The Reversible Removal of Naturally Occurring Organics Using Sodium Chloride Regenerated Ion Exchange Resins

By Michael Gottlieb, Published in Watertech, 11/10/93.

This is the first in a series of papers on the use of strongly basic anion exchange resins for the control and removal of naturally occurring organic substances from water.

My specific goals in this presentation are to show the mechanisms affecting organics behavior, give preliminary performance estimates for resin organic interactions, and to document the major steps in development of the knowledge that made this presentation possible. Therefore, a good deal of this presentation will be historical in nature.

Naturally occurring organic substances have long been recognized as being primarily aromatic hydrocarbons with carboxylic groups. For many years now it has been known that these substances can be removed by ion exchange resins and that the ion exchange phenomenon played an important part but not the complete role in their removal by resins. In an effort to explain the complex behavior of these substances other mechanisms were assumed to be involved. This was changed in a landmark effort by Symons[11] in a paper presented at the 1992 International Water Conference in Pittsburgh, PA. He showed that ion exchange was the only mechanism involved for the removal of the vast majority of TOC substances from natural sources, except for those with low molecular weights. Not only is the concept of an exclusive ion exchange mechanism new, so is the idea that the low molecular weight and not the opposite can pass through the resin bed, if the resin has sufficient gel phase porosity.

The presence of organic substances in influent waters generally causes problems in demineralizers such as, long rinses, poor quality, and reduced anion capacity. Because of Symons results, we now know that ion exchange kinetics and equilibrium relationships are the areas to be investigated. This means that resin characteristics must also be correlated to these relation-

ships. Today we can say that the mechanism for the removal of naturally occurring organics by ion exchange resins, as measured by the TOC test, is at least understood, if not well defined.

The naturally occurring organics are removed as ions. They have very slow diffusion rates. They are weak acids and therefore their ionic nature is affected by pH, temperature, and concentration. Since they have slower diffusion rates, contact time, especially during regeneration, is an important factor, equally as important as the regeneration dose.

Later I will show that in order to regenerate organic laden resins sufficient contact time is as important a factor as dose. Also, the higher the relative amount of water in the gel phase the less critical the time factor. As we shall

soon see, high water retention increases the removal capacity and lowers selectivity.

Lowering the selectivity coefficient of the organics against the regenerant increases the relative strength of the regenerant. For example, the higher water retention level of Type 1 porous gel resins gives them about 20% higher operating capacity for chlorides then the standard Type 1 gel resins in demineralizers regenerated at the same dose level of NaOH, even though the porous type has 15% lower total capacity([1]). This is because the Cl/OH selectivity coefficient is about 50% as great in the porous resin, which makes the OH ion a more effective regenerant against chloride.

In the case of organic ions, kinetic factors have a much greater impact on performance. They are at least as important as regenerant selectivity and dose level in determining the operating capacity, by the regeneration process.

Let us review now what we know about "organics" and the events leading up to this presentation. **Figure 1** shows the structure of the colored portion of the humic acid molecule according to Gjessing[4]. Given that it is well known that the source of organics in surface waters are vegetative, from decaying plant life. The sources of plant life include grasses, leaves, decaying tree limbs and soil humus. Humus is created from decaying roots and wood stock from plants. It is the "spongy" material in the earth and is known to have long lives and very high molecular weights.
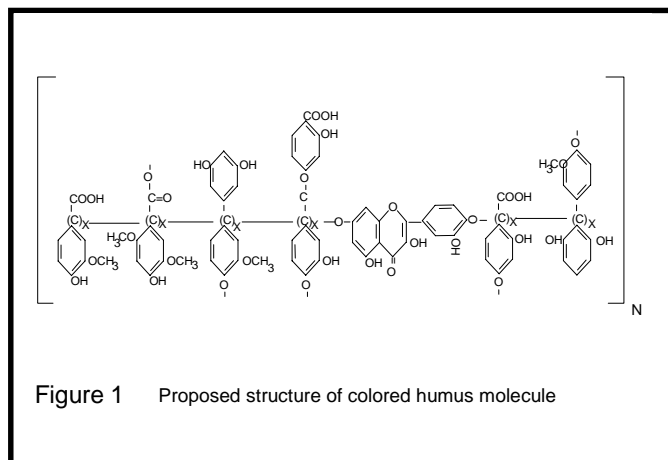

Figure 1   Proposed structure of colored humus molecule

Humus is acidic in nature. In concentrated form, organic acids act as biological preservatives. A few years ago, bodies were discovered that had been buried in peat bogs for over 100 years (which are primarily humic materials), they were found to still have their last meals undigested in their stomachs.

