PUROLITE®
ION EXCHANGE RESINS

Application Guide

Process Engineering Report

High Total Dissolved Solids (HTDS) Produced Water Softening

With

PUROLITE Shallow Shell Technology Resins

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ABSTRACT

The efficiency of an ion exchange resin is determined, in part, by how much excess chemical is used to drive the regeneration reaction while the operating costs of an ion exchange process is directly related to the degree of regenerant utilization and the volume of waste produced. . This paper demonstrates the use of shallow shell cation exchange resin in reducing operating costs by improving regenerant utilization and reducing waste in high total dissolved solids (HTDS) produced water applications.

HISTORICAL

Heavy oil deposits are typically flooded with steam to reduce the viscosity and increase the flowability of the oil. This method typically uses 2-3 gallons of water for every gallon of heavy oil recovered. During the process of recovery, the steam generated by boilers is condensed and becomes "Produced Water". A typical site is capable of generating 8,000-16,000 cubic meters (m^3) of produced water per day. The produced water is separated from the oil and is reused as make-up water for the steam boilers. Treatment steps needed to purify produced water to avoid scaling in the boilers are:

1. Oil removal (oleophilic resin, skimming, induced gas flotation, filtration)
2. Hot or warm lime softening
3. Magnesium oxide treatment (silica removal) and a final step of
4. Ion exchange softening.

Industry standards require hardness (calcium & magnesium), levels to be less than 0.2 ppm (as CaCO3) to avoid boiler fouling. Ion exchange resin softening is the critical factor in the treatment process to meet this stringent requirement.

Produced water quality is vastly different from municipal or well waters. The total dissolved solids (TDS) levels can range from a low of 2000 to >16,000 ppm, and total hardness of 50 to 300 ppm (as $CaCO_{3)}$. As the TDS of the water increases, removal of hardness to low levels becomes much more difficult requiring processes such as counter-flow regeneration with strong acid cation resin (SAC) and/or the use of weak acid cation exchange resin (WAC) in sodium (Na) form. WAC resin is much less affected by the salt concentration in the produced water and can generally produce water with significantly lower hardness leakage levels compared to SAC resin. Regeneration of WAC resin is accomplished by first regenerating the resin to the hydrogen (H) form with hydrochloric acid (HCl) then converting to the Na form with a sodium hydroxide (NaOH). The lowest level of hardness leakage is accomplished by a Primary to Polisher bed configuration.

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PURPOSE OF REPORT

Typical annual chemical and water consumption levels for conventional cation resin in a produced water system can range up to 400,000 kg of chemical and over 72,000 barrels of water for every cubic meter of installed resin. Regeneration cost for 2004 was estimated at $2500/m^3 of resin. This report demonstrates how the use of shallow shell resin technology (SST) has resulted in significant reduction in operating cost and improvement in quality of process effluent.

SHALLOW SHELL RESIN – Hybrid Ion Exchange Resin

The ion exchange process is very rapid, taking only a fraction of a second to go from 500 ppm TDS to nearly zero within the column. During the regeneration process the concentration of chemical needed to drive the regeneration reaction diminishes rapidly as it penetrates the resin bead. More chemical is required to keep the reaction driving toward the center of the bead. In the case of conventional resins, the larger beads are left with an un-regenerated core due to the relatively low regeneration level. This TDS equilibrates with its neighboring exchange sites diffusing TDS back to the surface where it is then rinsed off during service, resulting in leakage. This leakage necessitates longer rinses to reach quality, which consumes capacity and water. (See figure 1).

