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A New Ion Exchange Process For Softening High TDS Produced Water

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Abstract

Weak acid cation (WAC) resins are normally utilized for softening high TDS produced water. The main disadvantage of the WAC process is that the resins require regeneration with hydrochloric acid followed by sodium hydroxide. This is expensive and necessitates the utilization of exotic, corrosion resistant alloys for construction.

Strong acid cation (SAC) ion exchange processes employing only brine regeneration (i.e. no acid or caustic) are much simpler and less expensive, however the SAC process is normally restricted to low TDS (<3000 mg/L) waters. A new ion exchange softening flow-sheet that uses brine regeneration has been developed based upon the Recoflo short-bed ion exchange process. Recoflo makes it possible to use extremely high service flow rates through very short (15 cm) resin beds, while achieving low hardness leakages. The key to applying this to high TDS produced water is the use of high purity brine regenerant. A novel ion exchange process which employs only water for regeneration (i.e. no chemicals) has been developed for purifying the brine. This paper explains the rationale for the process using ion exchange equilibrium calculations and then shows pilot plant and field data.

Introduction

Heavy oil deposits require enhanced recovery techniques to improve their yield. Typically, wells are flooded with high pressure steam to loosen and lift the oil.

This method typically produces 2-3 gallons of water for every gallon of heavy oil. A typical site can generate 8,000-16,000 m^3/day (1,500-3,000 USgpm) of so-called 'produced' water mixed with oil. This produced water is separated form the oil and can be discarded in abandoned wells. This is seldom practical however, due to the large quantities of make-up water required for steam generation. Produced water can be used as make-up for the steam generators if a series of treatment steps are employed to purify the brine in order to avoid scaling in the boilers. These include:

- oil removal (skimming, induced gas flotation, filtration)
- softening (hot or warm lime)
- silica removal (magnesium oxide treatment)
- softening (ion exchange)

Ion exchange softening is a key step in the recycle process. It is generally considered necessary to reduce hardness levels to less than 1 mg/L (as CaCO$_3$) and preferably less than 0.2 mg/L. In an effort to avoid boiler fouling, the trend is to specifying even lower hardness limits - sometimes as low as 0.1 mg/L.

Ion Exchange Softening

Conventional water softeners such as those used in most domestic and industrial applications are normally strong acid cation (SAC) exchangers (designated as 'R' below) operated in the sodium cycle as per equation (1).

$$CaCl_2 + 2RNa \rightarrow 2NaCl + R_2Ca \qquad (1)$$
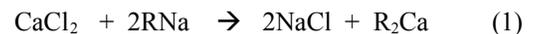
Regeneration is accomplished with sodium chloride brine according to equation (2).

$$2NaCl + R_2Ca \rightarrow CaCl_2 + 2RNa \qquad (2)$$

A chemical equilibrium is established between the ion exchange resin and solutions in contact with the resin. This is expressed by the standard equilibrium mass action expression:

$$K_{Na^+}^{Ca^{++}} = \frac{[Na^+]^2 [Ca^{++}]_R/2}{[Na^+]_R^{\,2} [Ca^{++}]/2} \qquad (3)$$

High levels of sodium in the feedwater compete with ion exchange sites on the resin so that the efficiency of the softening process is seriously impaired at high feedwater total dissolved solids levels. This has been discussed in detail by Anderson in 1981[1] and by Chen in 1984[2] in the context of produced water softening. Chen re-arranged and simplified the equilibrium expression showing that the hardness leakage level is directly proportional to the square of the total dissolved solids concentration of the raw water $[TDS]_f$ and directly proportional to the hardness concentration in the brine regenerant $[TH]_B$.

$$TH \; \alpha \; [TDS]_f^2 \, [TH]_B \qquad (4)$$

It is apparent that in order to achieve low hardness leakage levels on high TDS feeds it is necessary to employ a high purity brine regenerant. More recently, Mommaerts[3] pointed out again that it is theoretically possible to yield low hardness produced water with a TDS higher than 5000 mg/L using SAC resin, however to date there have been no takers.

Figure 1 shows the theoretical hardness leakage through a SAC softener as a function of TDS. It can be seen that if rock salt is used producing a brine regenerant containing 2500 mg/L hardness, it is not possible to soften produced waters below 1 mg/L at TDS levels beyond about 2500 mg/L. Even if brine from pan-evaporated salt containing about 250 mg/L hardness is used, it is unlikely that the required hardness leakages can be obtained. On the other hand, if purified brine containing 10 mg/L hardness is used, hardness leakages of less than 0.1 mg/L are readily achievable, at least theoretically, at TDS levels in excess of 15,000 mg/L.

