AN INTRODUCTION TO CONDENSATE POLISHING

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Deep-bed condensate polishing is an ion exchange process which is used to remove trace contaminants, both dissolved and suspended, from high-purity water. The reason for deep-bed polishing is to purify the same water which is recycled over and over again down to the ppb level of contamination.

With the advent of higher pressure boilers and more restrictive feed-water requirements of turbine manufacturers, the ion exchange equipment manufacturers were called on to meet the challenge of purifying very large quantities of water which contained very small quantities of both dissolved and suspended contaminants. The major dissolved contaminants were sodium, chloride, and silica, while the suspended contaminants were oxides of iron and copper.

Conventional mixed bed demineralizers consisted of in-place regenerated resins. The anion resin was regenerated with caustic and the cation resin with acid. While the new condensate polishers were similar in nature to the conventional mixed bed demineralizers, the high operating pressure and flow rate required changes. The polishers were externally regenerated to limit the cost of duplicating the regenerant headers, valves, and piping. With external regeneration facilities, the freshly regenerated resins could be rinsed down to quality without risking contamination of the high-pressure boilers with traces of regenerant acid or caustic.

Initially, most of the power plant piping contained substantial quantities of copper in the condenser tubing. In order to reduce corrosion of the systems, ammonia was added to raise the pH. However, in the process of providing corrosion protection the ammonia dissolved some of the copper piping, and therefore industry decided to use all iron piping. Ammonia was added to raise the pH to between 9.0 and 9.6. The presence of ammonia in the condensate feeding the ion exchange polishers created a higher load on the hydrogen-form cation resin. Run lengths grew shorter as the ammonia concentration in the feed water was increased higher and higher to reduce corrosion in the system. The relatively short length of run required more and more regenerant, and problems were encountered in performing the number of regenerations required to keep the units on line. The industry then started its early attempts at operating the polishers beyond the

ammonia break. However, as the ammonia started leaking into the effluent, the sodium started to increase.

$$R \cdot NH_4 + Na^+ \leftrightarrow R \cdot Na + NH_4^+$$

Let us examine the sodium equilibrium reaction with ammonia. We see that sodium in the influent to a polisher in the ammonia form produces ammonia in the effluent, with sodium being removed on the resin. The rate constant for this reaction is 0.75.

$$K = \frac{[NH_4^+][R \cdot Na]}{[R \cdot NH_4][N^+]} = 0.75$$

Assuming that the only cations present are sodium and ammonium, the sum of the sodium on the resin and the ammonium on the resin would be 100%.

$$R \cdot Na + R \cdot NH_4 = 100\%$$

Rearranging the equation,

$$\frac{[R \cdot Na][NH_4^+]}{[100 - R \cdot Na][Na^+]} = 0.75,$$

We see that sodium leakage in the effluent at equilibrium is a function of both the sodium on the resin and ammonia in the feed.

$$[Na^+] = \frac{[R \cdot Na][NH_4^+]}{[100 - R \cdot Na][0.75]}$$

1.   As sodium on the resin increases, so does the sodium in the effluent (at constant ammonia concentration).

2.   As the ammonium concentration is increased (pH of the condensate), the sodium in the effluent will increase.

3.   As the ammonium concentration is increased, less sodium can be tolerated on the resin.

Further treatment of the subject of ammonia, sodium, and kinetics is well presented in papers by Salem (1), Emmett (2), and Darji (3).

How then can we reduce the level of sodium on the resin? Emmett (2) has provided data on the regenerant level required to attain specific resin purity. This data holds for cation resin by itself, but what about that cation resin which has been backwashed into the anion resin and is suspended in the anion resin layer or the inert resin layer? How do we deal with the contamination of this resin which occurs during the sodium hydroxide

regeneration of the anion? The key to solving the problem of sodium is to obtain the best possible separation between the cation and the anion resins.