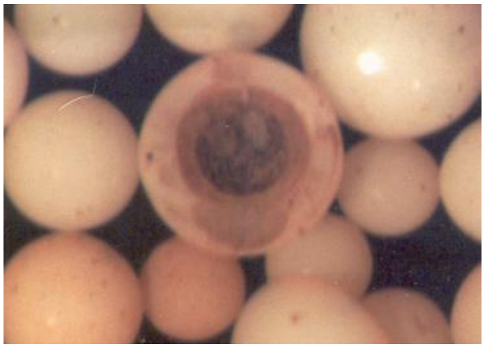

Figure 1: ***Standard resin with un-regenerated, (fouled) bead core***

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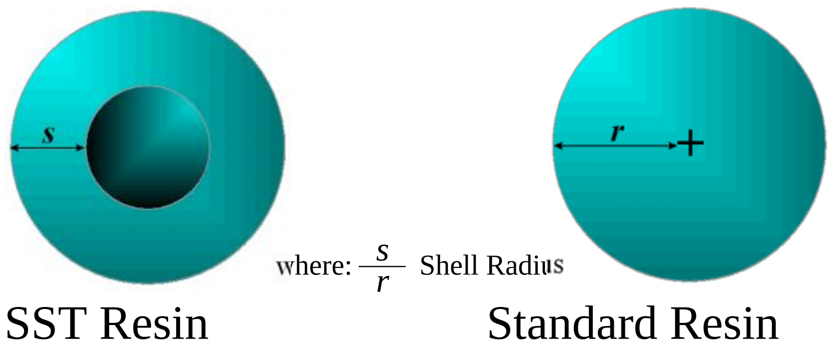
The volume of a resin bead is proportional to the cube of its radius. Example: if a bead "A" is half the size of bead "B", it will contain 1/8th the volume (½ x ½ x ½ = 1/8). Ninety five (95) percent of a resin's reactive sites are contained at about 60 percent of the radius depth, (See table 1). Producing a resin that only has functionality contained in the outer half of its shell, will improve the efficiency of regeneration by cutting the workload effort by 75%, thus reducing excess regenerant.



Shell Radius	.4	.5	.6	.7	.8	.9	1.0
Volume Ratio	78.4%	87.5%	93.6%	97.3%	98.7%	99.9%	100%

Table 1: ***Shell Radius and Volume Ratio.***

PUROLITE has perfected the process of shallow shell technology. All copolymer beads can be functionalized to the **same uniform** depth in a controllable manner. PUROLITE has been utilizing this manufacturing process since 1993 under the product name of SST-60.

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SST-SAC resin Produced Water Applications

Canada Case

When the original equipment was built in mid 1990s, it was designed to handle 350ppm TDS with 100ppm hardness. Six years later, the water source changed to 1500 ppm of TDS and 300ppm of hardness. With this change in water quality, the primary standard strong acid cation resin had to be regenerated every 6 hours with 15 lb/ft^3 of NaCl and only achieved 12ppm hardness leakage. The client decided to install Purolite SST-60 in the primary position and the service cycle went back to 20 hours with an average hardness leakage of 1.4ppm.

California Case

The original equipment was designed to handle 23000 BPD of 7500ppm of TDS with 225-ppm hardness operating at 160^{O}F. Two years after the water source changed, the client changed the resin to SST-80DL (an SST product developed for high temperature operation) netting the plant a 12000 BPD increase of purified produced water and an annual savings of $200,000 in chemical and water cost.

TDS – ppm	Hardness as $CaCO_3$	Primary leakage as $CaCO_3$	Polisher leakage as $CaCO_3$	Primary Cap as Kgr/ft^3
7500	225	5.6	0.4	18.2

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California Case

The original equipment was designed to handle 10000 BPD of 7500ppm of TDS with 200-ppm hardness operating at 210^{O}F. In March of 2002 the client changed the resin to SST-80DL (an SST product developed for high temperature operation) netting the plant a 2000 BPD increase of purified produced water and an annual savings of $80,000 in chemical and water cost.

TDS –ppm	Hardness as $CaCO_3$	Primary leakage as $CaCO_3$	Polisher leakage as $CaCO_3$	Primary Cap. as Kgr/ft^3
7500	200	4.6	0.4	19.4

Canada Case

In Nov 2003 Purolite's client, carried out a pilot project using SST-80DL in a 68ft^3 primary vessel followed by a 40ft^3 polisher running an average flow rate of 310 m^3/day. All the resin was regenerated with 20.4 lb/ft^3 of NaCl. The results of the SST-80DL testing are presented in Table 2.

