The Practical Aspects of Ion Exchange in the Service D.I. Industry

An examination of ion exchange resin selection and performance.

By Michael C. Gottlieb

Service ion exchange i.e., exchanging freshly regenerated canisters of ion exchange resins for exhausted ones at the customer location and bringing them back for regeneration at a central facility, is today one of the fastest growing segments of the ion exchange industry.

Let's examine ion exchange resin selection and performance in various multiple and mixed bed applications with an eye towards their usefulness in the D.I. service industry.

Most ion exchange products, and the various processes designed to optimize their performance in demineralizing systems, were developed for use in inplace regenerating systems. Likewise, the literature and engineering data describe how these products will work in inplace regenerating systems. Included are comparisons of how ion exchange technology and the various factors differ in "service" versus "inplace systems."

Economic Factors

Economical considerations are different in the service business than for inplace regenerated demineralizers. Inplace regenerated systems have low labor costs associated with regeneration because it is handled by maintenance personnel with other tasks to perform and is often automated.

Regeneration takes place usually one to three times a day, at regenerant levels geared to minimize chemical consumption. Labor plus chemicals vary between $1 and $10 per cubic foot. However, in the service business, the so-called regeneration step is actually a combination of the chemical process of regeneration, plus the service process of exchange and delivery associated with tank change out which can vary between $10 and $50 per cubic foot. The chemical regenerant costs are the only common factor between the two regeneration processes and are a less important factor in the service business.

The inplace regeneration plant usually regenerates at four to six pounds per cubic foot using inexpensive, but sometimes tricky, sulfuric acid for the cation resin and sodium hydroxide for the anion. The central regeneration center of a service D.I. company usually regenerates at eight to 10 pounds per cubic foot using more expensive hydrochloric acid and sodium hydroxide.

In inplace regenerating systems, the rule of thumb replacement rate for Type 1 porous anion resins is every six years, and for Type 2 resins, every four years. These numbers are based on general experience and include factors such as organic fouling. They also assume throughput rates of approximately 1 million gallons per cubic foot per year.

Generally speaking, service demineralization companies provide more comprehensive pretreatment. Also, service D.I. systems generally see much lower volume throughputs. These factors reduce the impact of organics and tend to extend resin life. However, the resins are used at higher regeneration levels where loss of capacity, due to aging, is ampli-

TABLE 1
STRONG ACID CATION

CAPABILITIES	LIMITATIONS
USEFUL ON ALL WATERS	OPERATING EFFICIENCY
COMPLETE CATION REMOVAL	
VARIABLE CAPACITY (REGEN. LEVEL)	
VARIABLE QUALITY (REGEN. LEVEL)	
GOOD PHYSICAL STABILITIES	
GOOD OXIDATION STABILITIES	
LOW FIRST COST	

TABLE 2
WEAKLY ACID CATION RESINS

CAPABILITIES	LIMITATIONS
● VERY HIGH CAPACITY	● ONLY PARTIAL CATION REMOVAL
● VERY HIGH OPERATING EFFICIENCY	● USEFUL ONLY ON SPECIFIC WATERS
	● FIXED OPERATING CAPACI TY*
	● POOR PHYSICAL STABILITY
	● HIGH FIRST COST
	● POOR KINETIC

* Changes only with water analyses

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fied. Since operating capacity is crucial to service business economics, it can make sense to replace resins more frequently.

Inplace regenerated demineralizers can run to the thousands of cubic feet. In such large systems, it often pays to use varied ion exchange process schemes and "non standard" resin types and processes, to reduce chemical consumption. Service-based systems are usually too small to use these approaches economically.

Performance Considerations

An important difference between the service industry approach to ion exchange and inplace regenerated systems is the impact of the feed water analysis. The performance of ion exchange resins can be greatly affected by the ration of ions in the incoming water, especially at lower regenerant levels. In the service business, a clearly-defined water analysis rarely exists. This is just the opposite for inplace regenerated systems. The service center regeneration plants often use various added chemical treatments, usually including a brine treatment which converts the cation and anion resins to the sodium and chloride forms, further complicating the relationship between regeneration and performance. However, the use of high regeneration levels of hydrochloric acid and sodium hydroxide insures conversion, regardless of the feed water.

