 0.6 ppb and sulfate concentration less than 1.5 ppb.
NEW LESS-SEPARABLE MIXED RESIN HELPS TO REDUCE REACTOR WATER SULFATE IN A BOILING WATER REACTOR (BWR) NUCLEAR POWER PLANT THAT DOES NOT HAVE THE BENEFIT OF OPERATING UNDISTURBED CONDENSATE POLISHER BEDS

The use of a deep-bed condensate polisher in a BWR primary cycle is to help maintain reactor water chemistry control. In this application the mixed resin bed functions to remove both ionic and particulate species from the condensate return stream. This minimizes the accumulation of insoluble iron (crud) deposits and contaminant...
ions, such as sodium, chloride and sulfate – which together create conditions conducive to inter-granular stress corrosion cracking (IGSCC) of BWR pressure vessels and reactor internals.

Identifying the major source of reactor water sulfate

In spite of the best efforts to optimize the performance of the deep-bed condensate polishers, meeting the EPRI guideline for final feed water iron and the operational target for reactor water sulfate does not come easy. Reactor water sulfate control and minimization continues to challenge many BWR stations. To this day, stations still report contributions to reactor water sulfate from one or more of the following sources:

- Ionic sulfate not removed by the condensate polisher resin during conditions of condenser inleakage
- Ionic and organically-bound sulfate (post-UV) in the effluent streams of the condensate polisher and reactor water clean-up vessels
- Cation exchange resin fines that are sufficiently small to pass through the screened under-drain laterals of the condensate polisher vessels

So a key part of determining the most cost-effective solution is to understand which of these sulfate sources is controlling reactor water sulfate levels. For most situations the answer is the presence of organically bound sulfur in the polisher effluent stream. Clearly the cation resin can be a source of sulfur due to the resins’ compositional structure and its thermal stability properties. However, the anion exchange resin readily adsorbs sulfate and low molecular weight organic sulfonates resulting from the cation resins’ natural decomposition mechanisms. But since cation resins are denser than anion resins, it seems logical that during the transfer of the mixed resins back to the service vessel a cation resin ‘heel’ can form at the bottom of the vessel. Consequently, sulfate species that leach from the cation resin will carry down stream and concentrate in the reactor water system. Having an underlay of anion resin is one approach to reduce this source of sulfate, as was demonstrated at Pennsylvania Power & Light’s Susquehanna Station.

Operating with undisturbed resin beds

Many plants have opted to retrofit their condensate polishers systems with non-precoat filters. These filters remove insoluble iron and are installed upstream of the mixed resin beds. This eliminates the need to transfer the mixed resin beds to an ultrasonic resin cleaning (URC) system since crud accumulation on the resin beds is reduced to negligible quantities. In this fashion the station can choose to operate the resin beds in an undisturbed mode. Today, many BWR stations are operating with undisturbed resin beds that were initially loaded with an underlay of anion resin.

An opportunity for a new, less-separable mixed resin combination

For BWR stations that cannot justify the expense (estimated between $4 and $10 million dollars) to retrofit their condensate polisher system with a non-precoat filter system, the task of controlling feed water iron and reactor water sulfate seems even more difficult. Such is the case at the Amergen Energy Oyster Creek Station in southern New Jersey. During Cycle 16 (November 1996 – September 1998), the station experienced abnormally high levels of elevated reactor water sulfate and the root cause was linked to residual cation resin remaining on the under-drain laterals following the resin transfer to the JRC (Japanese Resin Cleaner) system. At the time, all but one of the condensate polisher vessels contained a 1:1 equivalent ratio of Dowex HGR-W2 and SBR-C resins. The other vessel contained a new, less-separable combination of Dowex resin in the process of a field trial evaluation.

In the next refueling outage (17R) the under-drain laterals were replaced with a new higher strength design to alleviate pressure drop issues and improve resin transfer capability. In addition, the new Dowex less-separable resins were loaded in all vessels. This new resin mixture was selected because of performance advantages demonstrated in a full-bed field trial in the previous operating cycle. Specifically,

1. Reduced separability compared to standard resin mixtures (less tendency for resins to classify translating to better sulfate control).
2. Smaller cation resin bead diameter (approx. 500 microns) with uniform size distribution (results in a lower void fraction of the resin mixture and provides better crud filtration).

The differential pressure across the condensate polisher system is higher with this new resin pair (see Figure 3) but this was accommodated with the newly installed under-drain laterals.
New resin provides improved reactor water sulfate and feedwater iron control.

