

New ion exchange processes for brine purification

C. J. Brown^a, A. Russer^a and M. Sheedy^a

^aProsep Technologies Inc., subsidiary of Eco-Tec Limited.
1145 Squires Beach Road, Pickering, Ontario, Canada L1W 3T9

Three new ion exchange processes have recently been developed for purification of brine. The *PDP* (precipitator dust purification) process removes chloride contamination from byproduct sodium sulphate recovered from the electrostatic precipitator of a kraft pulp mill's recovery boiler. The *BDS* (brine de-sulphurization) process removes sulphate impurities from chlor-alkali cell brines, while a novel brine softening process is utilized to remove calcium and magnesium hardness from brine used for regeneration of brackish water softeners. The unique feature of these processes is that regeneration is accomplished with merely water, eliminating the handling and consumption of costly regenerant chemicals and their associated wastes. In addition, by utilizing a ion exchange technique called Recoflo, the height of the ion exchange resin bed can be reduced to only 30-60 cm. The basic equipment design, operation and application will be discussed and typical performance data will be presented.

1. INTRODUCTION

Huge tonnages of salt are consumed by industries such as chlor-alkali as a basic feed-stock. Prior to consumption of this salt it is usually necessary to purify the brine. The standard procedure is to use the classic lime/soda softening process to remove divalent cations. This is supplemented in some cases with barium to precipitate sulphate. While this process is well known and reasonably effective, its principle disadvantage is the mess and cost of disposing of the sludge generated by the process. The operating cost for treatment chemicals is also not insignificant.

Ion exchange has proven to be an extremely effective way of separating salts from water. In membrane chlor-alkali plants chelating ion exchange units are used to soften the brine to trace hardness levels. The primary disadvantage of ion exchange is that chemicals are consumed in regenerating the ion exchange resins after they become exhausted. These regenerant chemicals not only represent an economic cost but since they report to the waste in the form of neutral salts along with the original contaminants, an additional load of salt is discharged to the environment.

The alternatives for purification of salt are limited largely by economics. It is difficult to justify the use of significant amounts of energy or even inexpensive chemicals such as acid and caustic to purify a cheap commodity such as salt.

Alternative salt purification processes which do not consume chemicals or energy would be very attractive.

2. THE RECOFLO WATER ELUTION ION EXCHANGE PROCESS

2.1 Acid Retardation

In 1963 a new process for separation of strong acids from metal salts was introduced by Hatch [1]. Called *acid retardation*, the process was different from conventional ion exchange in that regeneration is achieved with only water. No regenerant chemicals are required. Consequently, economical recovery of a chemical as cheap as sulphuric acid can be considered. Although a few early attempts were made to commercially exploit the acid retardation process, it was not until 1977 when a system called the APU® (acid purification unit) was developed that the process became commercially viable. Since that time, the metals industry has embraced the technology, with almost 1000 APU's having been installed in over 40 different countries on applications such as purification of sulphuric acid anodizing baths [2] and nitric/hydrofluoric stainless steel pickle liquors [3].

2.2 The Recoflo™ Ion Exchange Process

One of the reasons that it took so long for the acid retardation process to become commercialized is that conventional ion exchange designs, originally developed for treatment of large volumes of water,

are not well suited to the treatment of small volumes of concentrated solutions.

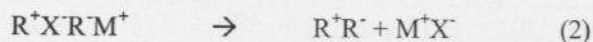
The APU takes advantage of an ion exchange technique call *Recoflo* which utilizes short resin beds (7.5-60 cm), fine resin particles (75-150 μm) and countercurrent regeneration. The Recoflo column contains no freeboard, thus avoiding one major cause of dilution. Fine mesh resins allow the use of very high flow rates, thereby helping to reduce equipment size and capital cost. Fine resins also tend to reduce axial dispersion of fluid in the column, further reducing dilution and intermixing. A number of patented innovations [4] which were introduced in 1985 to improve flow distribution, further enhanced the performance of the Recoflo process.

2.3 Amphoteric Ion Exchange Resins

A family of novel ion exchange resins has been developed 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 (1).



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 (2)).



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. There is also a striking similarity to the acid retardation process. The challenges faced in engineering a viable salt separation process are also similar to those encountered in the acid retardation

process ie. the treatment of small volumes of concentrated solutions. Consequently, it was possible to use the same basic process flow-sheet and equipment for these salt purification processes that was previously developed for the APU.

2.4 Basic Operation

There are two steps in the basic process: the "upstroke" and the "downstroke" (see Figure 1).