From a chemical consumption point of view, high regenerant levels and hydrochloric acid reduce chemical cost efficiency. However, overall cost efficiency is more dependent on transportation and labor costs which are reduced at higher operating capacities.

Resin Characteristics

The performance of an ion exchange resin also depends on the nature of the functional group, the polymer to which it is attached, and whether or not the polymer is a gel or macropore. Tables 1 through 4 show the features and benefits of each type of functional group, and Table 5 compares operating characteristics of weakly and strongly ionized resins. Since the weakly ionized resins, i.e. weak base and weak acid, are sensitive to water analyses, they simply will not work effectively in many cases, and are not widely used in the service business. Only the polystyrene matrix is fully approved for water treatment involving contact with food or ingestion by human beings making this polymer type the most widely used in this industry.

The porosity of an ion exchange resin affects the kinetics and capacity, usually in opposite directions. Most resins are made in gelular fashion by mixing the crosslinking agent with the polymer, allowing them to react in a suspension medium so that small beads are formed. An inert diluent can be added to the reacting mix and later extracted leaving discrete holes in the beads which are referred to as macropores. The gel phase also has some porosity which can be controlled by varying the ration of crosslinking agent to polymer.

TABLE 3

STRONGLY BASIC ANION RESINS

CAPABILITIES	LIMITATIONS
• COMPLETE ANION REMOVAL INCLUDING: SILICA AND CO_2	• LESS ORGANIC FOULING
• LOWER INITIAL COST	• LIMITED LIFE
• VARIABLE EFFICIENCY	• THERMODYNAMICALLY UNSTABLE
• VARIABLE QUALITY	• EFFICIENCY VS. QUALITY
• EXCELLENT KINETICS	
• SHORTER RINSES	

TYPE 1	VS. TYPE 2
BETTER THERMAL STABILITY	HIGHER OPERATING CAPACITY
BETTER CHEMICAL STABILITY	HIGHER REGEN EFFICIENCY
LONGER LIFE POTENTIAL	IMPROVED ORGANIC FOULING RESISTANCE
CAN BE REGENERATED AT HIGHER TEMPS. (SILICA)	
SHORTER RINSES	

Porous gel resins are resins that have lower degrees of crosslinking than "no porous gel resins." Macro porous resins can be made from either porous or non porous gels.

A full discussion of gel and macroporous resins is beyond the scope of this article. However, the following comments are intended as a summary.

In cation resins macro porosity allows higher DVB levels. This gives greater oxidation resistance, and thermal and physical stability. Macroporous cation resins are most often used in "inplace" regenerated condensate polishers of high pressure boilers and in chemically aggressive process applications. Since macroporous cation resins have lower operating capacities and higher first cost, they are rarely used in the service business. The primary cation resins used in the service exchange industry are the eight percent crosslinked, polystyrene gel type strong acid cation resins.

The macroporous structure gives anion resins improved organic fouling resistance over comparably crosslinked gel resins plus greater physical stability. They are most often used for color removal and organic scavenging and in inplace regenerated condensate polishers. Macroporous anion resins are not widely used in service D.I. units due to higher first cost and low operating capacity. Also, the more complete regenerant treatment process in the central regeneration plant

TABLE 4

WEAKLY BASIC ANION RESINS

CAPABILITIES	LIMITATIONS
• HIGH OPERATING CAPACITY REMOVAL	• ONLY PARTIAL ANION
• HIGH REGEN. EFFICIENCY	• DOES NOT REMOVE SILICA OR CO
• EXCELLENT RESISTANCE TO ORGANIC FOULING	• HIGH INITIAL COST
• GOOD THERMAL STABILITY	• LONG RINSES
	• POOR KINETICS

gives greater organic fouling resistance to all resins in service D.I. units. This eliminates much of the fouling resistance advantage of macropores.

