# CONTROLLING MECHANISMS OF
# Contaminant Ion Leakage
## IN CONDENSATE POLISHING SYSTEMS

**E**xtracting the maximum benefit from condensate polishing systems continues to be a top priority among many electric utility plants. With cost reduction pressures and increasing water quality standards, owners and operators continue to evaluate the resin handling procedures that affect corrosion product transport and contaminant ion impurity levels. In many cases, contaminant ion impurities are sourced from mixed resin separation and regeneration procedures. This article explores key mechanisms as they relate to regenerable condensate polishing systems.

### Effluent Water Quality

Remarkable progress has been made over the past decade to reduce the levels of contaminant ions in the effluent of regenerable deep-bed condensate polishers. In many pressurized water reactor (PWR) plants, polisher effluent purity is reported in parts per trillion (ppt) ranges; typical steady-state values are 5 to 15 ppt for sodium, 20 to 40 ppt for chloride and 20 to 50 ppt for sulfate. Certain fossil stations also report sub-parts per billion (ppb) levels of these same impurities in the polished condensate. However, other fossil stations are operating at much higher impurity levels.

Since the cation and anion resins are regenerated with solutions of sulfuric acid and sodium hydroxide, respectively, sodium and sulfate have been most affected by the improved product and procedural changes. Essentially, mixed resin charges are being returned to service with lower amounts of cross-regenerated cation and anion resins.

A review of the mechanisms that control the levels of sodium, sulfate and chloride ions is presented here. Knowledge of these controlling mechanisms is key to understanding and better defining opportunities for improved water quality.

### Sodium Leakage—Hydrogen Cycle

In the hydrogen cycle, equilibrium leakage appears to govern sodium levels in the polished condensate. That means the concentration of sodium ($Na^+$) and hydrogen ($H^+$) ions in the resin and solution phases at the bottom of the resin bed are in equilibrium. This is mathematically described by Equation 1.



**FIGURE 1:** Sodium Ion Displacement Based on pH

**Equation 1**

$$R\text{-}H + Na^+ \leftrightarrow R\text{-}Na + H^+$$
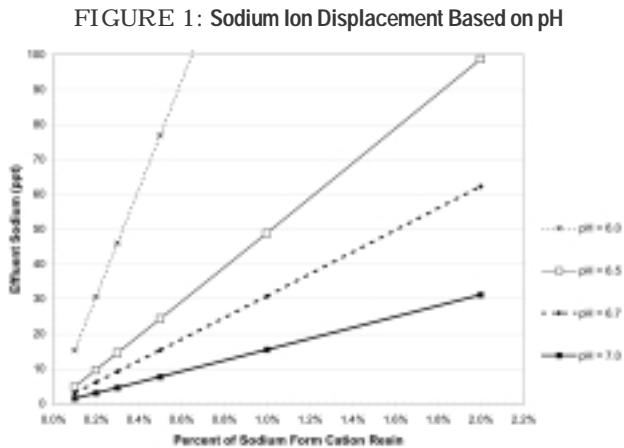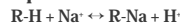
Where:
R = resin phase
K = the selectivity coefficient of $Na^+$ relative to $H^+$

According to Equation 1, sodium form resin (R-Na) and the hydrogen ion concentration in solution ($H^+$) at the bottom of the bed directly impact the sodium level in solution ($Na^+$) by shifting the equilibrium reaction from right to left. In order to achieve 5 ppt of sodium in the polisher effluent, sodium-form cation resin must be less than 0.33

percent when the effluent is at neutral pH conditions. (See Table A for the calculation exercise.) This especially is significant when considering the use of boric acid injection in the secondary cycle of PWR systems.

Anion resins show very low selectivity for borate species; therefore, the borate break occurs early on in the service cycle. The breakthrough of boric acid creates acid pH conditions and a larger driving force for sodium ion displacement as depicted in Figure 1.

Many PWR operators are attaining low ppt sodium chemistry with a conventional

regeneration system and some combination of the following.

- The use of gel, uniform particle size cation and anion resins.
- Leaving less than ⅛ inch of anion resin in the cation regeneration tank (CRT) following the anion resin transfer.
- Resin-on-resin regeneration.
- Skipping anion resin regenerations.
- Polishers taken off-line at the onset of amine breakthrough.