Once these substances dissolve in water, oxygen and sunlight oxidize them. Oxidation can cleave the carbon bond in the benzene ring. This reduces the overall size and molecular weights of the organic molecules.

The molecular weight of fresh aquatic humus has been extensively studied by several workers and summarized by Gjessing[4]. The molecular weights of humic acids range from 700 to 80,000+; fulvic acids from 200 to 300 for soluble species. Significant amounts of humic substances also exist as colloids which, when tested by light scattering and ultra centrifuge techniques, gave molecular weight values of 30,000 to 80,000. Therefore we know that the starting molecular weight of the organic materials in water can average well into the tens of thousands. Yet as we will see later, the average molecular weight of those substances in water comprising TOC are usually well below 10,000.

This may vary depending on climate conditions such as temperature, the amount of sunlight, oxygen concentration, water color, pH, and how long it's been in the water.

Once the concentrations of the organic acids are reduced by dilution, microbiological processes can begin. These are aided by the availability of oxygen and other nutrients. Microbiological attack is a form of oxidation. It also creates various chemical groups such as carboxylics, aldehydes, ketones, and hydroxyl to name some. Since these materials started out as plant life, they include other elements besides carbon and oxygen. They also have nitrogen, phosphorous and the whole range of elements associated with life. **Figure 1** is just one portion of the humic acid group of chemicals found in surface waters.

Surface waters contain several other classes of humus derived substances, including fulvic acids, lignins, and tannins. These are only the major constituents from plant sources. All of the various organic classes are similar in that they are based on multiple benzene rings and have significant carboxylic acid functionality. The biggest differences are molecular length and width. They also contain hydroxyls, ketones, aldehydes, sacchorides, etc. plus a minority of amides, amines and traces of mineral elements. The molecular shape is determined by the degree of branching in the polymer structure. Calculations based on Symons[11] data show that there are, on average, between 1 and 2 carboxylic groups per benzene ring (**Figure 14**). Several other studies of these materials have shown that the carboxylic content of humic substances varies usually between 3 to 12 milliequivalents per dry gram, which is similar. These substances behave like weak acid ion exchangers. Humic acid and lignin are used commercially as dispersants and chelants.

Humic substances form complexes with metals. **Figure 2** shows the structure of the humic acid complex with iron as proposed by Gjessing[4]. When iron is present in this form it is commonly referred to as "heme" iron. The difficulty in removing this form of iron is due to its non reactivity since the complex is only slightly ionized. Flocculation and filtration, or total destruction of the organic matter by

Figure 2   Proposed linkage with humus and iron
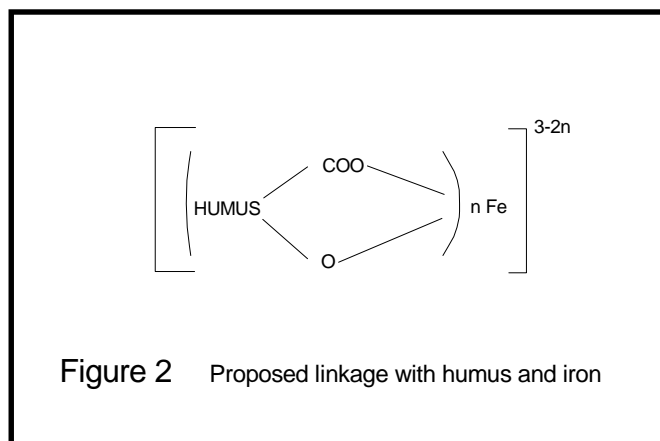
oxidation, are two of the common methods used for removing this form of iron. Many of the carboxylic groups on the humic acid molecules remain ionized, therefore they are free to interact with and be removed successfully by special purpose ion exchange resins, one of which I will discuss later. The presence of heme iron is the reason why most organically fouled anion resins also contain iron. They can also have copper, aluminum, zinc, manganese, etc. which also form complexes with humic acids.