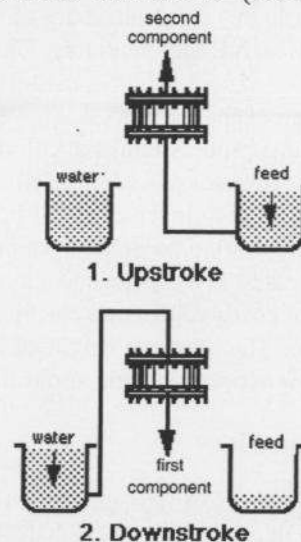


Figure 1. Recoflo Water Elution Operating Cycle

During the upstroke, feed solution bearing two components is pumped into the bottom of the ion exchange resin bed. The first component (MX) is sorbed by the resin particles according to (1) and a solution bearing a second component is collected from the top of the bed. Next, during the downstroke, water is pumped into the top of the bed, desorbing the first component from the resin according to (2) so that a solution of the first component is collected from the bottom of the bed. The total cycle typically takes about 2-10 minutes to complete and repeats successively.

2.5 Equipment Design

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 brine purification systems.

The resin bed is typically 30-60 cm (12-24 inches) in height. Scale-up is accomplished by increasing the bed diameter. Typical units range from small 'off-the-shelf' units 15 cm (6 inches) in diameter such as that shown in Figure 2, which processes 20-

200 litres per hour of feed solution (depending on the application), to large custom units up to 274 cm (108 inches) in diameter (see Figure 3) which process more than three hundred times as much. For still larger applications, multiple units are installed in parallel.

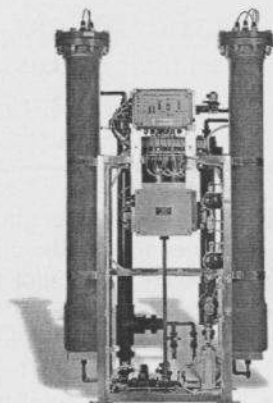


Figure 2. Small Recoflo unit for acid recovery operations.

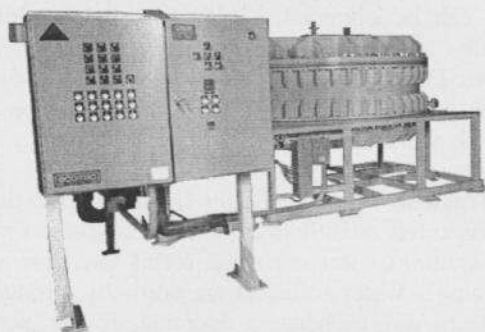


Figure 3. Large Recoflo unit with 274 cm (108 inch) diameter resin bed.

A major consideration in the design of a Recoflo system is adequate pre-filtration of the feed solution. The fine resin beds employed in the system will plug-up with any suspended material that is not filtered out prior to treatment. While it is possible to clean the resin, the procedure is inconvenient and a better approach is to provide proper filtration in the first place. Where the level of suspended solids is moderately high, such as in spent acid pickle liquors, good success has been obtained with backwashable, multi-media sand-type filters. Where solutions are relatively clean, such as chlor-alkali brines, disposable polypropylene cartridge filters may suffice.

3. APPLICATIONS

3.1 Chloride Removal

In kraft pulp mills, high levels of chloride can build up in the kraft recovery cycle under some circumstances. High chlorides are known to promote boiler plugging and some mills must shut down their recovery boilers for water washing as frequently as every three months. The lost production time associated with these shut-downs is very costly. As mills move towards higher levels of closure in response to environmental pressures, the current outlets for chloride are reduced. This will result in even higher chloride concentrations throughout the kraft recovery cycle and increased tendency for problems. The need for chloride removal is destined to become more universal and more pressing in the future.

An appreciable quantity of dust is collected from the electrostatic precipitator of a kraft recovery boiler. This dust consists primarily of sodium sulphate and sodium carbonate *salt cake*. Because of the relatively high volatility of chloride salts, there is a tendency for the chloride impurities to become enriched in the ESP catch. Some mills therefore deal with chloride contamination by purging a portion of the catch from the electrostatic precipitator to sewer. Since a typical kraft mill may collect as much as 100 tons per day of ESP dust, this approach can result in a significant loss of valuable pulping chemical. Moreover, discharge of such large quantities of salt cake to the environment is not allowed in some jurisdictions.

A resin was developed that is capable of removing chloride from concentrated sodium sulfate solutions. The sodium chloride is eluted from the resin with water as discussed above. The ion exchange unit is incorporated into a system called *PDP* (precipitator dust purification) that was developed for the pulp and paper industry [5].

Typical chloride removal results are shown in Table 1. As can be seen, the system has the capability to remove 96% of the chloride from the sodium sulphate feed while recovering 96% of the sodium sulphate content. Similar results are obtained for removal of chloride from sodium carbonate. As one might expect, the performance is dependent on operating conditions such as flow rate and throughput of feed and eluant per cycle. These parameters need to be optimized for each application, depending upon the requirements of the client.

