

Improved ion exchange processes for softening water

Technical Field

The present invention relates to an improved ion exchange process for softening water.

Removing hardness from water typically involves addressing the presence of soluble bicarbonates, carbonates and sulphates of calcium, magnesium and iron which are the

- 5 primary contributors to water hardness. There are several methods to soften water, and the choice of method depends on the degree of hardness and specific requirements. Temporary water hardness can be removed by boiling and removal of permanent hardness requires specialist treatment of water.

- 10 The presence of the solutes in hard water also leads to the build-up of scale, especially when used in industrial cooling or heating water pipes. Water used in industrial processes often contains dissolved minerals. When this water is heated, the minerals can precipitate and form solid deposits on the inner surfaces of boiler tubes and heat exchangers. The most common type of scale is calcium carbonate, but other scales may form depending on the specific
- 15 minerals present in the water. This accumulation can negatively impact heat transfer efficiency and overall system performance. The layer of scale acts as an insulating barrier, reducing the ability of the heat exchanger or boiler to transfer heat efficiently. This leads to increased energy consumption and decreased system performance.

- 20 One solution to remove hardness in water is to use mixed bed ion exchange resins, which can either be used in the acid and base form or, more commonly, in the saturated common salt (NaCl) form. These systems use resin beads that exchange sodium ions for calcium and magnesium ions in the water. Sodium ions are released into the water, effectively softening it. Periodically, the resin needs to be regenerated with a brine solution.

25 Background

In ion exchange processes using mixed bed ion exchange resins, the overall hardness is reduced but the acid and base required to generate the resins has to be used up. In the salt form this cost is reduced but the hard salts are replaced by NaCl, which can still lead to increased corrosion due to higher salinity levels.

- 30 Saline water is a general term for water that contains a significant concentration (i.e. ≥ 500 ppm) of dissolved salts (mainly NaCl). The salt concentration is usually expressed in parts

per thousand or parts per million (ppm). Saline water may include, but is not limited to, groundwater, brackish water, seawater, hypersaline water, brine, produced water or process water.

- 5 The term ‘ion exchange resin’ broadly refers to an insoluble matrix normally in the form of small (0.5 to 1 mm diameter) porous beads with a high surface area, fabricated from an organic polymeric material on which charged functional groups have been permanently attached. The functional groups may be weakly or strongly basic (e.g. -NH₂ or quaternary ammonium, -N⁺(CH₃)₃), or may be weakly or strongly acidic (e.g. -COOH or sulphonates, -
- 10 SO₃⁻). It will be appreciated to those skilled in the art that a reference to ‘weakly basic’ will refer to an ion exchange resin with weakly basic functional groups, ‘weakly acidic’ will refer to an ion exchange resin with weakly acidic functional groups, and so forth.

- To preserve the electrical neutrality of the ion exchange resin, a mobile counter-ion is
- 15 associated with each charged functional group. The mobile counter-ion may exchange with other ions of similar charge in an ‘ion exchange’ process. An ion exchange resin may be referred to as ‘spent’ when most or all of the mobile counter-ions associated with the charged functional groups have been replaced with other ions of similar charge.

- 20 Regeneration of a spent ion exchange resin may be achieved by reversing the ion exchange reactions referred to above, or by replacing one ion with another. Conventionally, the spent ion exchange resin may be regenerated by eluting the spent ion exchange resin with a relatively concentrated solution of the original mobile counter-ions.

- 25 However, thermally regenerable ion exchange resins are ion exchange resins with reduced adsorptive capacity at elevated temperatures. Heating thermally regenerable ion exchange resins has the effect of desorbing the counter-ions from the ion exchange resin.

- The requirements for acid/base ion exchange regeneration and the requirement for salt
- 30 regeneration and subsequent increase in salinity of the treated water has led to the introduction of other technologies, such as reverse osmosis (RO) and nanofiltration for water softening.