Symons also proved that nonionic adsorption played little or no role in the removal of these humic substances except for those of molecular weight less than 1000, which coincidentally, were not well removed by the ion exchange resins either as they are apparently unionized. Many of these also passed through the adsorbents and carbon indicating they may be alcohols, ketones or aldehydes.

Symons' experiments were conducted in two stages. The first stage was batch equilibrium studies using R.O. and U.F. to concentrate and fractionate the organics from Lake Houston water and dialysis to remove inorganic ions. His tests were conducted with several different ion exchangers, which covered a wide variety of types and were manufactured by a single supplier. The chloride form of the resins were contacted with specific molecular weight fractions of the extracted organics for one week and analyzed. The solutions were tested before and after for TOC and chloride. Both styrenic and acrylic polymers in their gel and also their macroporous versions of each were used as well as non ionic macroporous adsorbents. Crosslinking levels in the gel phase was varied in the gel resin, and also in the macroporous resins.

The results showed that less than 4% of the TOC values were removed by the adsorbents. Surprisingly those 4% had molecular weights of less than 1,000. This discovery is significant, because it caused us to re-examine our ideas and beliefs about the nature of "organics".

In the past, organics were invariably thought of as being of such high molecular weights that they could not fit into the gel phase of the resin. It was, until now, believed that naturally occurring organics were removed by a combination of adsorption and ion exchange ([6,7,10,12]).

Significantly the Symons[11] paper proved that the macroporous resins did not necessarily do better then gel resins. This had also been shown by others [1, 14, 15]. For the fist time we began to appreciate the importance of the gel phase. The lower crosslinked macroporous resins did better than higher crosslinked ones and lower crosslinked gel resins did better than higher crosslinked gel resins and higher crosslinked macroporous resins. Even for the very high molecular weights (above 10,000) the relative gel phase water retention was the only reliable predictor of removal performance. The gel phase water retention is controlled by the crosslinker level.

The second stage of Symons' studies were column studies. These were designed to measure the ability of an anion resin regenerated with 2N NaCl and .5 N NaOH to reversibly remove TOC contained in Lake Houston water. It was found that the sulfate ions offered significant competition for the ion exchange sites. Some of the lower molecular weight organic matter (less than 5,000) was less preferred than sulfates and were "dumped" off when runs extended beyond the sulfate breakthrough and reached concentrations higher than their inlet concentrations.

Since the organic matter is multivalent, electro selectivity will effect their apparent selectivity for the resin in the same manner as shown in **Figure 3** for the sulfate ions.

Figure 3   APPARENT SELECTIVITY- SULFATE / CHLORIDE
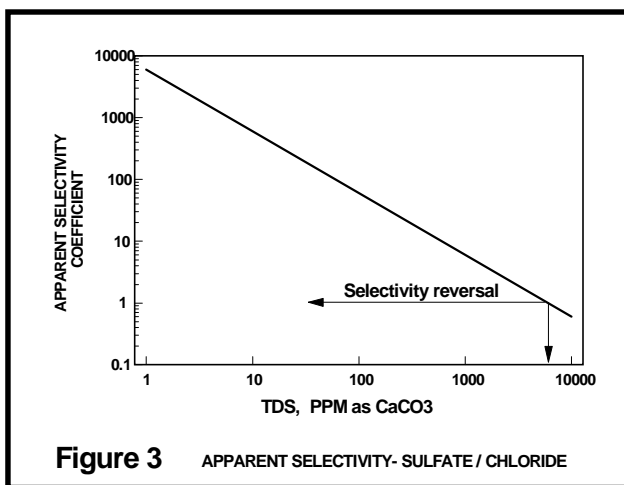
Symons work was focused on ways of reducing THM precursors. His study included activated carbon. When used alone granular activated carbon (GAC) could only treat about 1,000 bed volumes removing about 80% of the TOC before the onset of increased leakage. This is believed to be due to its limited capacity and because of surface blockage by large sized organics. The use of ion exchange ahead of the GAC let the GAC exclusively deal with the lower molecular weight unionized material passing through the resin. This combination removed 93% to 95% of the overall TOC influent with no indication of breakthrough at over 4,000 BV's of GAC. Of the 5% that was unremoved, 70% of it was less than 500 molecular weight and thought to be alcohols and similar materials. The resin was regenerated at the sulfate breakthrough using a salt/caustic combination.