Careful selection of resin screen sizes and densities is necessary to avoid cation resin beads in the anion resin layer. Since the degree of fluidization of a resin bead is a function of both its size, or diameter, and its density, large low-density beads and small higher-density beads can find themselves side by side when fluidized during a separation backwash.

Clumping of resins compounds the problem, especially when the resins are new. Clumping is caused by a strong surface charge on the resin which, by means of electrical attraction, draws resin beads together. This is especially true between the hydroxide-form anion resin and hydrogen-form cation resin. Once clumped, these resins resist separation. They also swell due to entrained water between the agglomerated clumps and you may find that the resin which fit in the tank very nicely with the cation below the separation point has now expanded above that point. Some resin manufacturers have addressed this problem by treating the anion resins with a proprietary chemical to partially foul the surface of the resin to prevent clumping. The cation and anion resins or cation and inert resins, when clumped, cling together, resisting ordinary efforts to separate them. A number of remedies have proven helpful in this regard, amongst which are the use of Triton X-100 in a 1/1000 dilution, or a complete exhaustion of the mixed resins, for example, using sodium chloride.

Once the resins have been separated as well as possible, it is still necessary (in a transfer demineralizer with a three-tank regeneration facility) to sluice the anion resin over to the anion regeneration tank. Usually, a small amount of anion resin (1/4" to 1/2") has been left behind to minimize transferring cation resin fines along with the anion resin into the anion regeneration tank. Once in the anion regeneration tank, this cation resin, either small beads or fragments from resin attrition, would be regenerated to the 100% sodium form.

Ion exchange resin manufacturers have provided the industry with a long desired goal, an inert resin which will form an interface between the cation and the anion resin. The inert resin, with size and density carefully selected, provides a separating layer between the cation and the anion resins after backwash. The intermixed zone has been reduced as far as possible by selection of resins which separate well without use of inert resins. The inert resin aids with the separation and also dilutes the intermixed resin. The use of inert resins permits transfer of the anion resin without either leaving behind a little bit of the anion resin, or taking along a little bit of the cation resin. These resins in effect optimize the separation. What we are doing, in effect, is providing a cation- and anion-free space between the cation and the anion bulk resins. Reality, as always, is somewhat less attractive than the ideal since no separation is really 100%, but we do have a much-improved system.

Three major processes have been developed in the last two decades to minimize sodium in the resin and hence reduce leakage.

1. Ammonium hydroxide treatment of anion resin.

2. Calcium hydroxide treatment of anion resin.

3. Floating anion resin with sodium hydroxide.

The first two processes use ammonia or lime to treat the anion resin after its regeneration with sodium hydroxide. The purpose of these treatments is to address the problem of the cation resin which has been transferred over with the anion resin. This resin has been regenerated with caustic and is now in the 100% sodium form. The last process makes use of a sodium hydroxide solution of density intermediate between that of the cation and anion resin to float the anion resin in the anion regeneration tank while permitting the cation to sink to the bottom. This separates out the cation resin, which has been converted to the sodium form. Let us take a look in detail at each of these three processes.

The ammonia wash system uses a weak solution of ammonium hydroxide, which is either passed once through the anion resin to waste, or recycled downflow through the regenerated anion resin, then down through the ammonia form cation resin before it has been regenerated. The ammonia will strip off sodium from those cation beads or fines in the anion vessel, which were converted to the sodium form during the anion regeneration. Recycle ammoniation deposits the sodium removed from the cation resin in the anion tank onto the cation resin in the cation regeneration tank. This cation resin is later regenerated with sulfuric acid. The cation resin regenerant level will have to be of such magnitude as to remove the additional sodium load as well as that sodium already on the resin.

The time required to strip the sodium from the contaminated cation resin in the anion tank is directly proportional to the actual quantity of cation resin contamination in with the anion resin. In practice, the weak ammonia solution is either passed through or recirculated for anywhere between 2 hours and 24 hours until the sodium is removed. If a lot of cation resin has been carried over with the anion resin, this time can become considerable.