TDS – ppm	Hardness as $CaCO_3$	Primary leakage as $CaCO_3$	Polisher leakage as $CaCO_3$	Primary Cap. as Kgr/ft^3
< 3000	327	2.4	0.3	27.6
3000 – 5000	377	3.6	0.6	25.5
> 5000	387	5.2	0.7	22.7

Table 2: ***SST-80DL on Water***

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The client conducted an additional pilot project using standard strong acid cation in the same primary and polisher units, while running the same flows and water chemistry. In this side-by-side comparison both the SST-80DL and STD SAC resin performed at the same throughput and leakage levels up to 4000 ppm TDS. Above 4000 ppm the standard SAC throughputs shortened and leakage from the primary increased on successive regenerations. At the 5000 ppm TDS threshold, the salt dose for the standard SAC was double to 40.8 lb/ft^3, but the SST-80DL stayed at 20.4 lb/ft^3. While both resins continued to operate at acceptable throughputs and leakages, the lower salt and water requirements for SST-80DL demonstrated a reduction in wastewater and operating cost by 50%. The results are presented in Table 3.

+ 5000 ppm TDS, 385 Hardness as CaCO3		
	SST-80DL	***Standard SAC***
Primary leakage, $CaCO_3$	***5.2***	***4.5***
Primary Operating Capacity, Kgr/ft^3	***22.6***	***25.4***
Polisher leakage, $CaCO_3$	***0.7***	***1.2***
NaCl dose, lb/CF	***20.4***	***40.8***
Yearly regeneration wastewater, US Gallons	***1,600,000***	***3,300,000***
Yearly regeneration cost for salt and water, (2004 data)	***$77,500.00***	***$163,900.00***

Table 3: ***Operating comparison SST-80DL Vs standard SAC resin***

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SST-Weak Acid Cation in Produced Water Studies

As stated earlier, weak acid cation resin operated in sodium (Na) form is also used in treatment of difficult sources of produced water. WAC resin is much less affected by salt concentration in the water to be softened, and regeneration is accomplished by regenerating the resin first to the hydrogen (H) form with hydrochloric acid (HCl), followed by conversion to the Na form with a sodium hydroxide (NaOH).

In Na form, WAC resins operate above a pH of about 4.8 preventing the formation of free mineral acid and exchanging divalent cations for Na ion. The chemical properties of sodium form WAC resin are quite different than the hydrogen form. The resin's exchange kinetics are much faster, and the capacity, when in the Na form, is about half that of the hydrogen form. The selectivity advantage for divalent cations for sodium form WAC resin is remarkably large, leading to very low leakage.

Std WAC Properties in Na Form	
Capacity (meq/ml)	2.0
Moisture Content (%)	45 – 55
Weight (g/l)	760

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SST-WAC Pilot study with Produced Water

Standard WAC field treatment systems have a primary unit followed by a polishing unit. The primary units are run to an exhaustion of 1ppm hardness (as $CaCO_3$) leakage, while the polishing unit further reduces the leakage to < 0.2 ppm as $CaCO_3$. Regeneration is accomplished by either counter-current in-situ or co-current mode in an external regeneration vessel. Current technical publications state chemical regeneration levels should be 6.5 eq/l (15 lb/ft^3) HCl followed by 6.0 eq/l (15 lb/ft^3) NaOH to achieve the target leakages. The following study demonstrates how these levels are a gross waste of regenerants.

Drawing on our expertise with SST chemistry Purolite developed and produced a WAC resin with a shallow shell. A pilot study was conducted in 2004, comparing a standard WAC resin, C-104H to SST-WAC. Leakage levels and operating capacities were documented. The following results show the capacities and leakages of the resins in the *PRIMARY* position.

The pilot study used 500 ml of SST-WAC and C-104H, in two side-by-side columns having a final bed depth of 36” in H^+ form. A simulated produced water consisting of 216 ppm Ca + 12000 ppm NaCl + $NaHCO_3$ @ pH 7.6 was used for all the pilot runs. The inlet water temperature was maintained at 80^0C and flow rate at 11 BV/hr.