Notwithstanding the theoretical calculations, conventional wisdom persists that for SAC resins, the practical upper for TDS is 3000 mg/L, when low hardness leakage (<1 mg/L) is required. There are several reasons for this:

- Large quantities of high purity brine regenerant are required.
- Salt of adequate purity for regenerant brine is not commercially available at a reasonable price.
- Lime softening, the standard technique for softening brine is a very messy process that is prone to upset and does not scale down economically for the quantities involved. Moreover, lime softening is not capable of achievable a brine hardness of less than about 10 mg/L.
- In the chlor-alkali industry, chelating ion exchanger resins are used to achieve sub-ppm hardness levels in saturated brine. This is not an attractive option since chelating resins need to be regenerated with both HCl and NaOH and undergo large volumetric change during regeneration. In addition, chelating resins are very expensive.
- SAC ion exchange resin capacities are low at high feed TDS levels.

At TDS levels above about 3000 mg/L, standard procedure is to employ weak acid cation (WAC) resins. WAC resins have a much higher affinity for hardness ions than SAC resins. Normally, WAC resins cannot be regenerated with brine, however. They must be regenerated using a rather complex two-step procedure that involves treatment of the resin with hydrochloric acid followed by sodium hydroxide. The use of WAC resin in the Na-form is extremely stressful on the resin beads due to the 60% change in volume as the resin is converted from H-form to Na-form. Use of hydrochloric acid mandates the use of exotic corrosion resistant alloys such as Hastelloy in the construction of the ion exchange equipment. This appreciably increases the cost of the system. WAC resins have a number of other disadvantages relative to SAC resins and generally speaking, SAC resins are preferred where it is feasible to use them.

Although WAC resins are always regenerated with acid and usually thereafter converted to the sodium form with caustic, it was suggested in 1970 that WAC resins could be regenerated with only NaCl brine, providing a large excess of regenerant were employed[4]. Mommaerts recently re-evaluated this concept[5]. It was reported that the results were rather 'disappointing', however. Leakages with a brine regenerated WAC resin were actually higher than that achieved with a SAC resin. In either case, hardness leakages were in excess of 0.1 mg/L at TDS levels above 1000 mg/L, even at feed hardness levels of only 2-5 mg/L.
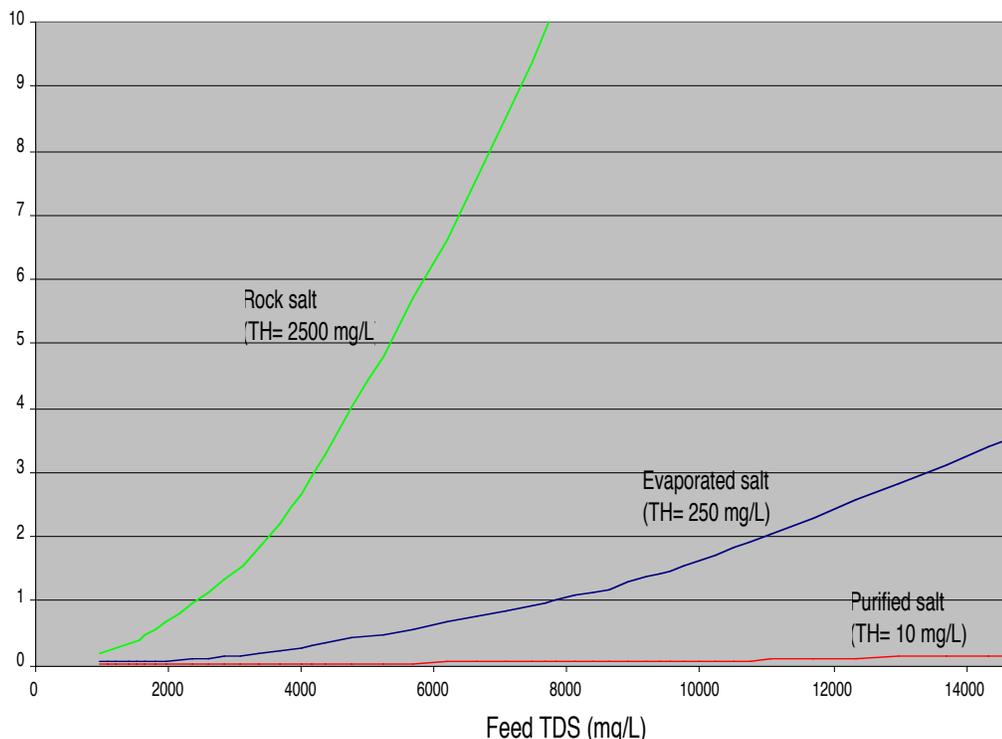
Figure 1: Effect of Feed TDS and Brine Hardness on Hardness Leakage