During the next operating cycle (Cycle 17) the reactor water chemistry was dramatically improved. Figure 4 shows a plot of the reactor water sulfate and the reactor water clean-up (RWCU) flow rate following Cycle 17 startup.

The startup plan called for two-pump RWCU operation at approximately 700 gpm until control could be maintained below EPRI Action Level 1 (5 ppb) with one pump. An outage of the RWCU system from 12/09/98 – 12/11/98 caused a sulfate increase, but the system was restored prior to exceeding reactor water sulfate of 20 ppb. The plant went to one-pump RWCU operation on 12/13/98, and sulfate continued to trend down to <1 ppb.
Based on these results, the Oyster Creek goal of controlling reactor water sulfate with one-pump RWCU operation was met.

Iron control results following the Cycle 17 startup are shown in Figure 5. After some initial results in the 4 – 5 ppb ranges, iron was down to 2.5 ppb on 01/20/99 prior to the loss of the moisture separator reheater. The impact of reheat loss can be seen in the 26 – 30 ppb CDI iron concentrations measured in the latter part of January and early February 1999. The reheater problems were repaired in February.

The process of cleaning all of the resin beds takes time and by late-February feedwater iron resumed a downward trend. This downward trend with operating time was expected at Oyster Creek where iron removal with standard resins has been observed to improve with resin age. After mid-May 1999, feedwater iron was controlled in the 0.7 – 2 ppb range.

![Graph showing iron control following Cycle 17 startup - Oyster Creek Station](image)

**Figure 5. Iron control following Cycle 17 startup – Oyster Creek Station**

Successful trial leads to installation of a new, high-capacity, less-separable resin. Based on the favorable results for reactor water sulfate and feed water iron control, the Oyster Creek plant continued to operate with one RWCU pump in service at 400 gpm. However, in late-Spring 1999, the plant began a battle with a small, continuous condenser leak. And in November 1999 a leak rate occurred that was estimated to be approximately 3.5 gpm. The resin beds maintained reactor water chemistry under good control during and immediately following the large leak; however, calculations suggested that the condensate polisher resin had over 20% of the original capacity exhausted due to all the exposure to salt water inleakage. So it was decided to begin replacing all the resin beds in December 1999.

All subsequent replacements were with a new, high-capacity, less-separable resin mixture with a cation exchange resin that had recently been developed by research scientists at Dow Chemical. Oyster Creek decided to install this new cation resin. The main reasons for this decision include:

- the new resin has a bead diameter that is 50 microns larger than the previous cation resin but still much smaller than the conventionally sized 10% cross-linked resin
- the new resin has 12% cross-linkage compared to 10% cross-linkage for the previous cation resin
The performance expectations for the new 12% cross-linked cation resin were improved resin stability, reducing organic sulfur release, along with somewhat improved selectivity for sodium, in addition to enhanced removal of insoluble iron.

Meeting the standards and goals set by Exelon

Amegern ownership includes Exelon and British Energy, so consequently, Exelon’s standards and goals are applied to Oyster Creek. The chemistry goals are tied to the Chemistry Performance Indicator (CPI) which is calculated from an equation with terms for reactor water quality and feed water iron concentrations. Oyster Creek was challenged to lower its’ CPI value to less than 1.1 and to achieve this goal Oyster Creek needed to control feed water iron below 2.1 ppb and reactor water sulfate and chloride below 2.0 ppb. Oyster Creek has met the reactor water sulfate and chloride goals each month so far in 2001. And feed water iron has been less than 2.1 ppb for most months in 2001.

Today, Oyster Creek operates with five beds of the new, less-separable mixed resin and 2 beds of the conventional mixed resin. As a result, year-to-date average CPI through September 2001 is 1.07.

Techniques to increase utilization of the cation exchange resin

In order to achieve the target for contaminant sodium, PWR stations need to maintain sodium leakage at levels near 5 parts-per-trillion (ppt) or less. In addition, the service cycle of the polisher resin cannot exceed the onset of amine breakthrough. Amine breakthrough occurs when the influent ethanolamine and/or ammonia have exhausted the cation exchange resin to the point at which these amine species appear in the polisher effluent as indicated by specific conductivity. Under these conditions the service cycle run length of the polisher bed is essentially the operating capacity the cation resin affords for amine pick-up. The term “percent utilization”, in this particular application, refers to the amine pick-up capacity relative to the total exchange capacity of the cation resin.