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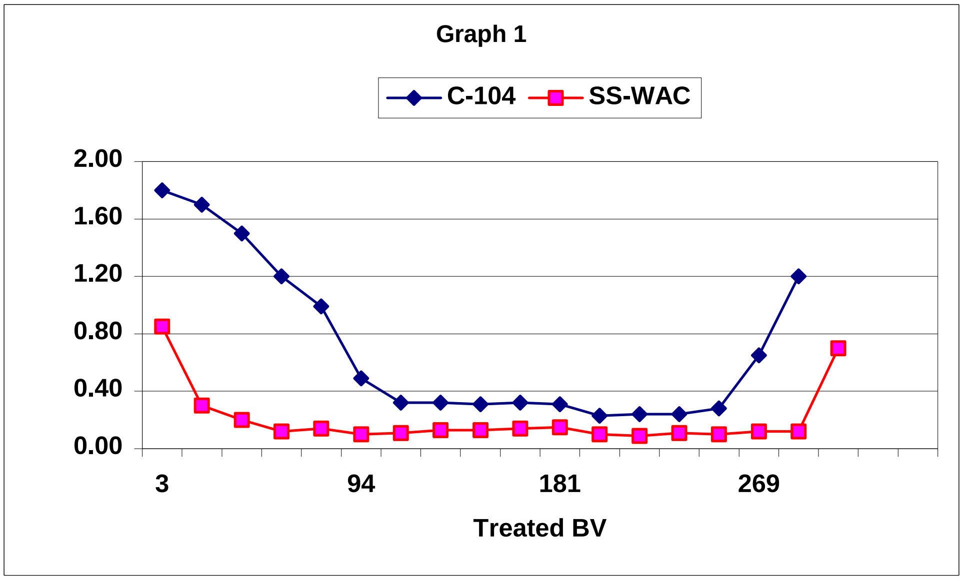
Cycle 1:

1. Both resins where regenerated with 9 lb/ft^3 HCl and 8 lb/ft^3 NaOH.
2. Swelling of the SST-WAC was 39% and the C-104 WAC was 45%.
3. The operating capacity of the SST-WAC was 29 Kgr/ft^3 and 19 Kgr/ft^3 for the C-104.

The leakage, as Ca is noted in Graph 1



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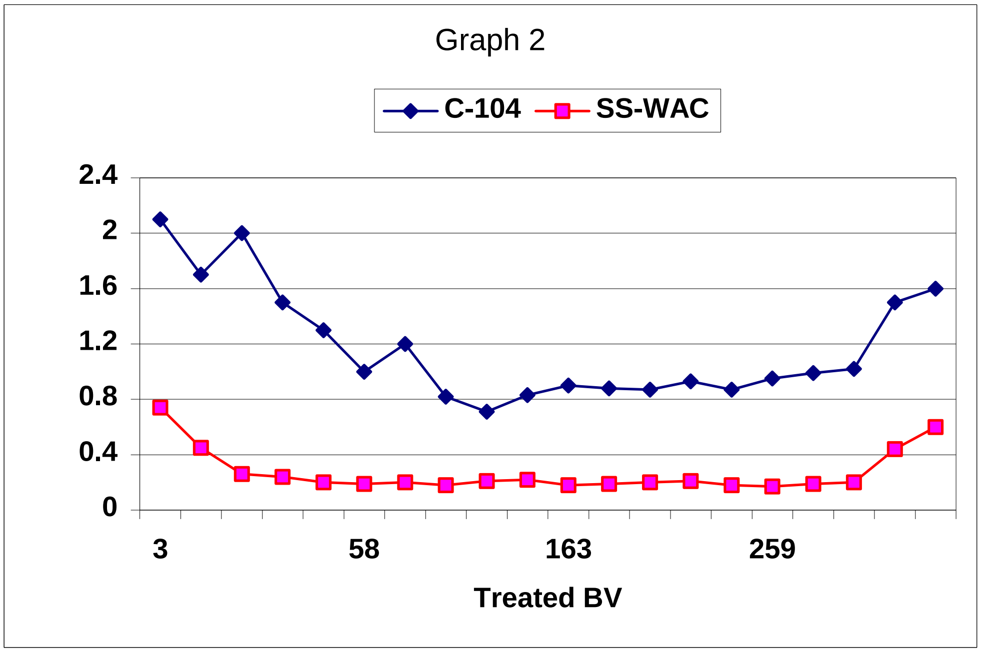
Cycle 2:

1. Both resins where regenerated with 6.8 lb/ft^3 HCl and 8 lb/ft^3 NaOH.
2. The operating capacity of the SST-WAC was 31 Kgr/ft^3 and 0 Kgr/ft^3 for the C-104.