The SACPlus Concept

A process flowsheet called SACPlus was devised for high TDS produced water softening. The idea was that the majority of the hardness in produced water (to say 10 mg/L) can be easily removed using rather conventional technology with strong acid cation resin. This primary softener can be regenerated with low purity brine, the spent brine containing appreciable hardness levels is discarded to waste. The remaining hardness, which is much more difficult to remove, can be removed with a secondary unit or polisher providing high purity brine is employed for regeneration. A large excess of brine will be required to achieve a usable exchange capacity, however. The spent brine from the polisher, which contains relatively low hardness concentrations, is purified by a brine purification unit. The purified brine is recycled for use in regenerating the polisher.

The primary softener is rather conventional technology. The polisher and brine purification steps however required further development.

Recoflo Ion Exchange

In order to make the SACPlus process viable it is essential to employ countercurrent regeneration for the polisher. The resin at the exit end of the resin bed must be completely regenerated in order for the process to function. It is also necessary to design the system to accommodate low exchange capacities. A patented[6] ion exchange technique called Recoflo™ proved to be ideal, particularly for the secondary or polishing stage. In addition to countercurrent regeneration, Recoflo uses short (15-60 cm) beds of fine mesh resin.

The process typically operates at extremely high flow velocities. For softening applications, velocities of 122 $m^3/h/m^2$ (50 gpm/ft^2) or 13.3 bed volumes per minute (100 gpm/ft^3) are employed, which are almost an order of magnitude higher than conventional ion exchange systems. To ensure that there is no channeling through the short bed of resin and to make sure that the exchange profile is maintained in the bed, the resin is maintained in a compressed state inside the vessel. This prevents resin movement and ensures optimal regeneration efficiency. The Recoflo process has been extensively used since 1972 in a wide variety of chemical recovery and water treatment applications.

A typical Recoflo softener is shown in Figure 2. This particular unit is fitted with a resin bed 152 cm (60 inches) in diameter and has a service flow rate of up to 227 m^3/h (1000 gallons per minute).
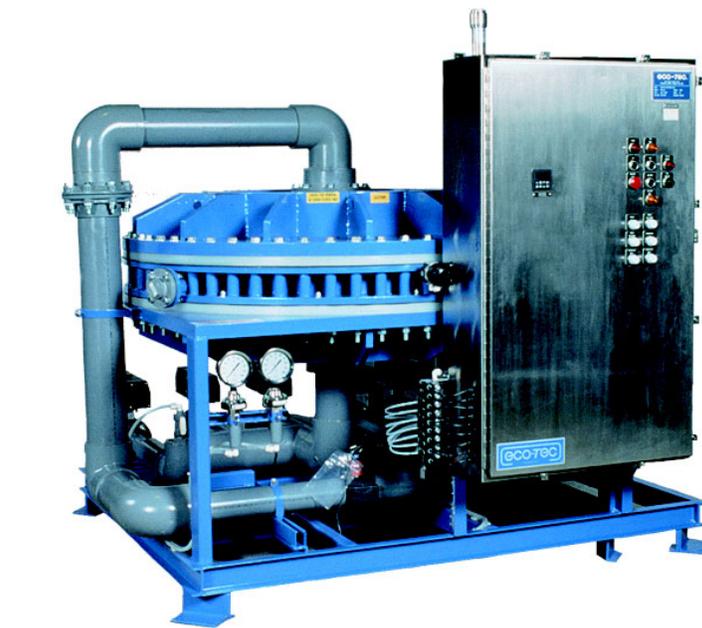
Figure 2: Recoflo Water Softener

Polisher Pilot Plant Results

Initial tests were conducted using strong acid cation (SAC) resin. Testing was performed on a fully automatic Recoflo softener pilot plant using resin beds 5 cm (2 inches) in diameter by 15 cm (6 inches) high. Extensive prior work at this scale has indicated that the results on this pilot plant can be reliably scaled up to beds up to 244 cm (96 inches) in diameter. For each experiment, composite samples of the softened water product as well as the spent regenerant were collected so that a material balance could be performed on the calcium and magnesium. Full service and regeneration cycles were repeated until a good mass balance between ions entering and leaving the system was obtained. This typically took 7-10 complete cycles.