Another related process called Forward Osmosis (FO) has been developed to overcome the high pumping pressures required with conventional RO processes. In the FO process a concentrated 'draw' solution is used to generate a higher osmotic pressure than feedwater. Using an appropriate RO membrane, water is drawn from feedwater across the membrane, without the need for expensive high-pressure pumping. The solutes used to create the concentrate draw solution are selected such that they can be readily removed from the diluted draw solution, to produce desalinated water. In one particular example, the draw solution is made from a concentrated mixture of ammonia and carbon dioxide. These solutes form a draw solution of concentrated ammonium bicarbonate (AB), which can then be decomposed, after use, by heating. The resulting gases (NH₃ and CO₂) can then be collected and re-used to form a new draw solution. Concentrated AB solutions could also be used to regenerate depleted mixed bed or mixed bead resins and in a similar process the AB can be subsequently decomposed, and the two gases collected and reused.

15 **Prior Art**

Mixed bed and mixed bead ion exchange (IEX) resins have been used to remove scale-forming ions such as Ca²⁺ and Mg²⁺ from hard water and to produce high quality water (i.e. comparable to distilled water). The resins can also be used for the desalination of fairly concentrated brackish water and even seawater, without the need for high pumping pressures, extensive pretreatment or high thermal energy input. However, utilization of an ion exchange process on a large scale for desalination is limited by the depletion of the resin and the need for large volumes of acid and base solutions for their regeneration.

This issue has been previously addressed by CSIRO in its 'Sirotherm' process. In this process a weak acid resin (WAR) and a weak base resin (WBR) were formed within the same resin beads, and these were shown to have a substantially reduced ion adsorption capacity at higher temperatures. For example, heating the ion exchange resin from 30⁰C to 80⁰C reduced the ion adsorption capacity by a factor of 8. This process has only been used to dilute brackish water. Attempts to synthesise strong acid/strong base single polymer resins has so far been unsuccessful.

Any references to background art do not constitute an admission that the art forms a part of the common general knowledge of a person of ordinary skill in the art. The above references

are also not intended to limit the application of the process and the system as disclosed herein.

Summary of the Invention

The novel regeneration processes proposed here are based on the use of ammonium bicarbonate (AB) to regenerate the resin into a usable form, specifically using concentrated AB solutions under enhanced pressure and increased temperatures. The methods disclosed herein can be applied to the softening of hard water, and can be used with mixed bed, strong acid and strong base resins, as well as weak acid and weak base mixed bed resins.

The methods could also be used with single polymer resins, that is with mixed resin beads, which contain weak acid and weak base groups on the same polymer. These resins can be of the type that have a reduced absorption density on modest heating.

Detailed description of the invention

According to one aspect, the present invention provides a process for softening hard water comprising the steps of:

- a) contacting hard water with a thermally regenerable ion exchange resin pre-saturated with ammonium and bicarbonate ions so as to replace 'hard' ions in the feedwater with NH_4^+ and HCO_3^- ions;
- b) heating the ammonium bicarbonate (AB) solution produced to decompose the AB, producing a soft product water of low salinity;
- c) collecting the emitted ammonia and carbon dioxide gases by bubbling through cool water to re-form the concentrated AB regenerant solution; and
- d) passing the concentrated ammonium bicarbonate solution through the hardwater exhausted resin, at elevated temperatures (up to 80°C) to partially decompose the AB and generate controlled partial pressures of NH_3 and CO_2 (up to 10 atm, in a sealed column) to drive the resin regeneration process.

In step b), the ammonium bicarbonate solution (water produced in step a) can be heated up to 80°C , under reduced pressure, if required, to thermally decompose the ammonium bicarbonate.

In a preferred embodiment of the present invention, the method described above could be

used with a thermally regenerable ion exchange resin comprising an amphoteric polymeric material of weakly basic (e.g. -NH₂) polymeric material and weakly acidic (e.g. -COOH) polymeric material.

- 5 The thermally regenerable ion exchange resin is selected to have a reduced ion adsorption capacity when heated from ambient temperatures to at least 70 °C. In one embodiment, said ion exchange resin may be heated to 80 °C. In another embodiment, said ion exchange resin may be heated to 90 °C. Heating to about 80 °C may reduce the ion adsorption capacity of said ion exchange resin by about eight times.

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The eluent may comprise from about 1 M to about 4 M ammonium bicarbonate.

