

Softening Methods of Waters with High Total Dissolved Solids

Soft water is required to generate steam without formation of harmful scale on the tubes of the boiler. Softening of low TDS (Total Dissolved Solids) water is done commonly with a Strong Acid Cation (SAC) exchange resin operating in the sodium form and regenerated with brine (Sodium Chloride). As the TDS of the water to be softened increases, removal of hardness to low levels becomes more difficult and processes such as counter-flow regeneration need to be used. As the TDS increases even higher, a weak acid cation (WAC) exchange resin has to be used. WAC resin is much less affected by salt concentration in the water to be softened, which also means that brine cannot be used efficiently for regeneration. Regeneration in this case, is done by regenerating the resin first to the hydrogen form with acid, followed by conversion to the sodium form with a sodium alkaline solution such as caustic (NaOH).

Weak acid cation exchange resins are also used very efficiently to reduce the alkalinity of water and this property can be used to soften and dealkalize waters that contain a higher level of alkalinity than hardness.

Low TDS water (< 5000 ppm) can be softened using SAC exchange resin in the sodium form (effluent hardness < 1ppm). This type of resin is similar to those used for home water softeners. As water, containing hardness (calcium & magnesium), flows over the resin in the sodium form, the calcium and magnesium are exchanged for the sodium from the resin. As a result, the effluent water no longer contains calcium or magnesium, which is soft water. This process is made possible because SAC resin has a higher selectivity for calcium and magnesium than for sodium.

After treating a certain volume of water, the SAC resin will become saturated with calcium and magnesium and therefore, will no longer soften the water. The resin needs to be regenerated by replacing the calcium and magnesium with sodium.

Since the resin has a higher selectivity for calcium and magnesium than for sodium, the only way to displace the calcium and magnesium off the resin, with sodium, is by feeding the sodium at a sufficiently high concentration. Normally 10 to 12% brine is used for regeneration.

Sodium Chloride is commonly used for regeneration because it is an inexpensive source of sodium. In some cases KCl is used as regenerant. This converts the resin to the potassium form, which is similar to the sodium form.

Most softeners are operating down-flow for service, which means that the water to be softened enters at the top of the ion exchange vessel and leaves from the bottom. Two methods are available for regeneration: Co-Current Regeneration, which consists of injecting the brine in the same direction as the service flow (from top of the bed down) and Counter-Current Regeneration (CCR), where the regenerant is injected in the opposite direction of the service flow (from the bottom of the bed up).

USA

Telephone: (1) 610-668-9090
Fax: (1) 610-668-8139
Email: info@puroliteusa.com

Europe

Telephone: +44 1443 229334
Fax: +44 1443 227073
Email: sales@purolite.com

Asia Pacific

Telephone: +86 571 876 31385
Fax: +86 571 876 31385
Email: pultalan@purolitechina.com

Co-Current Regeneration (CR)

As the brine is fed down-flow, to the resin bed, the sodium will displace the calcium and magnesium gradually lower and lower through the bed until forced out. This regeneration process is not absolute, but rather progressive. This means that as more fresh brine is being fed to the top of the bed, the resin in the upper part of the bed will find itself better and better regenerated.

Gradually, more and more hardness is pushed down through and out the bed. Providing sufficient brine is fed, the bulk of the hardness will leave the ion exchange resin bed. At the end of such co-current regeneration, the upper section of the resin bed is highly regenerated while the lower section, which only saw spent brine, will still contain some hardness. The amount of hardness left in the bottom of the bed will be directly related to the amount of brine fed to the resin bed.

When the resin bed is returned service, the hardness of the influent water will be very effectively removed in the upper part of the resin bed, which was highly regenerated. This softened water now contains 100 % sodium and this concentration of sodium ions will create a low level of regeneration effect on the resin in the lower part of the bed where some residual hardness was left by the end of the regeneration. This results in hardness leakage. The amount of leakage will be directly related to the amount of salt used for regeneration and also the level of TDS in the water to be softened. The more salt used per regeneration, the less hardness will be left at the lower part of the resin bed and therefore, the lower the leakage. Also, when the TDS of the influent water is high, the concentration of sodium ions, flowing through the bottom of the bed, will be high, and as a result, the driving force will be stronger, and more calcium and magnesium (residual hardness left on the resin at the end of the regeneration) will be driven off during the service cycle.

Regeneration of a softener is normally done with 6 to 8 lb/ft³. As the TDS of the water to be softened increases, the amount of salt has to be increased also in order to reduce the amount of hardness left in the lower part of the bed. Therefore, dosages of 15 to 20 lbs/ft³ may be required to achieve low hardness leakage when softening higher TDS water.