Analysis was conducted using atomic absorption spectroscopy. The limit of hardness detection for this method was 0.125 mg/L for calcium and 0.012 mg/L for magnesium (expressed as $CaCO_3$).

Synthetic brackish produced waters were prepared using NaCl in a deionized water background at a temperature of approximately 75°C. Hardness was added through addition of calcium and/or magnesium chloride to simulate the partially softened water being fed to the SAC polisher. Initial tests were done at a TDS level of approximately 4500 mg/L and 10 mg/L hardness. Subsequent experiments were conducted at approximately 7000 and 10,000 mg/L TDS at 10 mg/L and 25 mg/L hardness. Regeneration was performed using 150 g/L NaCl containing approximately 10 mg/L hardness. The regenerant was made up from reagent grade NaCl and additional hardness was added (either $CaCl_2$ or $MgCl_2$).

To avoid scaling in the steam generator, hardness leakage levels in softened produced water must be lowered well below 1 mg/L. The trend in the industry is toward lower leakage levels. For this work, a maximum leakage level of 0.1 g/L was considered acceptable. It will be appreciated that the task is considerably easier if higher leakages can be tolerated.

Tests were performed with a feed containing approximately 10 mg/L of hardness, all as magnesium. It was felt that this level could be fairly readily achieved by a well designed primary softener, counter-currently regenerated with brine. Because cation exchangers exhibit an appreciably higher preference for calcium ions over magnesium, it can be expected that the hardness leakage from this primary softener will be mainly magnesium. Because of magnesium's lower preference, attainment of the final hardness target will be much more challenging for the polisher than would be the case for a feed containing predominantly calcium.

It was found that in order to obtain the target hardness leakage of less than 0.1 mg/L the operating capacity was only 0.0925 eq/L (2.02 kgr/ft^3) at an average hardness leakage of 0.029 mg/L. This is only about 5% of the total resin capacity. This was obtained by regenerating with a dosage of 600 g/L$_R$ NaCl (as ~150 g/L solution) representing a dosage of about 110 times stoichiometric, based upon actual loading! The spent brine, which contains only about 1200 mg/L of hardness, is actually more pure than the brine produced by the virgin rock salt used by most conventional softeners! Clearly, some way of recycling the spent regenerant is necessary to make this process viable.

Subsequent tests with predominantly calcium hardness in the feedwater provided significantly higher capacities and lower hardness leakages confirming that a straight magnesium feed is the worst case scenario.

A perceived disadvantage of such low operating capacities is the expected short cycle times. The extremely high service flow rates characteristic of Recoflo would seem to exacerbate this. This is in fact not an issue, since even at these low capacities and high flows, the onstream time (37 minutes) is much longer than the offstream time for regeneration and rinse (7.5 minutes). Indeed, this is a much longer cycle time than employed in most Recoflo applications. Short cycle times and low operating capacities are characteristic of Recoflo and generally present no limitations or difficulties.

Although previous work by others indicated poor results using WAC resins regenerated only with salt, it was felt that the advantages afforded by Recoflo could make a sodium cycle WAC process viable. Our tests with the WAC resin on similar feeds were actually very successful. The operating capacity was increased to 0.196 eq/L, which while still low, is almost double that of the SAC resin at the same regeneration dosage of 600 g/L_R NaCl. Magnesium levels in the softened water were below the detection limit of 0.012 mg/L (as $CaCO_3$).

There was some concern that if the feed to a WAC polisher contained appreciable levels of calcium, the brine regeneration may not be effective, due to the higher selectivity of the resin for calcium. The tests were repeated with a feed containing about 80% Ca at the same regeneration dosage. Similar operating capacities were obtained with an average hardness leakage of only 0.023 mg/L. The marginally higher hardness leakage level is probably an indication of a slightly inferior regeneration.

