

Ion Exchange Resin

Methods Of Degradation

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As ion exchange resins age, two things happen. They swell and they lose capacity. A better understanding of the mechanisms of resin attrition allow us to make better decisions with respect to resin selection and timing of replacement.

BACKGROUND

Modern ion exchange resins consist primarily of a functional reactive chemical group affixed to a backbone polymer, usually, styrene. The functionalizing not only provides the reactive exchange site but increases the water permeability of the polymer as well. In fact, unless the polymer strands are tied together in some fashion, excessive swelling can solubilize the polymer completely.

The polymer strands of ion exchange resin are tied together by cross-linking. Most resins are cross-linked with divinyl benzene (DVB) which resembles styrene except it has two reactive groups:

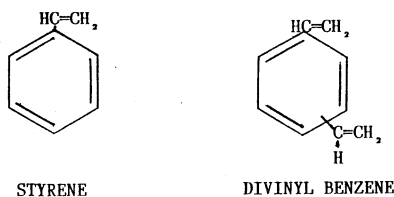
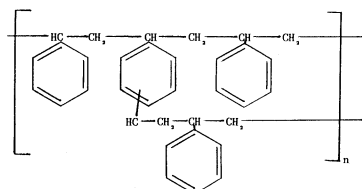


Figure 1

The chains of polystyrene (multiple links of styrene) are interlinked with the DVB, effectively tying the strands together. The higher the cross-linking, the tighter and tougher the

polymer structure becomes (and the lower the water permeability and residual moisture).



CROSS LINKED STYRENE DIVINYLY BENZENE

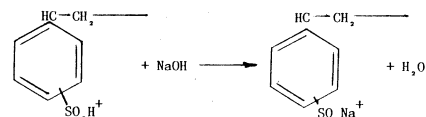
Figure 2

Typical ion exchange resin beads are made by a process known as suspension polymerization. Monomer (the unreacted styrene) and cross-linker are stirred together in water. Since the monomer is insoluble in water, droplets are formed (similar to the familiar oil and vinegar salad dressing). When the mixture is heated, the monomer droplets react to form polymer while retaining the spherical shape of the droplets. The "copolymer beads" are rinsed, dried and carefully screened for size uniformity to prepare them for functionalizing which converts them into ion exchange resins.

Cation Resins

These resins are functionalized

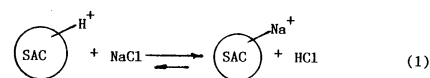
with sulfonic acid groups which are negatively charged and thus have an exchangeable positive ion. These resins are called strong acid resins because the functional group reacts like an acid.



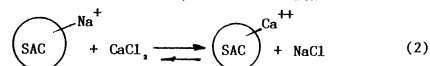
NEUTRALIZATION WITH A STRONG ACID CATION

Figure 3

These resins have the ability to neutralize a base (alkaline materials) or split a salt. Unlike with a real acid, the product of reaction remains insoluble and firmly attached to the resin. A typical reaction of SAC (strong acid cation) resins is as follows:



SALT SPLITTING/DEMINEERALIZATION



SALT SPLITTING/SOFTENING

Figure 4

Anion Resins

Anion resins are functionalized with amines which are positively charged and have an exchangeable negative ion. These resins are called strong base resins because the functional group reacts like a base. As an intermediate step, the copolymer is first reacted with methyl chloromethyl ether to prepare it for the amination step. This is shown in Figure 5.

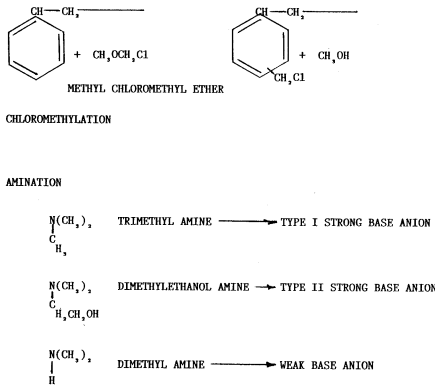


Figure 5

These resins have the ability to neutralize an acid or split a salt. Again, the product of reaction remains attached to the resin. A typical reaction of SBA (strong base anion) resin is as follows:

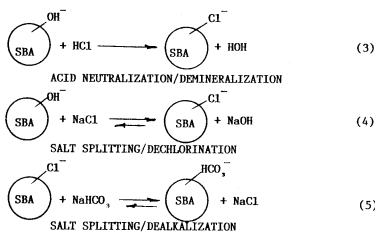


Figure 6

Depending upon the type of base chemical (amine) used, we can produce SBA resins in different ionic strength or basicity. Commonly, trimethyl amine is used to produce resins of stronger basicity called Type I SBA and dimethyl ethanol amine is used to produce resins of somewhat lower basicity which are called Type II. Type I SBA give superior removability of weakly ionized anions such as silica. However, being stronger bases, they are somewhat more difficult to regenerate and therefore result in lower capacities for a given amount of regenerant used.