Resin alone removed over 80% of the TOC. Significant organic fouling protection could be accomplished by the salt/caustic regenerated anion resin alone without GAC, since the lower molecular weight organic matter is more rapidly eluted from and therefore less likely to foul working resins.

For ultra high purity water systems requiring maximum reduction of TOC, a two stage organic removal process with the resin in front of the GAC would be required.

There are four major reasons for the reduction of TOC:

1. Bulk color or TOC reduction from water used for municipal or domestic use.
2. Maximum reduction of TOC for ultrapure water applications for semiconductor manufacturing and/or for municipal installations to remove THM precursors.
3. Prevention of organic fouling of demineralizer resins.
4. Reduction of organic substances in steam boilers.

Equilibrium relationships are very important to the regeneration process and to combat build up which leads to fouling. The efficiency of regeneration can be affected greatly by changing the salt concentration. Let us briefly review some of these relationships.

Table 1 shows the selectivity coefficients of the various ions for gelular Type 1 and Type 2 anion resins compared to the hydroxide ion. Those substances with the higher selectivities are more difficult to regenerate off of the resin with hydroxide. However, these resins are more easily regenerated with sodium chloride because the relative affinities of all the substances are lower against the chloride ion. For the Type 1's, the affinity of the chloride is from 11 (ResinTech SBG1P) to 25 (ResinTech SBG1) times higher than the affinities for the hydroxide ion. Therefore the selectivity coefficients for the listed substances against the chloride ion is 11 to 25 times lower. This makes the chloride ion significantly more effective as a regenerant than the hydroxide ion. Note the high values for lignosulfonate and benzene sulfonate. These are similar to the basic structure of the naturally occurring organics. It is believed that they have similar affinities for the resin as the humic substances and are therefore useful as models.

Table 1

Relative Affinities
(OH=1)

	Type 1 Standard Gel	Type 1 Porous Gel	Type 2 Standard Gel
Lignosulfonate	800	400	120
Benzenesulfonate	500	253	75
Salicylate	450	358	65
Citrate	220	110	23
Iodine	175	97	17
Nitrate	65	42	8
Bromide	50	31.1	6
Chloride	22	11.1	3
Bicarbonate	6	3.6	2.3
Hydroxide	1	1	1

The separation factor, which is the same as the selectivity coefficient for monovalent exchange, is what determines the efficiency of a regenerant. It can be used to calculate the theoretical regeneration level per unit of regenerant. In the case of multivalent ions the separation factor is more closely related to the apparent selectivity coefficient, which varies with the total ionic concentration as shown for the sulfate/hydroxide ion pair in **Figure 3**. When the regenerant concentration is about 10% the apparent selectivity and the selectivity coefficient are about the same. So we can use the selectivity coefficient as parameters.

The relative separation factor of chloride for the resin, during regeneration of a Type 1 resin with 10% brine versus 4% NaOH, is about 11 to 25 times higher than hydroxide. Therefore it is much more effective in removing organics.

The chloride cycle regeneration of organics can be seen to be as effective for Type 1 resins as for the Type 2's. The Type 1's are more chemically stable and can be made with higher water retentions (low crosslinker levels) therefore they can remove higher molecular weight organics than the Type 2's. This can best be seen in **Figure 4**, which shows the theoretical regeneration versus dose levels based on selectivity coefficients for chloride and hydroxide regenerations of lignosulfonate.
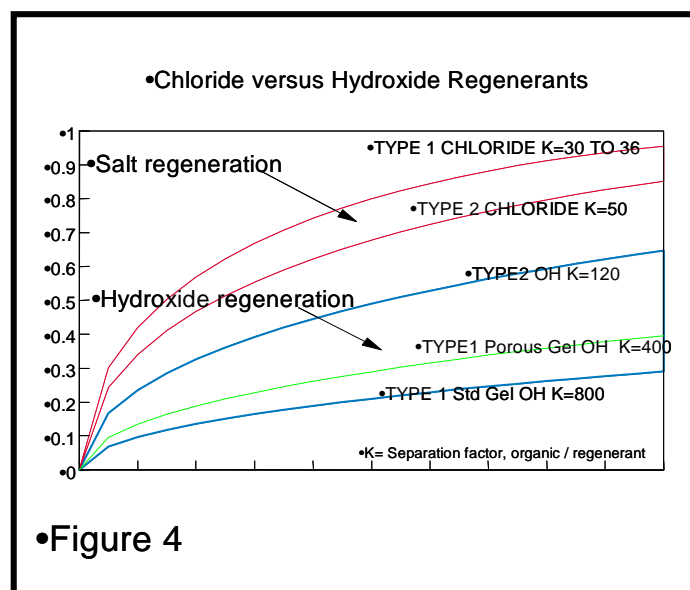
This gives a good picture of the effect on regeneration efficiency of the relative selectivity coefficients. Keep in mind these curves are based on the assumption that enough contact time has been given for the regenerant and resin to reach equilibrium. So we see that the porous Type 1 gel resins can remove TOC substances and be well regenerated with chloride regenerants. In reality this is not the case. For example, when brine regeneration was carried out in the same time as for inorganic ions (using short contact times and no prolonged soak) Sym-