The lime wash system uses a very dilute filtered calcium hydroxide solution to remove the sodium from the cation fines, exchanging calcium for the sodium on the resin. Some people have been reluctant to use the lime for fear of any calcium entering the boiler. The calcium itself is very strongly held on the resin, and sodium and ammonia are unlikely to remove any significant quantity of calcium. Any precipitated or suspended calcium in the form of hydroxide or carbonate is removed by a backwash followed by a

downflow rinse. An alternate method is in situ manufacture of calcium hydroxide by passing a calcium salt through hydroxide form anion resins as mentioned by Connelley (5). The lime solution is then filtered and applied as before. The time required to exchange the sodium will depend on the amount of cation resin present. The more cation resin present, the longer the time required.

In the third process, a sodium hydroxide solution of selected density is used to float the anion resin. These permits the cation resin fines to sink to the bottom of the anion regeneration vessel while the anion resin is being regenerated. The floating anion resin, free of cation fines, is transferred to the mix and hold vessel for rinsing. The cation resin is left in the bottom of the anion regeneration vessel and is subsequently transferred into the cation regeneration vessel along with the next charge of resin for regeneration.

Being engineers, we are inherently lazy people and hate to throw away a mold that works well. Let's try what worked for the cation resin, as far as equations go, for the anion resin. We note that, as the ammonia in the feed increased, both pH and hydroxyl ion concentration followed. For the anion resin, the increase in hydroxyl ion concentration tends to reverse the equilibrium, creating more bisilicate ions in the equilibrium reaction. Looking at the equation,

$$R\cdot OH + HSiO_3 \leftrightarrow R\cdot HSiO_3 + OH^-$$

The equilibrium constant K,

$$K = \frac{[R\cdot HSiO_3]\,[OH^-]}{[HSiO3^-]\,[R\cdot OH]}$$

has been assigned an approximate value of 5 by Venderbosch (4).

Rearranging the equation as we have done with the cation resin, we see that the bisilicate ion concentration is a function of the hydroxyl ion concentration and the amount of bisilicate or silica on the resin.

$$[HSiO_3^-] = \frac{[OH^-]}{5} \quad \frac{[R\cdot HSiO_3]}{[100-R\cdot HSiO_3]}$$

We can now see that:

1.   At any given pH, the silica concentration in the effluent will increase proportional to the silica concentration on the resin.

2.   As the pH increases, so does the silica concentration in the effluent.

3.   To maintain a low silica concentration as pH (hydroxide concentration) is increased less silica can be permitted on the resin.

The same three points are true for the chloride-hydroxide equilibrium.

Enough mathematics and theory for now. You may be willing to concede by now that the amount of cation resin in the sodium form, or anion resin in the chloride, bisilicate, or bisulfate forms, is important to the leakage of the same ionic species in an environment of ammonia. So what? How can this possibly have any bearing on methods of polisher operation? This becomes abundantly clear to anyone who has ever attempted to operate beyond the first few signs of ammonia in the effluent.

At the very beginning of this talk, we started to discuss ammonia. Almost all polishers start off life (after regeneration) as H-OH cycle mixed beds. Under these conditions the cation equilibrium is one between hydrogen and sodium until the ammonia (if any) works its way down the bed. **With a driving** force of OH- or NH4+ ions absent, the polishers do not require the same degree of conversion to the regenerated forms as when the ammonia does come through. The name of the game definitely becomes trying to avoid deterioration of effluent quality as the run passes from the hydrogen cycle to the ammonia cycle.

How can we observe the progress of the run and make intelligent decisions concerning the status of the resin? At the very start of the run, a recycle rinse, or rinse to drain, will push out that water which has been sitting idle in the standby polisher in contact with the resins. In a short time, we will be able to determine the health of the polisher by measuring both inlet and outlet specific and cation (Larson Lane.' conductance as well as ionic sodium and silica.