The TDS of the feed was increased to approximately 7000 mg/L at the same magnesium hardness level (10 mg/L). Similar operating capacities were obtained with average hardness leakages still less than 0.1 mg/L at the same regeneration dosage.

The magnesium hardness level in the 7000 mg/L TDS feed was increased to 25 mg/L. The operating capacity increased by more than 50% to 0.344 eq/L at the same regeneration dosage and there was no increase in leakage. The higher feed hardness apparently presented no problem. As predicted by the equilibrium calculations, the difficult part is removing the last little bit of hardness. In fact, as can be seen from equation (4), the feed hardness has no bearing on the hardness leakage.

The feed TDS was increased further to 10,000 mg/L and some preliminary tests were conducted. It was found that the increased competition provided by this higher TDS began to interfere with uptake of the hardness. Indications are that the resin operating capacity will be significantly reduced if the 0.1 mg/L leakage limit is maintained. Of course, if this limit can be relaxed somewhat, to say 0.5 mg/L, or if the feed contains more calcium, there should be no problem.

Because the WAC resin is regenerated with only salt, no significant volumetric change was observed in the resin. Since acid and caustic were not employed for regeneration, all of the advantages of using the SAC resin were retained. Despite the improvement with the WAC resin, the regeneration dosage is still extremely high and a way of economically purifying and recycling the spent brine is essential.

Brine Purification

As discussed above, the key to making SAC resins effective for softening of high TDS waters such as produced water is to employ high purity brine. Even if high purity brine is used, the regeneration dosages are very large so it will be necessary to purify and recycle the spent brine. To make the process viable a better way of producing high purity regenerant from spent brine was needed.

A family of novel ion exchange resins has been developed by Eco-Tec for separating different types of salts. Unlike conventional ion exchange resins, which are either cation or anion exchangers, these resins are amphoteric. Each resin bead has *both* cation and anion exchange groups. Although the mechanism is not fully understood, for discussion purposes, the freshly regenerated resin can be considered to be in the 'self-neutralized' form (R^-R^+) ie. the positive charge associated with the anion exchanger is neutralized by the negative charge associated with the cation exchanger. During the service or uptake cycle, the cation and anion associated with the impurity (eg. M^+, X) are taken up by the resin together. This is depicted in equation (5).

$$R^+R^- + M^+X^- \quad \rightarrow \quad R^+X^-R^-M^+ \qquad (5)$$

When the resin is contacted with water, the resin becomes less selective for the salt impurity and the resin self-neutralizes again, liberating the salt impurity (see equation (6)).

$$R^+X^-R^-M^+ \quad \rightarrow \quad R^+R^- + M^+X^- \qquad (6)$$
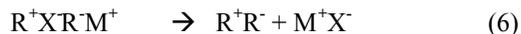
The anion and cation exchange functional groups on the resin are chosen to have high affinity for the salt to be removed (ie. MX) and a low affinity for the salt to be left behind. Obviously, a very different resin is required for each separation. The exact composition of the resins employed is proprietary, however the basic process is the same for each.

Figure 3: Typical Salt Separation Unit

The first successful implementation of this technology was a process called the APU (acid purification unit), which is used for removal of salt contaminants from strong mineral acids. Since 1978 over

500 of these APU systems have been installed in more than 40 countries in a wide variety of hydrometallurgical applications[7].

A process for removal of hardness ions (calcium and magnesium) from sodium chloride brines called BDH (Brine De-Hardening) was developed in 1998[8] using the Recoflo system. After the resin becomes loaded, the calcium and magnesium are regenerated from the resin with softened water. No additional chemicals are required. The process can be used at brine concentrations from about 5% w/w to saturation, containing hardness levels from a few mg/L to several thousand mg/L.

The system is assembled into a compact, skid-mounted unit which can be fully tested prior to shipment. This minimizes installation and startup costs. The same equipment design that has been used for over twenty years for APU systems is used for the BDH brine purification systems. The resin bed is typically 60 cm (24 inches) in height. Scale-up is accomplished by increasing the bed diameter up to a maximum of 274 cm (108 inches). A typical salt separation unit of this type is shown in Figure 3.

Typical BDH pilot plant brine purification results are shown in Table 1. As can be seen from Table 1, both the calcium and magnesium contaminants were removed well below the 10 mg/L level required for this application.