It is interesting to note that as the service cycle proceeds, the residual hardness left, at the lower part of the bed, will be gradually depleted and as a result, hardness leakage, due to this process, will be decreasing gradually as the service run progresses. This means that the lowest leakage will be obtained towards the end of the service cycle just before the hardness break.

Counter-Current Regeneration (CCR)

The leakage problem experienced with co-current regeneration is due mainly to the presence of residual calcium and magnesium left in the lower part of the bed at the end of the regeneration. To overcome this problem, regeneration can be done counter-current: the brine is injected opposite the direction of service flow. In most cases the brine is injected into the bottom of the vessel and exits through a distributor at the top of the resin bed. The advantage of counter current

USA

Telephone: (1) 610-668-9090
Fax: (1) 610-668-8139
Email: info@puroliteusa.com

Europe

Telephone: +44 1443 229334
Fax: +44 1443 227073
Email: sales@purolite.com

Asia Pacific

Telephone: +86 571 876 31385
Fax: +86 571 876 31385
Email: pultalan@purolitechina.com

regeneration is that, the lower part of the bed constantly sees fresh brine and the hardness is displaced upwards into the resin bed.

At the end of regeneration, the resin in the lower zone of the bed will be highly regenerated while the resin in the upper zone will not be as perfectly regenerated. Therefore, there will be very little residual hardness left on the bottom of the bed, and this will reduce the hardness leakage to a minimum. During the softening cycle, the water will be softened gradually as it progresses down the resin bed and the last traces of hardness will be removed in the lower part of the resin bed. This allows to effectively soften water with higher levels of TDS. It also allows using lower levels of regenerant while still achieving low levels of hardness leakage during the service cycle. This is due to the fact that if insufficient salt is used for regeneration, the hardness present in the resin bed will be driven up into the bed but may not be sufficiently removed. Such a situation would lead to a shorter service run but the water produced would still contain low levels of hardness. This CCR process allows to soften higher TDS water.

For best results, it is necessary to use low hardness salt, because otherwise hardness coming from the brine will be left in the lower part of the resin bed, resulting in unwanted leakage. As the brine is fed to the lower part of the bed, equilibrium will be established between the hardness in the brine and the hardness on the resin. This means that the resin is not converted 100% to the sodium form; some hardness will be left on the resin. As outlined earlier, the higher the TDS, the higher the driving force to drive residual hardness off the resin.

SAC-SAC system

In order to optimize the system and to achieve lower levels of hardness leakage, two resin beds can be used in series: Primary – Polisher. The primary column will be regenerated with the spent brine from the polisher. The polisher, in second position, will be regenerated in a counter-current mode, while the primary is usually regenerated in the co-current mode. This allows softening a higher volume of water per cycle resulting in a much more efficient operation. It also provides lower levels of leakage since the polisher will see much higher dosages of salt.

Weak Acid Cation Exchange Resins

To soften water with TDS higher than 5000ppm (guideline) it is necessary to use an ion exchange resin, which is not affected by the presence of salts. Weak acid cation exchange resins are used for this purpose. WAC exchange resins are different in structure and their properties are significantly different. These resins show a very high selectivity for divalent ions such as calcium and magnesium under alkaline conditions. As the name implies, the active group is a weak acid (such as carboxylic acid). As a result this resin, in the H-form, can only split salts from weak acids, such as bicarbonate or carbonate (from carbonic acid) but not from strong acids such as chlorides, nitrates and sulphates. Passing a solution of sodium chloride over a WAC resin in the H-form will convert very few sites to the Na-form. Since regeneration is normally done with a

USA

Telephone: (1) 610-668-9090
Fax: (1) 610-668-8139
Email: info@puroliteusa.com

Europe

Telephone: +44 1443 229334
Fax: +44 1443 227073
Email: sales@purolite.com

Asia Pacific

Telephone: +86 571 876 31385
Fax: +86 571 876 31385
Email: pultalan@purolitechina.com

strong acid (Hydrochloric acid or Sulphuric acid), regeneration is very efficient and the resin until fully regenerated will use 100% of the acid.

In the hydrogen form this resin can only remove cations (such as calcium, magnesium or sodium) associated with alkalinity. This means that, in theory, water with a higher alkalinity than hardness could be fully softened and dealkalized at the same time. To fully soften water, regardless of level of alkalinity, the resin must be used in the sodium form. Passing sodium alkaline solution (such as NaOH) over the H form WAC resin will neutralize, the H-sites and convert the resin to Na form. Na form WAC resin has a much greater affinity for divalent ions, calcium and magnesium and will exchange the monovalent ions, sodium and in the process soften the water.