The leakage, as Ca is noted in Graph 2



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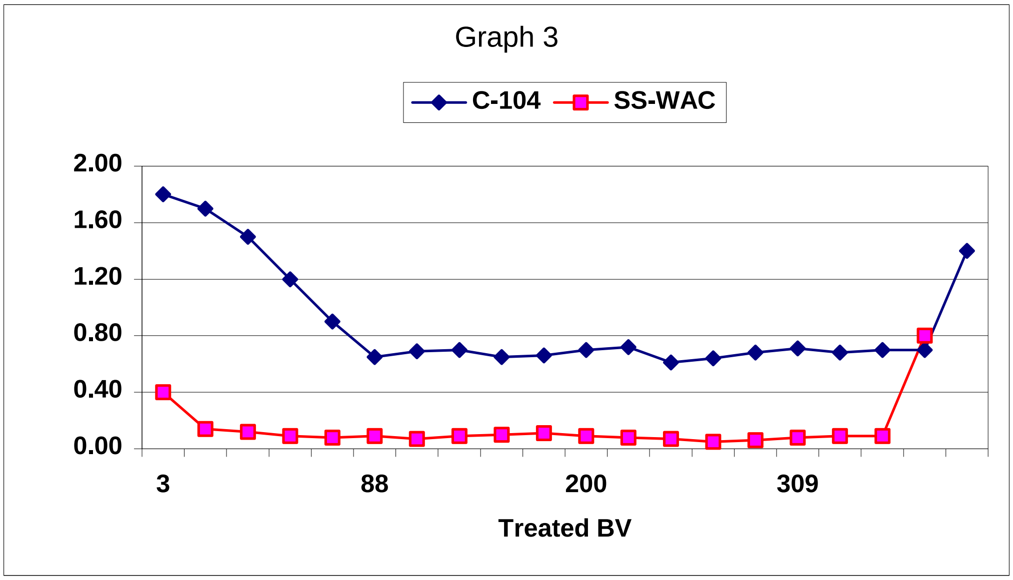
Cycle 3:

1. Both resins where regenerated with 9 lb/ft^3 HCl and 8 lb/ft^3 NaOH.
2. The operating capacity of the SST-WAC was 35 Kgr/ft^3 and 21 Kgr/ft^3 for the C-104.

The leakage, as Ca is noted in Graph 3



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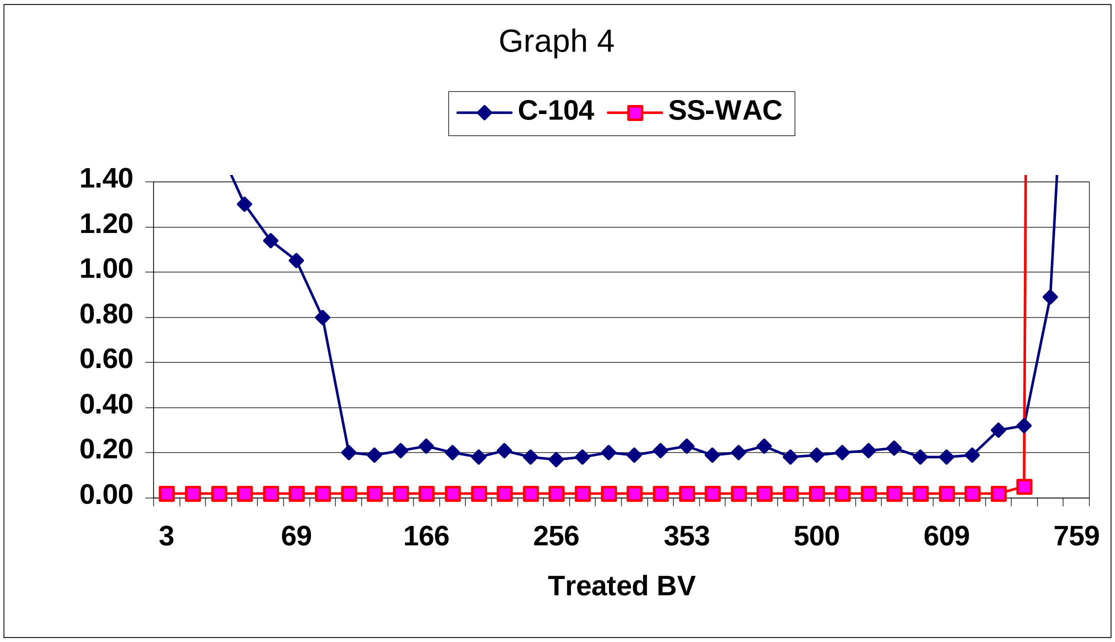
Cycle 4:

1. Both resins were regenerated countercurrent with 7.1 lb/ft^3 HCl + 8 lb/ft^3 NaOH.
2. The operating capacity of the SST-WAC was 55 Kgr/ft^3 and 50 Kgr/ft^3 for the C-104.

The leakage, as Ca is noted in Graph 4



Graphs 1-3 show that SST-WAC, regenerated co-currently provides the same, if not lower, leakage as standard weak acid regenerated counter currently (as seen in Graph 4). This suggests that expensive counter current systems can be eliminated from new capital equipment budgets, replacing them with cost effective external regenerated, (co-current) systems.

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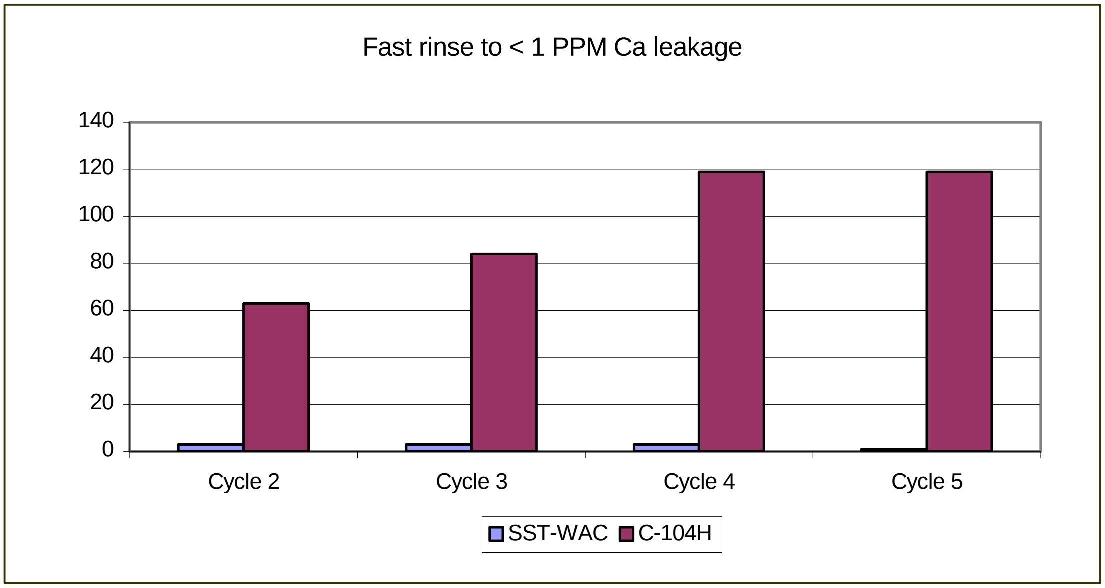
Fast Rinse Improvements

The explanation for the superior performance of the shell resin lies in its ability to allow a more complete regeneration than its conventional cousins at any given regenerant level. The results of the pilot study demonstrate this clearly. During pilot studies, it was observed that the rinse requirements for the shallow shell resin were very short. The study showed the final rinse volume for SST-WAC is 2 L of water per L of resin, with conventional resin at 20 to 50 times as much.



Summary

- *Efficient utilization of regenerants is apparent with short diffusion path resins. Shallow shell resins minimize regenerant use, while providing higher capacity, lower rinse requirements and lower the leakage in service.*

- *Field experience with SST SAC resins has resulted in increased throughput run lengths by a factor of 2 to 3 time's Vs SAC resins with significantly lower hardness leakage and reduced waste water regeneration*

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- *With potential savings of 46,600 kilograms of HCl and 41,000 kilograms of NaOH yearly per M^3 of WAC-SST resin, there's an obvious payback on this type of resin above and beyond the cost of the resin itself.*

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