Table 1: BDH Pilot Plant Brine Softening Results

	Relative volume	Total Hardness (mg/L)	[Ca] (mg/L)	[Mg] (mg/L)	[NaCl] (g/L)
Feed	1	1685	570	62.5	108
Purified brine	0.922	3	1.2	0.00	101
Removal			99.8%	99.9+%	7.8%

It can be seen that recovery of the sodium chloride values using the BDH processs is about 92%. As a result, it is possible to reduce the overall regenerant consumption on the polisher softener from a gross value of about 50 times stoichiometric using the WAC resin to a level of less than 5 times stoichiometric. This is on the same order of magnitude as a conventional softener on a potable water application and sufficiently low to make the process attractive.

The SACPlus Process

The overall SACPlus process is shown in Figure 4. Both service (on the left) and regeneration cycles (on the right) are illustrated. The first step in the process is removal of the bulk of the hardness from the filtered

produced water using a primary strong acid cation unit (SACI). This is designed to lower the hardness to less than about 25 mg/L The SAC1 unit is regenerated in the conventional manner with brine typically made up from rock salt. Counter-current regeneration is recommended to minimize the salt consumption.

The secondary softener or polisher (SAC/WAC2) unit contains either SAC or WAC resin, depending upon the feed TDS and hardness leakage specification. This SAC/WAC2 unit lowers the hardness to the final target level (eg. <0.1 mg/L). This unit is regenerated with purified brine containing a hardness level of less than 10 mg/ L. The spent brine is collected for subsequent recycle to the BDH unit. Regenerant rinsewater from the

SAC/WAC2 unit can be used to dissolve rock salt for regeneration of the primary softener SAC1.

The BDH unit produces purified brine by treating the spent regenerant from the SAC/WAC2 unit as described above. A small amount of salt makeup is added to the spent SAC/WAC2 regenerant solution to replace sodium actually consumed in the softening process as well as losses in the BDH process. The BDH unit is regenerated using softened produced water from the SAC/WAC2 unit. The spent BDH water regenerant, which is similar in composition to the raw produced water, is recycled around to the inlet of the primary softener unit SAC1 or an upstream lime softener.

Field Results

Although a complete SACPlus system has not yet been installed in the field, the basic principal is currently being demonstrated on the industrial side. The system consists of two Recoflo SAC softeners, each 244 cm (96 inches) in diameter, and a BDH brine purification system. The entire

skid-mounted system, which has a maximum service flow capacity of 1136 m^3/h (5000 gpm) is shown in Figure 5.