There are two types of strongly basic anion resins. Type 1 and Type 2. The Type 1 is available as a porous or "standard" porosity grade. Since the porous version gives higher capacity, superior resistance to organic fouling, and is comparable in cost, it is the one used for this discussion. Table 3 shows the major difference between Type 1 and Type 2 resins. The Type 2's offer excellent fouling resistance and much greater operating capacity. In general, the Type 2 gels are the most widely used anion resins in the service industry, whereas Type 1 porous gels are most widely used in the inplace regenerated industry. The difference in operating capacity of Type 1 and Type 2 resins, on a long-term basis, depends on whether they are used in separate beds for bulk ion removal, or in mixed beds. Additionally, performance in mixed beds depends on whether they are used for polishing, or for bulk ion removal in "working mixed beds." I'll examine their performance in various applications in more detail in next month's issue. ❑

TABLE 5

ION EXCHANGE RESINS CHARACTERISTICS

STRONGLY IONIZED	WEAKLY IONIZED
● FULLY IONIZED	● IONIZATION -FUNCTION OF pH
● FIXED NUMBER OF EXCHANGE SITES	● NUMBER OF EXCHANGE SITES VARIES LOW TO HIGH
● RATE OF NEUTRALIZED FAST T 1/2<5 MINUTES	● RATE OF NEUTRALIZATION SLOW T 1/2 . 10 MINUTES
● REGENERATION MASS ACTION CONTROLLED EXCESS REGENERANTS REQUIRED	● REGENERATION pH CONTROLLED ESSENTIALLY 100% EFFICIENT
● OPERATING CAPACITY DOMINATED BY EQUILIBRIUM FACTORS	● OPERATING CAPACITY DOMINATED BY KINETIC FACTORS

The Practical Aspects of Ion Exchange in the Service DI Industry, Part 2

An examination of bulk ion removal and polishing applications.

By Michael C. Gottlieb

In the February issue of *Water Technology*, I talked about the general considerations of the practical aspects of ion exchange in the service deionization industry, delving into the economic factors, the performance considerations and resin characteristics. This article will focus on bulk ion removal including separate and mixed beds, and mixed bed polishers and low TOC polishers.

Bulk Ion Removal Applications

Separate Beds. Figures 1 and 2 show the changing capacity curves of Type 1 porous and Type 2 anion resins in separate bed service on a high chloride water. In this case the Type 2 resin gives the most capacity. A Type 2 will always start off with a higher capacity, it also tends to lose it more rapidly than the Type 1, but still retains its advantage. The rate of loss depends on the regenerant level and water analysis. Generally speaking, on a long-term basis, a Type 2 will out perform a Type 1 resin on waters where weak acid ions are less than 50 percent.

FIGURE 1

AGE VS. OPERATING CAPACITY

TYPE 1 POROUS GELS

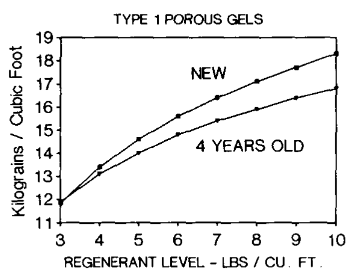
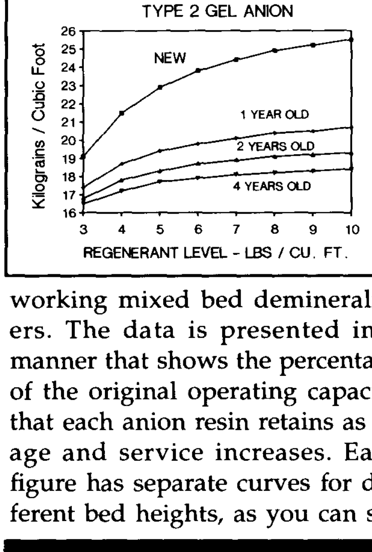


FIGURE 2

AGE VS. OPERATING CAPACITY

TYPE 2 GEL ANION

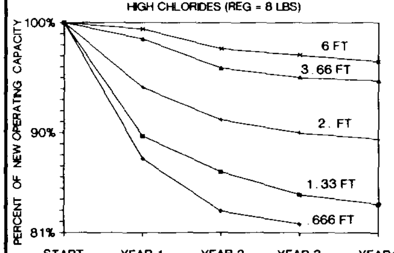


Working Mixed Beds. Figures 3 and 4 show the capacity retention of the same two resins, on the same kind of water, but in working mixed bed demineralizers. The data is presented in a manner that shows the percentage of the original operating capacity that each anion resin retains as its age and service increases. Each figure has separate curves for different bed heights, as you can see mixed beds can be sensitive to bed height. The data in Figures 3 and 4 are based on operating flow rates of two gallons per minute per cubic foot. Figure 5 shows four-year projections of the relative performance of a Type 2, compared to a Type 1, resin in mixed beds of various depths.