mons[11] showed that the same brine could be reused up to 9 times without loss of capacity or quality in TOC reductions. So it is obvious that much longer relative regeneration times are needed for organic ions.

Before discussing the importance of contact time to the regeneration of the organic acid form anion resin, let us first review the effect of contact time on the regeneration of softeners. The common cations come to 80 to 90% of equilibrium in about 5 minutes[10]. It is standard practice to design softeners with regenerant times of about 30 minutes.

Figure 5 shows how the change in regenerant contact time affects operating capacities of softeners. Significantly the effect on operating capacity is about the same degree as the relative attainment of equilibrium versus time.

Due to their slower diffusion rates, the regeneration of organics is considerably more rate sensitive than for common inorganic ions. It has been shown that the equilibration times for aquatic organic matter is measured in hours [12], not minutes. For example, aromatic amines [10], like diphenylamine, reached less than 10% of final equilibrium after 4 hours. The same phenomenon has been shown to apply to anion resins ([5], [6]).

•Chloride versus Hydroxide Regenerants

•TYPE 1 CHLORIDE K=30 TO 36
•Salt regeneration
•TYPE 2 CHLORIDE K=50
•TYPE2 OH K=120
•Hydroxide regeneration
•TYPE1 Porous Gel OH K=400
•TYPE 1 Std Gel OH K=800
•K= Separation factor, organic / regenerant

•Figure 4

Large molecular sizes make for slower gel phase diffusion rates, so does higher selectivity and valence. Wilson[12] studied Type 2 resins that had been fouled, by equilibrating them with brine/caustic solutions in batch equilibrium experiments. He studied the amount of organics removed from the resin as a function of time. It was found that over 16 hours was required for what only appeared to be equilibration. However, it took only 4 to 6 hours to reach 70% to 80% of the 16 hour amount. Wilson's data is shown in **Figure 6**. Data such as this could be used to construct an operating capacity factor curve similar to that of **Figure 5**.

A comparison of **Figures 5 and 6** shows remarkable simi-

Figure 5 CAPACITY FACTORS vs BRINE INJECTION TIMES
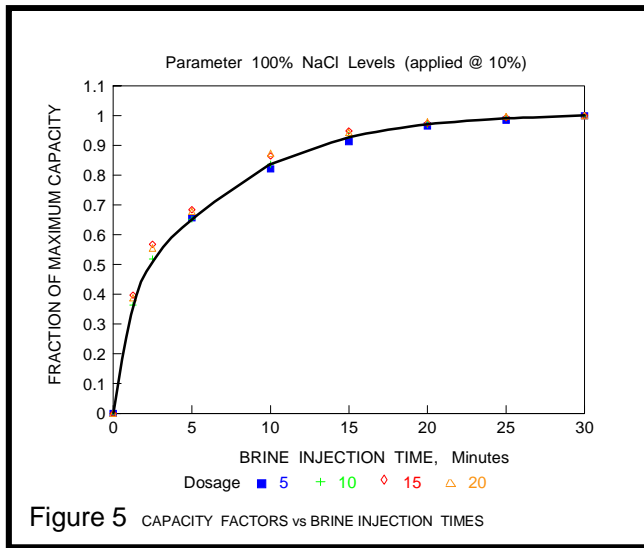
larity and might be identical except that the X axis for the inorganic exchange is measured in minutes compared with hours for the organic exchange. Using time as a parameter, we should be able to project operating capacities in a similar manner to the capacity versus the regenerant level curves used in inorganic ion exchange. The impact of resin characteristics on diffusion rates is quite significant, it will therefore be necessary to establish separate time factor curves for each type of resin. This will be addressed in more detail in later chapters of this work.