The feedwater to the SAC softeners is pretreated by warm lime softening and depth filtration. The SAC softeners are regenerated with purified brine from the BDH system. In this particular system the spent brine from the softeners is not being recycled, however. Due to the fact that a supply of inexpensive pan-evaporated salt is available and disposal of spent brine presents no problems, a decision was made to use virgin pan-evaporated salt to make up brine as feed to the BDH system. The BDH system removes most of the hardness from this brine before it is used on the SAC softener. Although some problems relating to inadequate pretreatment are currently being dealt with, some preliminary results are shown in Table 2. This early data indicates the process will perform as expected when fully operational.
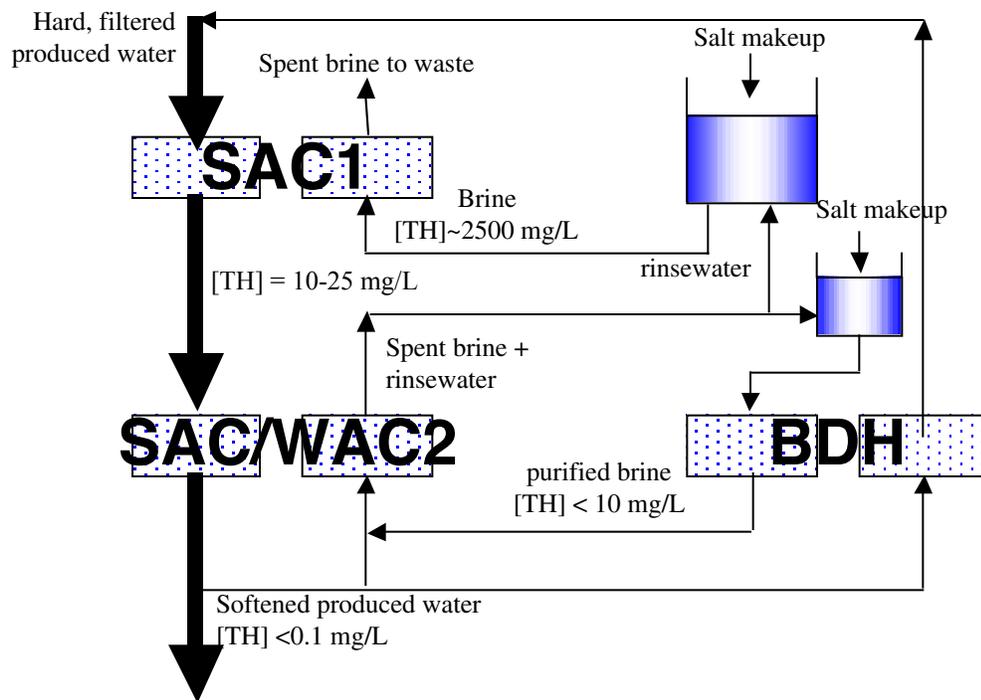
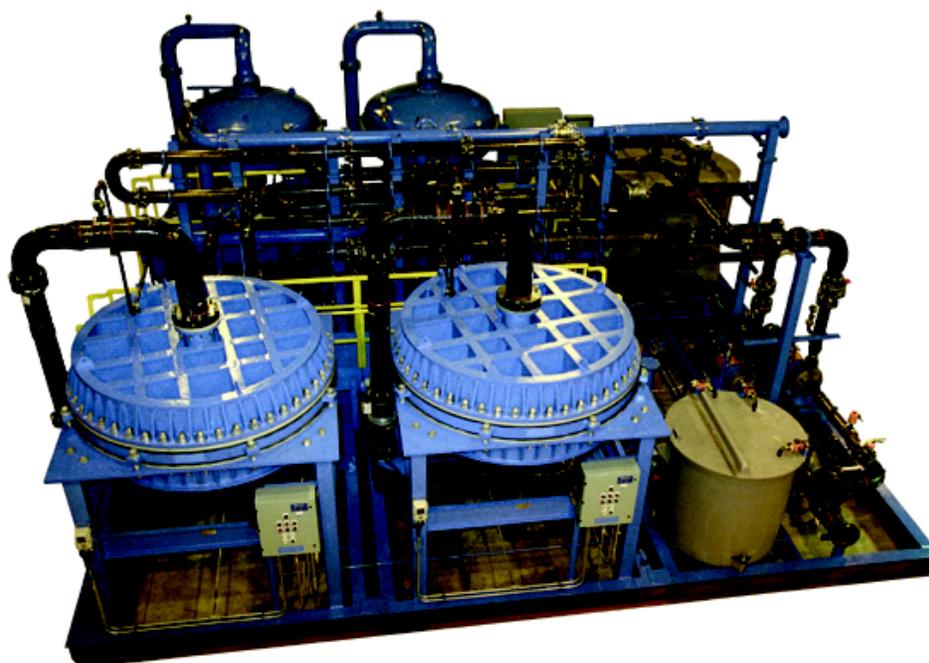

Figure 4: SACPlus System Layout

Figure 5: Full Scale Refcoflo SAC Softener/Brine Purification System.

Table 2: Preliminary Field Results

	TDS (mg/L)	Total Hardness (mg/L)	[Ca] (mg/L)	[Mg] (mg/L)
Produced water feed (after lime softener)	3040	3.38	0.92	0.26
Softened produced water	3130	0.15 (spec = <0.2)	0.038	0.014

Conclusion

Use of a novel ion exchange process called Recoflo has made it possible to utilize either strong or weak acid cation resin to soften produced waters at TDS levels up to 7000mg/Lto levels of residual hardness below 0.1 mg/L. By utilizing large dosages of high purity brine it is possible to eliminate the use of acid and caustic, even for regeneration of WAC resins. The softener equipment is extremely compact, utilizing resin bed heights of only 15 cm (6 inches) in height that operate at flow rates up to 50 gpm/ft^2. The key to making the process viable is a new process called BDH which allows recycle of excess brine from regeneration of the secondary (i.e. polishing) softeners. The BDH unit is extremely simple, utilizing a novel ion exchange resin which is regenerated with merely water. This new produced water softening system called *SACPlus* is bound to find widespread application in the softening of oil field produced water in the coming years.

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