Weak acid cation resins, in the H-form, are used very efficiently for removing alkalinity from water. This process is mostly efficient when the alkalinity is associated with hardness. In fact, the resin does not remove alkalinity as such, but removes the cations associated with alkalinity, thereby converting the bicarbonate and carbonate to carbonic acid. The carbonic acid, so formed, can then be removed in a scrubber (decarbonator or degasser) that will blow off the carbonic acid as CO₂. Water, dealkalized in such a way, will have a pH varying from 3.5 to 6.5; therefore, the pH is normally adjusted with caustic after the decarbonator. It then goes through a regular SAC sodium cycle softener to remove the residual hardness.

In order to minimize the amount of caustic required for pH adjustment, WAC resins used for dealkalizing are regenerated with a minimum of acid (105% of stoichiometric, based on the amount of cations exchanged). This will leave an intentional “heel” of hardness in the lower zone of the resin bed and cause a higher hardness leakage but at the same time less acidic water. The softener downstream will pick up the extra hardness.

WAC resin, in the H-form, does not have much ability to remove cations from salts of strong acids (such a chloride, nitrate or sulfate) therefore, in theory, no free mineral acidity (FMA) would be expected in the effluent. However, this is not absolutely true and it is found that during the early part of the service run, some FMA is generated by resin that has been fully converted to the H-form. This is due to the fact that this resin has a limited amount of exchange sites with salt-splitting capability. This prevents WAC resin from being fully regenerated at stoichiometric acid dosages and leads to the presence of residual cations, mostly calcium and magnesium, being left on the resin at the end of the regeneration, unless higher acid dosages are applied.

During co-current regeneration, the acid is fed from the top to the bottom of the bed and calcium, magnesium and sodium (if any) are driven down the bed. Unless sufficient excess acid is used, there will be hardness left at the bottom of the bed. Since, the top of the bed will have seen a constant supply of fresh acid, it will be fully converted to the H-form. When such a resin bed is put in service, some FMA will be generated in the upper part of the resin bed and this acid will have a regenerating effect on the resin on the lower part of the resin bed, resulting in a slow release of hardness. This is the reason why water containing more alkalinity than hardness cannot

USA

Telephone: (1) 610-668-9090
Fax: (1) 610-668-8139
Email: info@puroliteusa.com

Europe

Telephone: +44 1443 229334
Fax: +44 1443 227073
Email: sales@purolite.com

Asia Pacific

Telephone: +86 571 876 31385
Fax: +86 571 876 31385
Email: pultalan@purolitechina.com

be fully softened with WAC resin in the hydrogen form, unless all hardness is removed from the resin bed; this requires a substantial excess of acid.

Dealkalizing and Softening in one step

There is, however, a method to soften and dealkalize water in one step (only for water containing more alkalinity than hardness). In order to reduce this initial hardness leakage it is necessary reduce the amount of FMA produced within the bed at the beginning of the run. This is done by feeding two bed volumes (2 BV) of a 5% brine solution (NaCl) after the acid displacement rinse (before the final rinse) This technique will significantly reduce the hardness leakage experienced at the beginning of the service run which typically lasts for 10 to 15% of the service run. The hardness leakage in the effluent from such a system will, however, still be higher than out of a WAC resin in the sodium form. This is due to the presence of carbonic acid, but being a weak acid it will not generate high levels of hardness leakage.

As outlined above, when the alkalinity exceeds the hardness, it is possible to soften water with WAC resin in the H-form. However, the pH of the effluent will be on the acidic side for a large part of the service run and therefore, when this water is used for boiler feed-water, the pH needs to be adjusted (often with the use of caustic).

Feeding caustic to the effluent of a WAC unit in order to maintain a steady pH acceptable to the boilers is not simple because the pH of the effluent from the WAC unit will rise gradually during the service run from 3.5 to 6.5 (depending on the water characteristics). This means that the amount of caustic required maintaining a steady pH will vary during the service run. Also the quantity of caustic fed will have to be adjusted according to the flow-rate.

This variation of pH during the service run does not exist when the WAC resin is used in the sodium form. But then it will not reduce alkalinity.

Operating the WAC resin in the H-form may seem more economical since it does not require the use of caustic for the conversion to the Na-form. However, the fact that caustic has to be used to adjust the pH of the effluent should not be overlooked and the apparent saving of caustic may not be as high as expected.