Type II SBA regenerate more easily, therefore higher capacities can be obtained. Type II's are used for dealkalization and nitrate removal

because higher capacities can be obtained with brine (NaCl) regeneration and 100% removal of the offending ions is not necessary. Type I's are typically used for complete demineralization and polishers.

Weak Base Resin

In addition to the SBA's described, anion exchange resins can be made with even weaker bases such as dimethyl amine to produce resins called weak base anions (WBA). WBA cannot split neutral salts like SBA's. However, they can neutralize acids (reaction #3) and can therefore be used in conjunction with SAC (reaction #1) to demineralize certain waters:

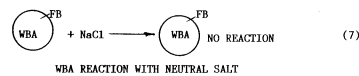
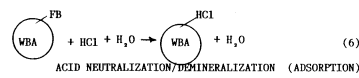


Figure 7

Note that the reactive mechanism of WBA is different. Neutralization of acid is accomplished by the complete adsorption of the acid rather than the exchange of its anion group.

Regeneration of WBA with a base such as caustic (NaOH) or ammonia (NH₄OH) effectively neutralizes the adsorbed acid off the resin, leaving the resin in what is called the "free base" form. WBA regenerate very easily and have high capacities for acid adsorption.

Mechanisms of Resin Attrition

As ion exchange resins age two things happen: they swell and they lose capacity. With age and use ion exchange resins are subject to oxidation. Oxidation breaks down the cross-linking of the polymer backbone, weakening the bead and causing it to swell. These beads are more easily broken and the fines (fragments) are subsequently backwashed out of the column. For any particular ion exchange resin, the relationship between the degree of cross-linking and moisture content of the polymer is so interrelated that one property can be used to qualitatively measure the other. Moisture content, which is easily measured, is an excellent yardstick to measure cross-linking (which is difficult to determine without complex equipment).

Therefore, a simple measurement of moisture can reveal a wealth of in-

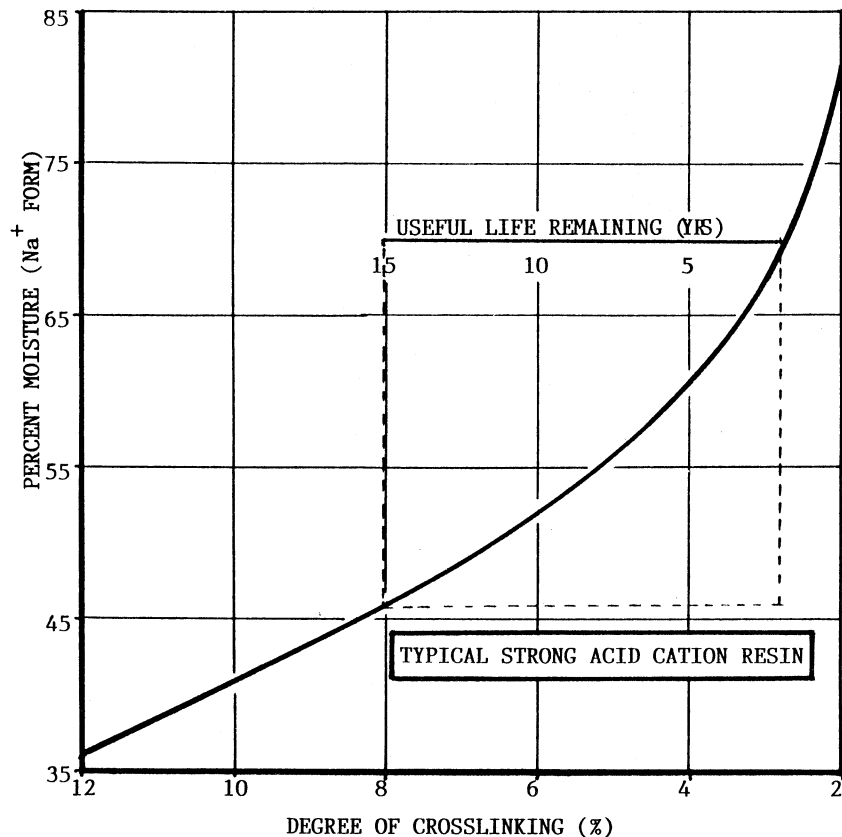


Figure 8

formation regarding the life expectancy or "age" of the remaining resin. The chart on the preceding page shows the relationship of moisture and cross-linking for a typical styrene DVBSAC resin.