FIGURE 3

TYPE I "WORKING MIXED BEDS"

HIGH CHLORIDES (REG = 8 LBS)

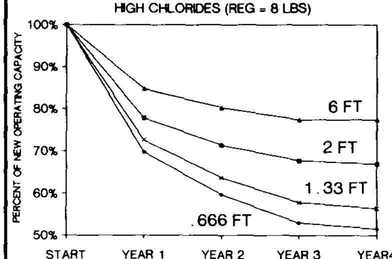


The height of the polishing zone, which remains unused, is the same, regardless of the overall bed height of the resin. Therefore, the working portion of the bed increases in percentage as bed height increases. At the higher bed heights, both resins retain their capacities to a much higher level. Below two feet, the bed depth capacity loss is quite noticeable for both kinds, but more severe for the Type 2 anion resins. Changing the flow rate changes the polishing zone height and the percentage utilization, in a manner similar to changing the bed height. As anion resins age, their functionability changes, and

FIGURE 4

TYPE 2 "WORKING MIXED BEDS"

HIGH CHLORIDES (REG = 8 LBS)



they become more sensitive to flow rate and bed height.

In the service industry, flow rates are usually in the area of one-half to two gallons per minute per cubic foot (compared to two to four gallons per minute in inplace regenerated systems). Bed heights are usually in the three to six foot range (usually tow tanks in series). Although the Type 2's age more rapidly than the Type 1's, they still tend to provide better

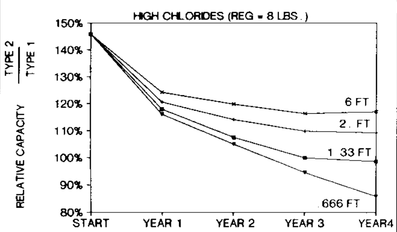


FIGURE 5
RELATIVE CAPACITY OF TYPE 2 VS TYPE 1 IN WORKING MIXED BEDS AT VARIOUS BED HEIGHTS

value in "working" mixed beds over 2 feet deep at normal flows.

Figure 7 shows the ever-changing optimum ratio of anion to cation resin to balance the cation capacity, which is stable, and maintain maximum mixed bed operating capacity. This ratio depends on the changing anion operating capacity, which is determined by its age, regeneration level, temperature, bed height, flow rate and the kind of ions being removed. Figure 7 is valid therefore only for two-foot beds,

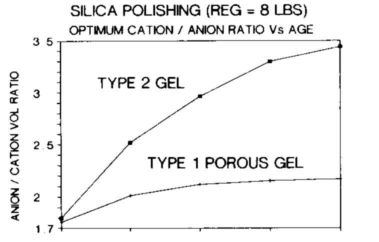


FIGURE 6
MIXED BED

seeing high chloride waters and where the anion resin is regenerated at eight pounds per cubic foot.

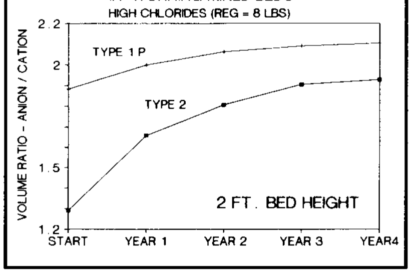


FIGURE 7
AGE VS ANION / CATION RATIO IN "WORKING MIXED BEDS"

Figure 8 is the same as Figure 7, but bed heights have been changed to six feet to show the effect of increasing bed height (or lowering flow rates). The Type 2, though less stable than the Type 1, usually provides higher long-term operating capacities in bulk ion removal applications, including mixed beds, therefore the required ratio of anion to cation resin is usually lower. This gives higher operating