### Sodium Leakage—Ammonia Cycle

In the ammonia cycle, sodium and ammonium ions ($NH4^+$) in the resin and solution phase at the bottom of the resin bed are in equilibrium. This is described in Equation 2.

**Equation 2**

$$R\text{-}NH_4 + Na^+ \leftrightarrow R\text{-}Na + NH_4^+$$
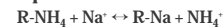
Where:
R = resin phase
K′ = the selectivity coefficient of $Na^+$ relative to $NH_4^+$

In this environment, the competing ion concentration ($NH_4^+$) also is a function of pH. At pH equal to 9.0 hydroxyl ($OH^-$), and therefore $NH_4^+$, is at a solution concentration near 10–5 equivalents per liter. Compared to the hydrogen cycle, this may be 100 times greater than the competing $H^+$ concentration at a pH equal to 7. Consequently, sodium leakages are greater with ammonia cycle operation.

Many stations operating in the ammonia cycle cycle choose a 20 percent cross-linked macroporous cation resin rather than the 10 percent cross-linked gel cation resin. This decision stems from the higher sodium selectivity coefficient, K' of the macroporous resin. But, as shown by Equation 2, sodium leakage also is governed by the amount of sodium form cation resin, R-Na, at the onset of the amine cycle. So, reducing this term is a direct way to reduce sodium leakage. This has been the essence of power plant sodium reduction initiatives throughout the past decade.

### Sulfate Leakage

The governing mechanisms for sulfate leakage have only been discussed to a limited extent. Let's first start out by
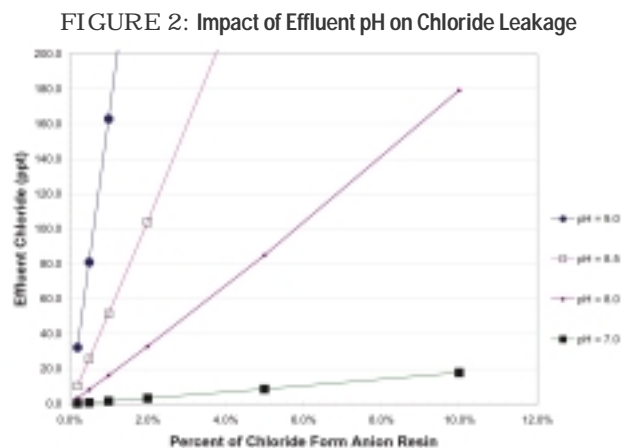


**FIGURE 2:** Impact of Effluent pH on Chloride Leakage

reviewing what we do know about sulfate. Sulfate ($SO_4^{-2}$) is a divalent ion that exchanges with monovalent hydroxide ($OH^-$) according to Equation 3.

**Equation 3**
$2 R\text{-}OH + SO_4^{-2} \leftrightarrow R_2SO_4 + 2 OH^-$
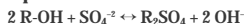
Where:
R = resin phase
$K'' =$ the selectivity coefficient of $SO_4^{-2}$ relative to $OH^-$

The mathematical treatment of the selectivity coefficient is more complex than for monovalent-monovalent exchange. The expression for $K''$ is given below and shows it to be a nonlinear function of hydroxide ion concentrations in the solution and resin phases (Equation 4).

**Equation 4**
$K'' = \dfrac{[OH^-]^2 [R_2SO_4]}{[SO_4^{-2}][R\text{-}OH]^2}$

According to Equation 4, the selectivity coefficient is not a constant and varies with concentration terms. In general, the anion resin becomes more selective for the divalent (sulfate) as R-OH declines but more selective for the monovalent (hydroxide) as R-OH increases. In practice, this means that sulfate selectively is held by the resin during service conditions but easily released during regeneration conditions. This explains the common practice to leave behind some anion resin in the CRT.

Some PWR operators leave behind as much as a ½ inch in the CRT; yet, when the bed is returned back to service, the polisher effluent contains less than 50 ppt of sulfate at steady state conditions. Along the same lines, the sulfate-hydroxide selectivity relationship has allowed for the skipping of anion regenerations in many PWR plants without a significant compromise to effluent sulfate levels. One end user went more than six months without regenerating the anion resin. Sulfate occupied nearly 40 percent of the total exchange sites on the anion resin due to cross-regeneration in the CRT; yet, effluent sulfate remained below 50 ppt during steady-state service cycle conditions.