The inlet specific conductance, when compared to the inlet cation conductance, lets us know how much ammonia is being fed. The pH would also be a means of verifying ammonia feed. The inlet cation conductance, with the influence of any masking ammonia removed, permits us to examine the sum of any influent chlorides and sulfates as their corresponding acids. The effluent specific conductance (usually 0.1 microsiemens) informs us that the ammonia is being removed by the polisher. The effluent cation conductance (if greater than the specific conductance) indicates anion leakage of chlorides and/or sulfates. The Larson Lane column acts as an analytical tool to change the ammonia or sodium chloride into the corresponding acid, namely hydrochloric. The quantity of anion leaking can be estimated by dividing the cation conductance less the pure water blank, which is 0.055 at 25'C., by approximately 0.007 and obtaining the leakage in ppb as $CaCO_3$. For example, a cation conductance of 0.13 microsiemens would indicate an anion leakage of approximately 11-ppb.

Sodium and silica leakage are generally determined by means of continuous inline analyzers. Grab samples are very susceptible to contamination and are not reliable in the range of sodium and silica concentration generally found in condensate.

Suspended matter can be determined using membrane filter stain tests and comparing the stain to a standard chart, or by means of total iron and/or copper analytical testing.

The diagnostic tool used to monitor suspended solids during the run is pressure drop across the bed. When a resin bed becomes fouled with crud, the pressure drop will increase or, if no flow-balancing devices are in use, the flow through that unit with the most service (more crud) will decrease.

On the H-OH cycle, the service run continues until the ammonia is no longer being completely removed by the cation resin (often 3-5 days). The first indication of ammonia break is a gradual rise in the specific conductance of the polisher effluent. As the ammonia and the hydroxide concentration increase in the effluent, the concentration of both sodium and silica start to increase. The level of sodium or silica leakage, as mentioned previously, is determined by the regeneration level that the resin receives or, correspondingly, the concentration of sodium or silica on the resin and on the degree of intermixing and on any condenser leakage that may have occurred.

When operating beyond the ammonia break, the run proceeds until the inlet and outlet conductivities are the same. At that point, the cation resin is fully ammoniated. Ammonia is now passing unchanged through the cation resin. Sodium influent to the polisher is removed by the cation resin and the equivalent amount of ammonium ion exits the polisher. The level of sodium leakage is determined by the influent pH, which is also now the effluent pH, and the amount of sodium on the resin. Similarly, the chloride and silica are exchanged for hydroxide anions and their leakage is controlled by the equilibrium reactions discussed earlier. Once the cation resin is fully ammoniated, the run can continue until the cation resin is either exhausted with respect to sodium and leakage exceeds what is tolerable, or when the pressure drop reaches intolerable levels. High silica caused by anion exhaustion is also a reason for terminating the run.

In spite of the best metallurgy and the tightest condensers, sooner or later all plants experience condenser leakage. The seriousness of a condenser leak is proportional to the concentration of solids in the cooling water, and the magnitude of the leak. What matters to the polisher is the quantity of solids, both dissolved and suspended, which are flooding into it and occupying its capacity. During a condenser leak, the influent dissolved solids are increased by the cooling water, which is leaking through the ruptured condenser tube into the recirculating condensate stream. The cation resin will exchange ammonium ions for sodium and hardness, while the anion will exchange hydroxide ions for alkalinity, chlorides, sulfates and silica. The increase in the effluent ammonium and hydroxide levels causes a shift in the equilibrium and the sodium, chloride and silica levels in the effluent will rise. The magnitude of the leak and the degree of regeneration of the resins, as well as how much sodium, silica, and chloride are on the resin, will determine if the plant can continue to operate with the leak. The run length and the time required to regenerate will decide if the leak can be tolerated for a longer period. When operating with a detectable condenser leak, increased regenerant is recommended to remove the added ionic contaminants. In order to keep the sodium and silica leakage in range, operation is usually restricted to the H-OH cycle during a condenser leak and the run is terminated when ammonia starts leaking into the effluent.