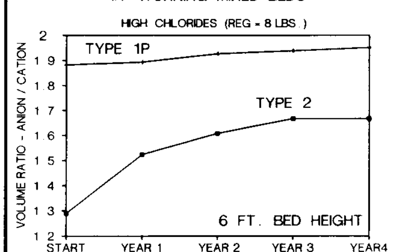


FIGURE 8
AGE VS ANION / CATION RATIO IN "WORKING MIXED BEDS"

capacity per cubic foot of mixed bed and a low capital cost as well. Operating capacity is not the only criteria by which resins are selected. Here again the difference between the service industry's use of ion exchange resins and inplace regenerated equipment is apparent. Most inplace regenerated demineralizers are used to supply purified water to steam turbines and boilers. In the service industry, the product water is mainly used in process applications where taste and odor is important. Type 2 resins have much lower and less offensive odor and are often automatically selected for this reason.

Type 2's are heavier than Type 1's and more difficult to separate without specialized equipment or brine enhanced backwash steps. Inplace systems are not normally able to do this and usually are limited to the Type 1. On the other hand, the service center regeneration plant process can usually handle the Type 2 quite well.

Polishing Application

Mixed Bed Polishers. So far we have only discussed operating capacities for bulk ion removal in "two beds" and in working "mixed beds." In "polishing mixed beds," the ion content is primarily silica and/or sodium.

If multiple beds were used for bulk ion removal, then sodium leakage is much greater than silica, and the capacity of the polishing bed is determined by the cation resin. Here, the anion resin has little affect on overall performance.

When mixed beds are used for bulk ion removal ahead of the polishing mixed bed, which often occurs in the service DI business (and almost never in inplace regenerated systems), then silica is the predominant ion and the polishing mixed bed capacity is determined by anion resin performance.

The chemical stability of the anion resin is key to its long-term silica-removing capacity since silica removal occurs only at strongly basic anion resin sites. Whether the functional group of the anion resin is a Type 1 or Type 2, has little to do with the silica operating capacity. When new, both resins exhibit similar silica removal capacities. As they age, the Type 2 anion resin can loose two to three times as much of the original capacity for silica as the Type 1.

Figure 6 shows the optimum anion to cation ratios for polishing mixed beds which operate primarily for silica removal (two-foot bed depth at two gpm per cubic foot). As anion capacity declines, more is needed to equal the cation capacity which remains constant. Therefore, the ratio of anion to cation changes in the direction of increasing anion resin. The rate at which this ration changes is determined by several factors. The major ones are bed height, flow rate, regeneration level, temperature, age in service, and the type of resin. It can be seen that the mixed bed, with a Type 1, stabilizes at a ratio of 2:1, whereas the mixed bed with a Type 2 continues to require more and more anion resin so that anion to cation ratio can exceed 3:1 in less than two years. By comparison, Figures 7 and 8 show the change in ratios in "working" mixed beds.

The Type 1 porous resin is almost always the better resin for polishing mixed bed whose capacity is dominated by silica removal. However, in applications that also require water of low taste and odor, such as in pharmaceutical, cosmetics, good processing and humidification, the Type 2 resin will still be selected because it has less odor. This is an important fact to remember.

In the service industry, most deionized water is used in processes such as pharmaceutical, rinsing, product dilution, food preparation, humidification etc. Most of these applications involve close contact of the purified water with people. Type 2 anion resins give off lower, and less offensive, odors. They are often automatically preferred for such applications, even in cases where the Type 1 may give equal or better operating capacity.

Low TOC Polishers. Service demineralizers are increasingly used as polishing units in semi-conductor manufacturing processes where 18 megohm water with low TOC values is required. The Type 1 anion resin provides lower TOC values than Type 2 anion resins because of their greater porosity. Also it is important to note that the Type 1 resin is more stable and will provide long-term organic removal capability, whereas the Type 2 may loose much of its capacity for organics, much like the case for silica.

It is also worth noting that the Type 1 porous anion resins tend to foul more rapidly than their Type 2 counterparts. Therefore, they are less desirable in applications where organics are present and low TOC effluents are not a requirement.

Knowing how the resin's performance drops off in mixed bed applications, allows for more precise selection or changes in resin ratios to maintain maximum throughputs between those expensive pickup and delivery changeouts. Inplace regeneration systems are usually constructed with fixed ration applications due to equipment limitations. ❑

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All capacity data courtesy of ResinTech Technical Center.

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