Many operators have on-line ion chromatographs that are equipped to measure sulfate in the ppt range. This has enabled some very interesting data collection, particularly the concentration-time profile for sulfate during the initial part of the service cycle. In many cases, the sulfate profile exhibits a long tail that has endured for many hours before reaching a steady state equilibrium leakage value—unlike sodium, which has a very sharp and quick approach (minutes) to a steady-state, flat-line profile. Why are the concentration-time profiles so different for sodium and sulfate in some cases? If an operator measures less than 10 ppt sulfate in the hot well, then why does it sometimes take more than 20 hours for effluent sulfate to fall from 300 ppt to 30 ppt?

### Conversion of Bisulfate to Sulfate Form
During cation regeneration, bisulfate ($HSO_4^-$) is the predominant species in the sulfuric acid. Hence, anion resin in the CRT initially is converted to the bisulfate form according to Equation 5.

**Equation 5**
$R\text{-}OH + HSO_4^- \leftrightarrow R\text{-}HSO_4 + OH^-$
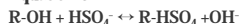
As the sulfuric acid is rinsed out of the interior of the anion resin bead, the exchange site converts from the bisulfate to the sulfate form according to Equation 6.
**Equation 6**
$2R\text{-}HSO_4 \rightarrow R_2SO_4 + H_2SO_4$
The diffusion rate of sulfuric acid out of the bead and into the surrounding bulk solution may determine the conversion rate and therefore the rinse down behavior. Surface fouled anion resins will impede the diffusion rate of $H_2SO_4$ exiting the anion resins; hence, the conversion of anion resin from the bisulfate to the sulfate form. This partly may explain the long, sluggish rinse down behavior associated with "aged" or "surface-fouled" anion resins. Consequently, it is common to see sulfate excursions in the steam generators of PWR plants linked with anion exchange resin that has been tested and deemed kinetically impaired. Regardless of the source of anion resin kinetic impairment, the same symptomatic associations seem to exist.

### Chloride Leakage
The equilibrium leakage of chloride can be described according to Equation 7.

**Equation 7**
$R\text{-}OH + Cl^- \leftrightarrow R\text{-}Cl + OH^-$
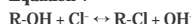
Where:
R = resin phase
$K'' =$ the selectivity coefficient of $Cl^-$ relative to $OH^-$

As shown by Equation 7, as the level of chloride form resin (R-Cl) at the bottom of the bed increases, equilibrium shifts to the left and the chloride level in solution ($Cl^-$) increases. Figure 2 depicts the impact of effluent pH on chloride leakage for conditions in which effluent chloride levels are controlled by chloride-hydroxide equilibria. Notice the sensitivity of the effluent chloride leakage with pH conditions. This illustrates the importance of maintaining a uniform mixture of cation and anion resin through the entire depth of the bed. With a uniform mixed resin bed the anion resin at the bottom (outlet) of the bed is leaking chloride in response to neutral pH conditions. However, a non-uniform mixed resin bed with anion resin classified near the upper section will start to show increased chloride leakage due to alkaline pH conditions.

Actually, resin samples analyzed from condensate polisher systems generally contain chloride at levels near 1 percent of the total anion exchange sites. At neutral pH conditions the calculated chloride leakage is 1.6 ppt based on chloride-hydroxide equilibria. (See Table B for the calculation exercise.) But chloride leakages from PWR plants typically are at levels near 25 ppt. So the implication is that chloride leakage is a result of pH conditions between 8.0 and 8.5. This can occur only with significant classification of the anion and cation resins. Clearly, an opportunity exists to improve effluent water quality by assuring the uniformity of a mixed resin bed throughout the entire depth of the bed.
Continued improvement of effluent water quality with regenerable deep bed condensate polishing remains a high priority for many power stations, especially PWR nuclear power plants. Efforts to better understand the

controlling mechanisms for effluent chloride and sulfate impurities is the most sensible approach to achieve improved water chemistry in the downstream process equipment. **WQP**

**About the Author**
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