In another embodiment of the present invention, the resin used in the process described above could be a standard mixed bed resin of two separate polymer beads of a weak acid resin and a
15 weak base resin.

In a further embodiment of the invention, the gases emitted from thermal decomposition of the product water containing ammonium bicarbonate, can be passed through a suitable zeolite packed column to separate out ammonia gas, as a valuable product, from the NH₃/CO₂
20 mixture. The zeolite can easily be regenerated for reuse by low temperature heating, which will completely displace the absorbed CO₂.

The thermally regenerable mixed bead ion exchange resin may comprise a basic polymeric component formed by the polymerisation of secondary or ternary amine monomers of both
25 the aromatic and aliphatic types. Examples of useful secondary amine monomers of the aliphatic types include unsaturated monomers of the allylamine type such as triallylamine, diallylamine or derivatives thereof. It is often desirable to crosslink such basic polymeric components with a crosslinking agent during the polymerisation step. Suitable crosslinking agents include, but are not limited to, aliphatic dialdehydes such as glutaraldehyde, glyoxal,
30 and paraldehyde. In a preferred embodiment of the invention, the thermally regenerable ion exchange resin comprises a copolymer of acrylic acid and ethylene glycol dimethacrylate and a copolymer of polyethylenimine crosslinked with glutaraldehyde. The thermally regenerable

ion exchange resin is selected to have a reduced ion adsorption capacity when heated from ambient temperatures to at least 70 °C. In one embodiment, said ion exchange resin may be heated to 80 °C. In another embodiment, said ion exchange resin may be heated to 90 °C.

Heating to about 80 °C may reduce the ion adsorption capacity of said ion exchange resin by a factor of 8, and when required, at the same time, ammonium bicarbonate decomposes to CO₂ and NH₃ at similar temperatures. That is, the ammonium bicarbonate-loaded ion exchange resin is heated to enhance the desorption of ammonium bicarbonate therefrom.

In another aspect of the present invention, it provides an apparatus for treating hard water which comprises:

- An ion exchange column containing, thermally regenerable ion exchange resin pre-saturated with ammonium and bicarbonate ions so as to replace 'hard' ions in the feedwater with NH₄⁺ and HCO₃⁻ ions;
- A means for passing hard water through said ion exchange column;
- A means for collecting the treated water containing ammonium bicarbonate and a means for heating said ammonium bicarbonate solution to decompose the ammonium bicarbonate into ammonia and carbon dioxide;
- A means for bubbling ammonia and carbon dioxide into cool water to re-form the concentrated AB regenerant solution;
- A means for passing the concentrated ammonium bicarbonate solution through the hardwater exhausted resin in the ion exchange column, at elevated temperatures (up to 80⁰ C) to partially decompose the AB and generate controlled partial pressures of NH₃ and CO₂ (up to 10 atm, in a sealed unit) to drive the resin regeneration process.

In yet another preferred embodiment of the present invention, the feed water can be degassed prior to entering the ion exchange column. This can be achieved by flowing the feedwater through a membrane, hydrophobic, hollow-fibre, de-gassing unit. De-gassing levels up to 99 % can be achieved using this method. Alternatively, the feedwater can be de-gassed by passing the solution through a bed of Teflon (or other hydrophobic plastic) beads or small

tubes, under vacuum suction. De-gassing levels up to 99 % can be achieved using this method.

5 This degassing process will increase the volume of hard water which can be treated by increasing the access to ion exchange sites. Degassing may also improve the efficiency of resin regeneration, for example, by inhibiting the decomposition of ammonium bicarbonate solutions.

10 The degassing step of the present invention can also be achieved by other processes including the following:

- Use of a pump to push water along a pipe to an aperture of suitable small diameter to facilitate removal of dissolved air;
- Collecting the water and the released air bubbles in a chamber on the other side of the aperture, noting that air is released because of the pressure difference;
- 15 • Directing the water/air bubble mixture into a hydro cyclone which will separate the air bubbles from the degassed water; and
- Directing the degassed water into the ion exchange column.