Oxidants such as chlorine, ozone, oxygen, peroxide, UV light, combined with heat, speed the de-cross-linking of resins.

In addition, strong acids such as nitric and chromic acids have oxidizing capabilities (as do permanganate and perchlorate ions).

Effects Of Chlorine

As a rule of thumb, the life expectancy of a SAC resin used in a typical softening application can be predicted by simply dividing the number 10 by the ppm of free chlorine in the feed water. For example: 2ppm Cl, 10 divided by 2 = 5 years.

At the beginning of this article, we mentioned that as ion exchange resins age they swell and lose capacity. While oxidation and subsequent de-cross-linking may explain the swelling, does oxidation affect functionality as well? The answer is definitely yes-- and sometimes!

SAC resins used for softening and D.I. have very stable functional groups.

SAC used for hot lime polishers, for instance, frequently see temperatures of 290 ° F or more and survive for 20 years or more. Softening hot water with conventional 8% DVB resins is not uncommon. The limitation is simply that resin beads are thermoplastic and soften at elevated temperatures. This can cause the beads to become easily deformed and break under the higher pressure drop that results. Nonetheless, these cation fragments (fines) keep on working. For proof, simply look closely at the resin in a 30-year-old residential softener.

Do we suggest that SAC be replaced at 30 year intervals? No, indeed. The reason is economics and concern for salt efficiency.

A brand new cubic foot of SAC resin is expected to yield a capacity represented by the chart in Figure 9.

As the resin ages, swells, and breaks apart, the same volume of salt is required to regenerate it. Fewer beads actually occupy that original cubic foot of space due to swelling. Therefore, the capacity drops and the salt efficiency (Killograins removed/lb. salt) drops dramatically. The resin still softens but the cycle is shorter. The unit becomes more expensive to operate.

Let's say that after 19 years, the

capacity of a cubic foot of resin is 70% of original capacity and 10 lbs. of salt are used to regenerate the resin every other day. That's 3 lbs. of excess salt times 180 cycles per year or 540 lbs. of wasted salt per year. At \$.10 per lb., you're spending \$54 per year more than you have to for the softening capacity you get. It doesn't take too much math to figure the pay back for rebedding, let alone the benefits of lowering the amount of salt down the drain. Do the calculation again - this time increasing the frequency of regeneration by 30% as well. Now we have 257 cycles per year instead of 180. That wastes 540 lbs. of salt from the 180 cycles plus, we consume 770 lbs. more for the subsequent 77 cycles to maintain softened water. This is a waste of 1310 lbs. of salt per year and \$131.00. Even assuming \$.05/lb. for salt and 80% of original capacity, we still waste 810 lbs. of salt and \$40.50 per year. This level of performance can arrive in 5 to 7 years depending upon the water supply (level of oxidizers). With more expensive regenerants such as muriatic acid (HCl), the break even point is upon us even sooner.

With SBA resins, the mechanisms of degradation are twofold. In addition to the physical breakdown of the resin due to de-cross-linking, we experience chemical degradation as well. Chemical or functional degradation refers to the actual loss of the reactive site.

SBA reactive sites are far more sensitive to temperature degradation than their acidic cation cousins. Salt forms of SBA's (dealkalizers) have upper limits of 180 ° F, while hydroxide forms (demineralizers) are limited to 120 ° F for Type I's and 100 ° F for Type II's. Degradation actually occurs at temperatures of 60° F or less. It's just more precipitous at elevated temperatures.