WAC in Na Form operated in Counter-current regen

WAC resin can be regenerated in a counter-current mode by injecting the acid from the bottom of the bed. In doing so, the resin at the bottom of the bed constantly sees fresh acid and, as a result, there will be very little hardness left on that resin at the end of the regeneration. This allows the use of lower dosages of acid while still maintaining very low hardness leakage during the service cycle. After the acid injection, the acid should be displaced; this is also done up-flow. The caustic used to convert the resin to the Na-form and the displacement rinse should also be injected from the bottom of the bed up. The final rinse will be done down-flow at a rate close to the service

USA

Telephone: (1) 610-668-9090
Fax: (1) 610-668-8139
Email: info@puroliteusa.com

Europe

Telephone: +44 1443 229334
Fax: +44 1443 227073
Email: sales@purolite.com

Asia Pacific

Telephone: +86 571 876 31385
Fax: +86 571 876 31385
Email: pultalan@purolitechina.com

flow rate. (Note: in down-flow regeneration, it is perfectly all right to inject the caustic down-flow, providing the diameter of the vessel exceeds the bed depth)

In order to operate a counter-current regenerated system efficiently, it is important to prevent migration of the resin from the top of the bed down to the bottom. If this occurs, some resin that is still loaded with hardness may find its way to the bottom of the bed and this would alleviate the advantages of having a hardness-free lower zone of the bed. In order to prevent such resin migration in normal counter-current systems, the resin bed is held down either by a water-block or with an air-block or by operating with minimal freeboard as in a Packed-Bed. Due to the large volume change of the beads (60 to 80%) from H-form to Na-form, it is impractical, in this case, to provide a proper air-block or water-block for the resin bed. A swelling of 60% from the H-form (as shipped) to the Na-form (fully converted and rinsed) means that 1-ft³ will swell to 1.6ft³.

However, if the regenerants are injected at a sufficiently low flow rate, there will be less risk of bead migration and full advantage of the counter-current regeneration will be achieved. Injecting the acid at a low flow-rate is only possible when hydrochloric (HCl) is used. Using sulphuric acid for regeneration does not allow low flowrates because of the potential danger of calcium sulfate precipitation within the resin bed.

Regenerating WAC resin with Brine

This is not impossible in theory but it is clear that capacity can be expected to be very low. This may not necessarily be a problem when used for polishing. To get more concrete evidence of this, lab scale testing has been done.

WAC resin was first converted to the Na-form with caustic, and then fully exhausted with hardness (effluent hardness equal to influent). Then the resin column was regenerated with a salt dosage comparable to when installed as the polisher column after a SAC primary. Results showed that a higher than expected amount of hardness was regenerated off the resin. However, even so, a lot of hardness was remaining on the resin after this regeneration. Regeneration was done counter-current.

The resin was then fed a low hardness water (2 to 5 ppm) with various levels of TDS (1000 to 5000 ppm). Results are posted in table 1. Results were not as expected but indicate that sodium has more of a driving force on WAC resin than originally expected, both during the regeneration process and thereafter in the service mode.

This is an illustration of the need to feed 45% excess acid (stoichiometrically) based on the total capacity of the resin — H-form) for a co-current regeneration of WAC-Na resin to achieve low hardness leakage, as this minimises the “heel” of hardness left at the bottom of the bed. When the polishing zone of the WAC-Na resin has zero hardness, there will be no hardness leakage, even in the presence of higher concentrations of sodium.

USA

Telephone: (1) 610-668-9090
Fax: (1) 610-668-8139
Email: info@puroliteusa.com

Europe

Telephone: +44 1443 229334
Fax: +44 1443 227073
Email: sales@purolite.com

Asia Pacific

Telephone: +86 571 876 31385
Fax: +86 571 876 31385
Email: pultalan@purolitechina.com

These results indicate that the selectivity of WAC-Na resin for Calcium over Sodium is not as high as expected. Secondly, the reason WAC-Na resin can soften higher TDS water is strictly due to the ability to regenerate WAC resin 100%, thereby leaving no or very little hardness on the resin by the end of the regeneration process. This further confirms the value to consider CCR for regeneration of WAC resin used in the Na-form.

The use of WAC resin in the Na-form is extremely stressful on the resin beads due to the shrink-swell experienced every regeneration. The change in volume from H-form to Na-form varies from 60% to close to 100% for certain resin.

Additional notes:

WAC-H resin can be used to dealkalize and soften water containing more alkalinity than hardness in one step, providing a brine wash applied after the acid regeneration.

The ability of WAC-Na resin, to remove hardness from high TDS water, is based on the possibility to easily regenerate WAC resin to zero hardness with acid. The amount of acid required to achieve this is approximately 145% stoichiometric in the co-current mode (based on total capacity of the resin — H-form).

The presence of residual hardness in the lower zone of the WAC-Na resin bed will lead to hardness leakage, even with low TDS water.

USA

Telephone: (1) 610-668-9090
Fax: (1) 610-668-8139
Email: info@puroliteusa.com

Europe

Telephone: +44 1443 229334
Fax: +44 1443 227073
Email: sales@purolite.com

Asia Pacific

Telephone: +86 571 876 31385
Fax: +86 571 876 31385
Email: pultalan@purolitechina.com