20 While various embodiments of the present invention have been described above, it should be understood that they have been presented by way of example only, and not by way of limitation. It will be apparent to a person skilled in the relevant art that various changes in form and details can be made therein to suit different situations without departing from the spirit and scope of the present invention. Thus, the present invention should not be limited by any of the above-described exemplary embodiments.

The claims defining the invention are as follows:

1. A process for softening hard water comprising the steps of:
 - a) contacting hard water with a thermally regenerable ion exchange resin pre-saturated with ammonium and bicarbonate ions so as to replace 'hard' ions in the feedwater with NH_4^+ and HCO_3^- ions;
 - b) heating the ammonium bicarbonate (AB) solution produced to decompose the AB, producing a soft product water of low salinity;
 - c) collecting the emitted ammonia and carbon dioxide gases by bubbling through cool water to re-form the concentrated AB regenerant solution; and
 - d) passing the concentrated ammonium bicarbonate solution through the hardwater exhausted resin, at elevated temperatures (up to 80°C) to partially decompose the AB and generate controlled partial pressures of NH_3 and CO_2 (up to 10 atm, in a sealed column) to drive the resin regeneration process.
 - e) repeating steps a) to d).
2. A process according to claim 1 wherein the ammonium bicarbonate (AB) produced in step a) is heated up to 80°C in step b) under reduced pressure, if required, to thermally decompose the ammonium bicarbonate to produce a soft product water of low salinity.
3. The process according to claim 1, wherein the ion exchange resin is a mixed bead, thermally regenerable resin, comprising an amphoteric polymeric material of weakly basic polymeric material and weakly acidic polymeric material.
4. The process according to claim 3, wherein the thermally regenerable ion exchange resin comprises a copolymer of acrylic acid and ethylene glycol dimethacrylate and a copolymer of polyethylenimine crosslinked with glutaraldehyde.
5. The process according to claims 1 and 3, wherein the thermally regenerable ion exchange resin is selected to have a reduced ion adsorption capacity when heated

from ambient temperatures to at least 70 °C.

- 5 6. The process according to claim 1, wherein the ion exchange resin is a mixed bed resin, comprised of two resin beads, a weakly basic polymeric material and a weakly acidic polymeric material.
- 10 7. The process according to any one of the preceding claims, wherein the regenerant solution comprises a concentrated solution from about 1 M to about 4 M ammonium bicarbonate.
8. A process according any one of the preceding claims where feed water is degassed prior to entering the ion exchange column.
- 15 9. A process according to claim 8 where the feed water is degassed up to 99%.
10. An apparatus for treating hard water which comprises:
- a) An ion exchange column containing, thermally regenerable ion exchange resin pre-saturated with ammonium and bicarbonate ions so as to replace 'hard' ions in the feedwater with NH_4^+ and HCO_3^- ions;
 - 20 b) A means for passing hard water through said ion exchange column;
 - c) A means for collecting the treated water containing ammonium bicarbonate and a means for heating said ammonium bicarbonate solution to decompose the ammonium bicarbonate into ammonia and carbon dioxide;
 - 25 d) A means for bubbling ammonia and carbon dioxide into cool water to re-form the concentrated AB regenerant solution; and
 - e) A means for passing the concentrated ammonium bicarbonate solution through the hardwater exhausted resin in the ion exchange column, at elevated temperatures (up to 80⁰ C) to partially decompose the AB and
 - 30 generate controlled partial pressures of NH_3 and CO_2 (up to 10 atm, in a sealed unit) to drive the resin regeneration process.

11. An apparatus as defined in claim 10 further comprising a means for degassing the

feed water.

5 12. An apparatus as defined in claim 11 wherein the means for degassing feed water comprises a microporous hollow fiber membrane inside a device designed to enhance flow dynamics which takes full advantage of the large membrane surface area for efficiently stripping dissolved gases.

10 13. An apparatus as defined in claim 13 wherein the de-gassing unit comprises a pump to push feed water along a pipe to an aperture of suitable small diameter to facilitate removal of dissolved air for collecting the water and the released air bubbles in a chamber on the other side of the aperture and a means for directing the water/air bubble mixture into a hydro cyclone which separates the air bubbles from the degassed feed water.