What ratio of cation resin to anion resin should we use? Resin ratio is a term which has been loosely tossed around a great deal. Consider the 2:3 cation:anion ratio (by volume), which is the so-called stoichiometrically equivalent mixture. Referring to Table 1, we find that the capacity of an 8% crosslinked cation (measured in the sodium form) is 2.0 meq/mL. That of a porous gel anion (measured in the chloride form) is 1.1 meq/mL. With a 2 parts cation: 3 parts anion ratio, each cubic foot of mixed resin will have an ultimate capacity of 0.8 meq/mL. of both cation and anion capacities as shown.

TABLE 1
ULTIMATE CAPACITIES

	CATION meq/mL			ANION meq/mL		
	H+	Na+		OH-	Cl	
*8%	1.8	2.0	*Type 1	1.25	1.45	
*10%	2.0	2.2	**Type 1	1.1	1.3	*Gel
Macro	1.7	1.75	Macro	0.9	1.0	**Porous gel

If the same resins, the 8% gel cation and the porous gel anion, are supplied in the hydrogen and hydroxide forms, the picture changes. The cation capacity decreases from 2.0 to 1.8 meq/mL. and the anion capacity decreases from 1.3 to 1.1 meq/mL. The cation contributes 0.72 meq/mL. to the mixture and the anion only 0.66 meq/mL.

With a 10% gel cation, the cation in the hydrogen form has a capacity of 2.0 meq/mL. and contributes 0.8 to the anion's 0.66 meq/mL. Suffice it to say that the 2:3 ratio should be used as a guide and not as a panacea, especially since we are talking about a balance of ultimate capacities, not operating capacities.

How do you intend to design your polisher? Will it operate exclusively on the H-OH cycle with a pH 9.2 influent? With a normally leak-free environment, the cation resin will be hard at work removing ammonia while the anion will be on hand just in case of a condenser leak. This does not need a balanced system. A 2:1 ratio of cation:anion would seem appropriate with the anion there as an "insurance policy."

If the designer is using a brackish cooling water with total dissolved solids in excess of 500 ppm, and is anticipating certain pinhole leaks, more anion may be justified. If the "design" leak condition would limit operation to the H-OH cycle, then the cation load would consist of the leak itself, namely the calcium, magnesium and sodium in the leak, plus the ammonia in the feed. Perhaps a 1:1 ratio by volume might be suitable.

With operation beyond the ammonia break, consideration of operating conditions becomes critical. The quantity of sodium, chloride and silica which can be removed is determined by the pH of the influent condensate. Some of the anion capacity is required to remove the carbon dioxide, which has entered the cycle along with air inleakage. Any

leak which would contribute chlorides, sulfates, C02, silica and alkalinity would also have entered the calculation.

We have spoken about condensate polishers which operate on the ammonia cycle. Some condensate polishers operate exclusively on the H+ - OH- cycle. Typical of these are those used in purifying condensate for use in a boiling water reactor. In this case, the stoichiometrically equivalent ratio would have to be considered since the NRC Regulatory Guide #1.56 requires that the capacity utilization of both anion and cation be limited to half the total or ultimate capacity.

During operation for extended run lengths, the resin in the polishers can become fouled with crud or oxides of iron and copper. In order to successfully regenerate these resins, they must be cleaned and this can be accomplished by a combination of air scrub and backwash. To successfully clean resin, it helps to have the capacity of scrubbing and backwashing the resins individually after separation in order to obtain sufficient fluidization of the cation.

You will probably have more questions now than you had at the start of my presentation. I hope so. The subject of condensate polishing is as complex as it is fascinating. Remember that the mathematical equations are valid for two component systems. They do, however, give an insight as to what is actually happening in the system and can be used to explain certain of the curious behavior of the resin systems.

References:

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