While no long-term field data is available on the PDP system yet, extended laboratory tests have

indicated that the resin should be very stable in this application [5].

The economics of the PDP system appear to be very favourable, when the lost production time due to boiler shut-downs and/or the value of purged salt cake are taken into consideration.

Table 1
Typical Chloride Removal Results

	Relative volume (L/L feed)	[Na ₂ SO ₄] (g/L)	[NaCl] (g/L)
Feed	1	198	18.3
Waste	1	11.0	17.5
Purified salt	1	188	0.31
% removal		5.6%	95.6%
Mass balance		0.3%	-2.4%

3.2 Brine De-Sulphurization

The susceptibility of membrane chlor-alkali cell performance to brine purity is well known and documented. One of the more troublesome impurities is sulphate. Since the sulphate content of most salts is too high, some means of sulphate removal is required. In the simplest case this may be a simple purge of depleted brine from the circuit to sewer. This is becoming unacceptable due to the value of the salt as well as environmental restrictions. Precipitation techniques based upon calcium or barium are also being used. The effectiveness of calcium sulphate precipitation is limited. Barium sulphate precipitation is much more effective, however handling and disposal of barium salts, which are deemed hazardous, can be problematic.

Ion exchange processes employing weak base resins have been proposed for removal of sulphate contamination from brine [6]. Given that significant quantities of sodium chloride 'regenerant' are consumed to recover the original sodium chloride brine, it's not too surprising that this approach has not been adopted by the industry. A process that employs a powdered inorganic ion exchanger in a slurry has also been proposed [7]. This process appears rather cumbersome and messy and will be expensive to operate, since the ion exchanger must be regenerated with NaOH.

The BDS (brine de-sulphurization system) process uses a water elutable resin that is capable of removing sulphate from a concentrated sodium chloride solution. Typical results are shown in Table 2.

Table 2
Typical sulphate removal results

	Relative volume (L/L feed)	[Na ₂ SO ₄] (g/L)	[NaCl] (g/L)
Feed	1	6.00	203
Waste	0.381	6.82	21.3
Purified salt	1.11	3.06	174
% removal		43.4%	4%
Mass balance		0.1%	-1%

As with the PDP system, the operating parameters of the unit can be adjusted to suit the client's needs. These particular results were an attempt to maximize productivity (ie. minimize capital cost) and minimize the waste volume. While the NaCl recovery efficiency is about 96%, the brine purity is not exceptionally good (43.4% sulphate removal). This is not considered a disadvantage however, since the low removal efficiency can be compensated for by increasing the flow of feed that is treated by the system. If necessary, removal efficiencies of over 95% can be obtained. Although the process is actually somewhat more effective in treating saturated brine, a typical flow-sheet would probably locate the BDS system so that depleted brine from the cells would be treated.

3.3 Brackish Water Softener Brine Purification

Substantial quantities of salt are consumed in the regeneration of ion exchange resins used for water softening. Water softeners are normally strong acid cation (SAC) exchangers operated in the sodium cycle, to remove calcium and magnesium hardness from water. Rather impure brine can be used to regenerate a SAC resin used to soften a potable water supply to levels as low as about 1 mg/L hardness. The ability of a SAC softener to achieve the lower hardness levels sometimes required by boilers is compromised by the hardness of the brine, however. The problem becomes exacerbated as the total dissolved solids (TDS) of the feed increases and the waters become brackish. The high sodium in the brackish feed-water competes with the hardness ions for uptake on to the resin. In fact, 5000 mg/L TDS is normally considered the practical upper limit for use of SAC resins operated as a sodium cycle softener [8].

At TDS levels above about 5000 mg/L, standard procedure is to employ either weak acid cation WAC resins or chelating resins. WAC resins are normally employed for softening brackish waters such as oil-field produced water prior to recycle to the steam

generator and chelating resins are normally used for softening chlor-alkali brines. WAC resins and chelating 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. WAC and chelating resins have a number of disadvantages relative to SAC resins and generally speaking, SAC resins are preferred, where it is feasible to use them.

The TDS limit at which a given hardness can be met using SAC resins can be increased well beyond 5000 mg/L by using purified brine for regeneration. Recent work has shown that feeds containing up to 12,000 mg/L TDS can be softened to hardness levels of less than 0.2 mg/L with a Recoflo SAC softener, providing that it is regenerated with brine containing less than 10 mg/L hardness. A commercial system has recently been sold to an oil producer in Western Canada for softening oil field produced water containing a TDS of 4000 mg/L to hardness levels of less than 0.2 mg/L. The 350 m³/h capacity system, which will incorporate Recoflo softeners fitted with SAC resins, is regenerated with purified brine. The brine will be purified using a novel resin in a Recoflo brine softener unit.