Those of you who have ever handled SBA resins are no doubt familiar with the amine odor (fishy smell) that is associated with it. No matter how much rinsing, the odor seems to persist if water is allowed to stagnate in the resin bed. That's because the functional amine groups are actually coming off the resin. The resin is losing capacity from both the physical attrition of the bead and the chemical attrition of the reactive site itself. With the price of caustic going through the roof, it doesn't take much capacity loss to reach a break even point. What's more, anion resins, in

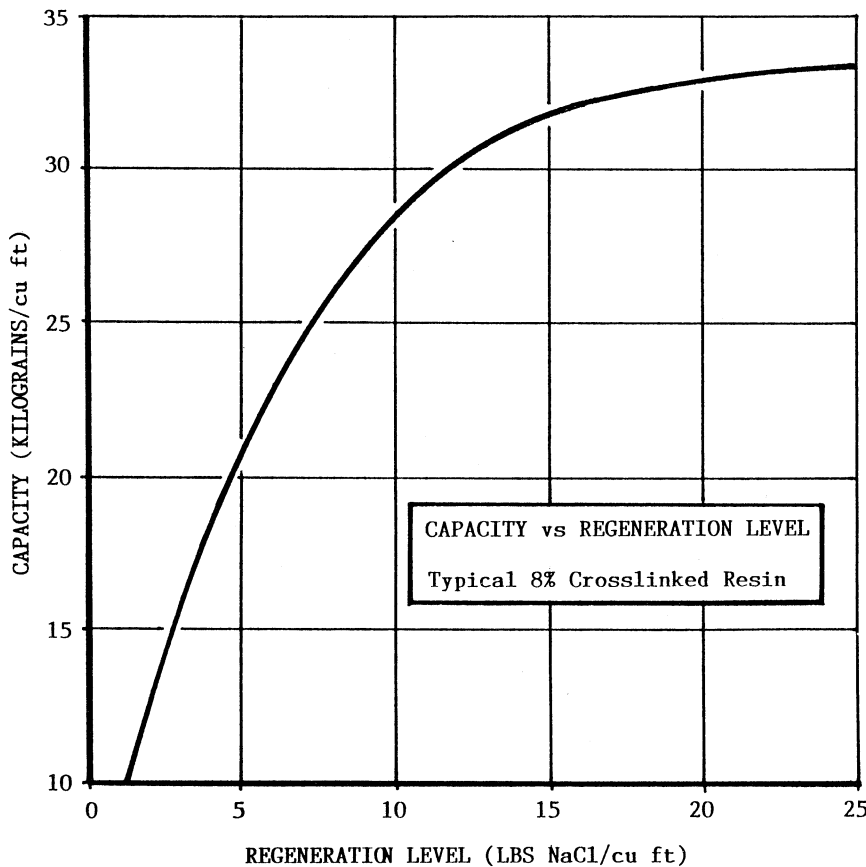


Figure 9

general, are not as highly cross-linked as cation resins and physical attrition is more rapid. SBA's have a useful life of 3-5 years. Seventy percent of original strong base capacity is generally the replacement point.

We emphasized strong base capacity here for a very good reason. That has to do with the actual chemical change that occurs as SBA resins degrade. Earlier we mentioned that WBA (weak base) resins also have the capacity to neutralize acids (demineralizers). Type II SBA degrade by about 10% loss of reactive group (quatarnary) and 90% from conversion of the reactive group to a weak base (tertiary). Therefore, Type II's retain their ability to act as demineralized resins longer than Type I's, whose degradation mechanism is just the opposite. Salt splitting (true strong base functionality) degrades more rapidly for Type II's, however, due to their increased sensitivity to temperature. This makes Type I's the resin of choice for mixed bed polishers.

Old Type II's still have utility for their WBA functionality. However, they will require higher levels of re-

RESIN SELECTION CRITERIA

	ANION			CATION	
	Type I	Type II	Weak Base	8% X-link	10% X-link
Hi-Flow Softening				++	+++
Heavy Metal Removal	+		+	+++	++
Operating Capacity	+	++	+++	+++	++
Regeneration Efficiency	+	++	+++	++	+
Temperature Stability	+	-	++	+++	+++
Chemical Stability	++	+	++	++	+++
Silica Removal	+++	+			
Organic Removal	++	+	+		
Fouling Reversibility	+	++	+++		
Osmotic Shock Resistance	+	+	+	++	+++

Figure 10

generant than WBA and will have lower capacities since, by the time they arrive at this point they will have lost a significant number of sites.