Means to increase utilization of the cation exchange resin
Engineers at Millstone Station explored two changes to the resin handling and regeneration procedures: 1) in-vessel mixing of the freshly regenerated mixed resin, and 2) extending the regeneration of the cation exchange resin. The in-vessel mixing uses compressed air to re-mix the condensate polisher resin in the service vessel immediately following the transfer from the mix and hold tank. This redistributes the cation resin equally throughout the vessel and consequently more of the cation resin settles in the useable portion (upper section) of the service vessel. Unit 2 first implemented this procedure in February 1996 and Unit 3 put into practice in August 1999. Extending the regeneration is a simple approach that involves regenerating the cation resin until 95% or more of the ethanolamine elutes from the cation resin bed. Sampling and analyzing the regenerant effluent makes possible an elution curve (see Figure 6) that can be used to determine the time required for completing the regeneration step. Figure 7 shows that the system at Millstone reaches the desired endpoint after approximately 90 minutes.

Figures 8 and 9 show the cation resin utilization performance for Millstone Station Units 2 and 3. After the initial five or six service cycles, both units show fairly consistent cation resin utilization over the next ten service cycles, near 75%. This is a significant improvement compared to a utilization range of 45% to 65%; reported in 1996 from a survey of 8 different PWR units in the United States.

Condenser inleakage causes high chloride in the steam generators

High TDS conditions existed in the hotwell during re-start preparations for Unit 2 due to ingress of seawater from the coolant side of the condenser. Although the condensate polishers provided ion exchange capacity to remove the majority of the contaminant ions, the steam generators were showing unacceptably high chloride levels. Efforts to correct this problem proved futile even after applying twice as much regenerant NaOH for the anion exchange resin, carefully examining the resin separation and regeneration process, and analyzing the bulk regenerant NaOH for high chloride impurity. The root cause of the problem was finally discovered when engineers at Millstone measured the elution of contaminant ions from the anion resin.

![Figure 6: Ethanolamine Elution Curve during Regeneration of Charge #6 Cation Resin / Millstone Station, Unit 2](image-url)
Figure 7. Regeneration Efficiency of Cation Resin -- charge #6 at the Millstone Station, Unit 2
Extending the NaOH regeneration to correct the problem

Figure 10 is an example elution curve for one of the four condensate polisher charges that was exposed to abnormally high levels of free mineral acidity (chloride and sulfate) due to the condenser inleakage situation. As can be seen in this plot, about 150 minutes of NaOH regeneration is required to remove most of the contaminant sulfate and about 300 minutes is required to achieve efficient removal of the contaminant chloride. This amount of NaOH is much higher than standard recommendations that this author has seen reported in the literature. The results speak for themselves. Figure 11 shows the impact on steam generator chloride levels once the extended NaOH regeneration was applied to all four condensate polisher charges.
Figure 10. Elution of Anions during Regeneration of Charge #5 Anion – Millstone Station, Unit 2

Figure 11. Steam Generator Chemistry – Millstone Station Unit 2

The other important item to note from Figure 11 is the absence of a steam generator sulfate excursion prior to the extended NaOH regenerations. This is explained by the concentration-dependent selectivity in the
exchange between divalent and monovalent ions. Although excess sulfate remained on the anion resin following the regenerations up to mid-July 1999, the sulfate remained on the anion resin during the service cycles due to its extremely high affinity for strong base anion resin under conditions of low hydroxide concentrations. Conversely, under conditions of high hydroxide concentration (i.e., during NaOH regeneration), the sulfate possesses much lower selectivity and is more easily displaced when compared to chloride (see Figure 10).

CONCLUSIONS

Condensate polishing is an application with many different design and operational aspects. The past decade has brought new challenges for improved water quality with respect to both soluble and insoluble contaminants. Nonetheless, the endeavors to understand the compositional complexities of the ion exchange resin bead and the convoluted dynamics of ion exchange chemistry and chemical engineering mechanisms occurring within the mixed bed condensate polisher have brought new ideas and expectations for ion exchange resin in deep-bed condensate polishers than ever before.

The new products and procedures presented here are a collaboration of a great deal of effort on the part of researchers, consultants, system engineers, station chemists, lab technicians and others. The studies discussed in this paper unequivocally demonstrate the merits of:

1. A specially designed cation resin to achieve greater than 95% insoluble iron removal efficiency
2. A less-separable mixed resin for improved control of reactor water sulfate in BWR primary cycles
3. Applying increased levels of regeneration chemicals and retrofitting the service vessels with re-mixing capability to improve the operation of deep-bed condensate polishers in PWR secondary cycles

REFERENCES