While the SAC softeners themselves are remarkable in that they achieve very high hardness removal efficiencies at extremely high flow rates with only 15 cm high Recoflo beds, the key to the process is the brine softeners. They provide a simple, convenient means of producing high purity brine on demand, at very low operating cost.

The brine softener resin removes calcium and magnesium chloride from concentrated brine during the upstroke. The calcium and magnesium is then eluted from the resin with water during the downstroke. The height of the resin bed is only 30 cm (12 inches). Typical pilot plant brine softener results are shown in Table 3. The brine that was treated in this case was made up with vacuum pan salt to a concentration of approximately 10% w/w, which is the concentration employed for regeneration of the SAC unit. Included in the table is the entrained volume of feed solution (ie. feed void) which is displaced from the bed prior to regeneration each cycle. The feed void would normally be recycled to the feed tank and processed in subsequent cycles.

Table 3
Brine softening results – dilute vacuum pan salt

	Relative volume	[Ca] (mg/L)	[Mg] (mg/L)	[Na] (mg/L)
Feed	1	37.25	0.80	40,300
Purified brine	0.966	0.0	0.00	38,500
Feed	0.0808	36.0	0.80	28,000
Void				
Waste	0.417	81	1.7	300
Removal		99.9+%	99.9+%	0.4%
Mass balance		-2%	-3%	-1%

As can be seen from Table 3, both the calcium and magnesium contaminants were removed down to below the limits of detection employed (Ca = 0.1 mg/L, Mg = 0.01 mg/L). This indicates the high removal capability of the process, although the purity produced under these conditions may be higher than required for the intended use. Alternate conditions have been developed which would provide higher productivity (ie. lower capital cost) at somewhat lower removal efficiency.

Table 4 shows the results obtained in treating a saturated solution (292 g/L) of vacuum pan salt. Note that the higher brine concentration did not adversely effect the removal efficiency, even considering the higher hardness concentration. Complete hardness removal was obtained with 99% recovery of the NaCl values.

Despite the use of purified brine for regeneration of the SAC unit, a considerable excess of brine beyond the stoichiometric quantity is required to obtain satisfactory SAC softening efficiency. An alternative to using fresh, purified brine for regeneration is to purify and recycle the spent brine regenerant from the SAC unit. Results obtained on a simulated SAC spent brine regenerant are shown in Table 5. Although the hardness of the SAC spent brine is considerably higher than in the fresh brine made from vacuum pan salt, it is still relatively dilute. Because of the higher brine softener feed hardness concentration compared to fresh brine, the volume of feed processed each cycle is considerably less and lower flow rates were employed. As a result of the decreased amount of feed treated, the amount of NaCl lost each cycle is more significant. Under these conditions almost 8% of the salt is lost.

Table 4
Brine softening results – saturated vacuum pan salt

	Relative volume	[Ca] (mg/L)	[Mg] (mg/L)	[Na] (mg/L)
Feed	1	106	2.00	114,800
Purified brine	0.968	0.0	0.00	113,100
Feed	.0775	326	6.70	82,400
Void				
Waste	0.382	203	3.9	2,790
Removal		99.9+%	99.9+%	1.0%
Mass balance		-3%	0%	1%

Table 5
Brine softening results – spent regenerant recovery

	Relative volume	[Ca] (mg/L)	[Mg] (mg/L)	[Na] (mg/L)
Feed	1	570	62.5	42,400
Purified brine	0.922	1.2	0.00	39,780
Feed	0.238	1400	150	29,130
Void				
Waste	1.23	225	24	2,580
Removal		99.1%	99.9+%	7.8%
Mass balance		8%	5%	4%

3.4 Chlor-Alkali Brine Softening

Membrane chlor-alkali cell brines are currently softened using a two-stage process. Primary softening is performed using the lime/soda precipitation process to reduce hardness to a few mg/L. This is then supplemented by chelating ion exchangers to obtain final hardness levels of less than 0.05 mg/L.

It is technically feasible to use the Recoflo brine softening process to achieve comparable results to the lime-soda process, but there may be little incentive to replace an existing installation. For new plants, the primary issue is capital cost. The lime-soda process is relatively inexpensive for large scale plants. For small plants, the BDH system may be competitive, particularly for packaged turn-key plants, when installation and start-up costs are taken into consideration. The Recoflo system is very compact and can be quickly started up and easily operated with minimal labour requirements.

The above results indicate that the process may even be capable of matching the final purity currently offered by chelating units. One potential disadvantage of the BDH system is the relatively

large volume of wastewater produced from the water elution. This issue is currently being addressed.

4. CONCLUSION

Novel ion exchange technology has recently been developed for separation of alkali metal salts. A number of brine purification applications have been developed which appear particularly attractive. The process is very simple and since only water is consumed to regenerate the ion exchange resins, the operating costs will be extremely low. The equipment, which is similar to that currently widely utilized for purification of waste acid, is very compact.

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