SUMMARY

We have described only four basic resins at this point: SAC, SBA I and II and WBA. However, each resin manufacturer produces and sells

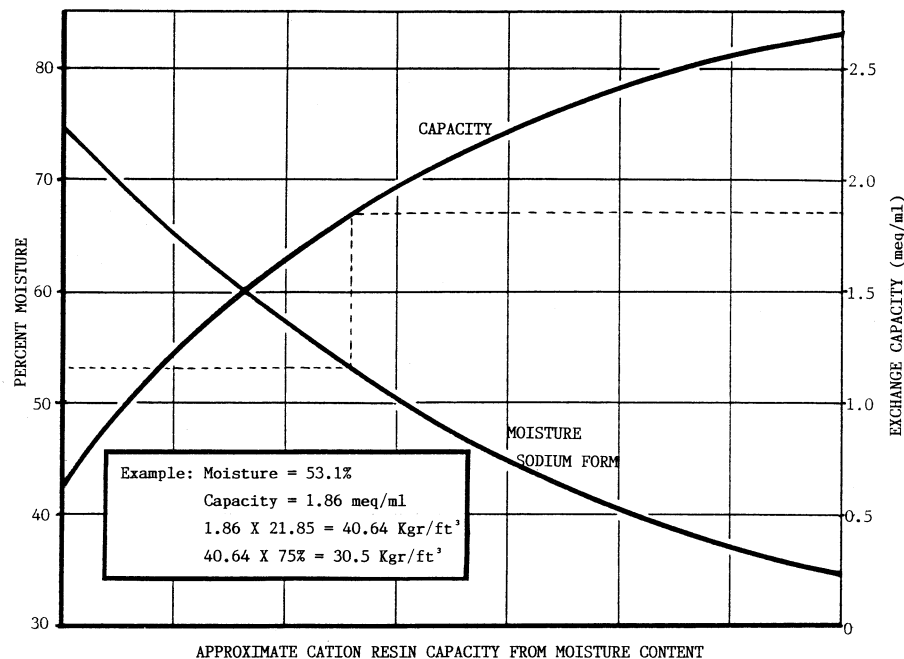
dozens and dozens of different ion exchange products.

The table below attempts to simplify the problem of initial resin selection based upon water analysis and intended end use. The life of the resin is going to be relative to its purpose. Similarly, a racing car will not outlive the family sedan. The higher the expected performance, the shorter its useful life (at that level of performance).

The table in below gives a general view of the remaining life (capacity) of resin based solely on moisture content.

While moisture is a good approximation of the physical condition of an ion exchange resin, the whole picture must take into consideration the actual capacity as well. To do this, the capacity, usually reported as meq/ml or meq/gm (milliequivalents/gram), must be compared to the new resin or typical values for new resin. By comparing the remaining capacity per dry gram of resin to the original value, the percent capacity loss can be calculated. Have these analyses done by a qualified lab. Keep in mind also that an analysis for capacity may not reveal a capacity loss due to fouling of the resin by organics, iron, scale, etc. If fouling is suspected, the resin must first be cleaned before its true capacity and life can be evaluated. Consult your resin supplier if interpretation of results is in question.

Also keep in mind that "total" capacity does not mean "column" capacity or kinetic capacity. Total capacity is meant to measure the total ability of a resin to react (all the way to complete breakthrough). Actual



1. Read moisture on left. Follow right to moisture curve.
2. At intersection, go vertically to capacity curve.
3. At intersection, go right to read capacity in meq/ml (milliequivalents/milliliter)
4. 1.0 meq/ml is equal to 21.85 Kgr/ft³ (kilograins/cubic foot as CaCO₃).
5. Use 75% of this value to estimate actual column capacity.(with 15'lbs salt)

Figure 11

Continued on page 51

Ion Exchange Resins

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capacity will be less because the run will normally terminate at very low levels of breakthrough.

CONCLUSION

Moisture analysis coupled with relative capacity (versus original) are usually sufficient indicators in determining useful life of an ion exchange resin. For SAC softening resins, moisture alone is usually good enough (since the relative capacity per dry gram will not change appreciably during its life). Microscopic (visual) examination is useful in determining if the resin is worth trying to save in the event of fouling.

Use a qualified lab for all resin testing. Don't be afraid to seek a professional opinion before expensive rebedding.

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Don Brodie is also a chemical engineering graduate from the University of West Virginia and began his

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Both Michaud and Brodie have been frequent contributors of technical articles for *Water Conditioning & Purification Magazine* in the past.



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