Wilson varied the concentration of the brine and found that the amount of organics pushed off of the resin varied directly with the concentration of the regenerant his results are presented in **Figure 7**. This shows the importance of equilibrium relationships.

pH not only affects ionization levels in weakly acid material, it can also affect solubility. For example phenol, an aromatic carboxylic acid, is soluble to about able 7.5% in cold water as the acid, but as the sodium salt its solubility reaches almost 20%. Wilson also changed the regenerant formulas by adding various levels of either NaOH or hydrochloric acid. The effects of these factors on organic elution are presented in graphical form in **Figure 8**. The acidification of the brine regenerant significantly reduced the regeneration. Adding sodium hydroxide to the brine

Figure 6 TIME VS HUMIC ACID REMOVED
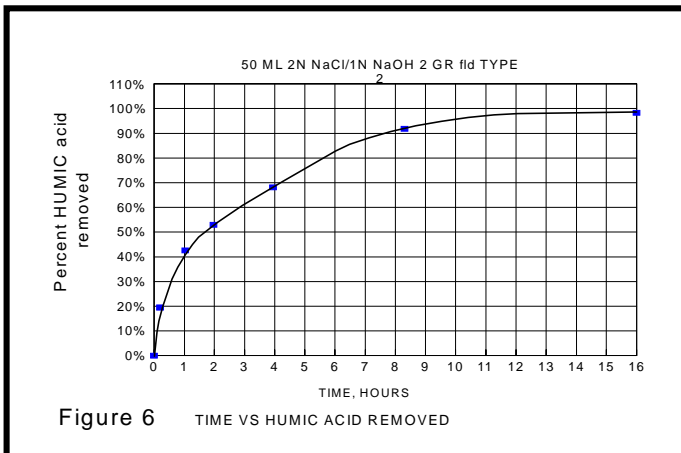
was very beneficial. The more NaOH that was added the higher the amount of organic matter regenerated off of the resin.

The pK of the carboxylic groups in humic acids has been determined to be between 1 and 6 (Gjessing[4]). When the

Figure 7 NaCl CONC VS HUMIC ACID REMOVED
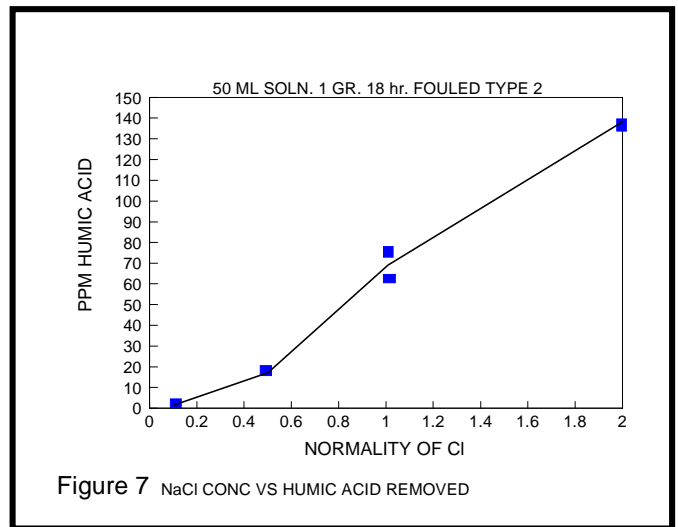
brine is alkaline these groups become fully ionized. In order to keep them ionized and soluble at the high concentrations of regeneration, excess hydroxyl groups are required. Adding caustic to the brine does both.

At ResinTech Inc. we have developed a test protocol for fouled anion resins. First we determine total and salt splitting capacity in the normal manner. Then the sample undergoes a comprehensive organic fouling treatment process, which includes hot brine and caustic. Then we retest the resin and make a before and after comparison. Typically the only difference we see is in salt splitting capacity. The total capacity usually stays the same while the salt splitting capacity increases after treatment.

The total capacity test requires the resin to be treated with hydrochloric acid followed by elution with $NaNO_3$. The low pH created by the acid forces the organic acids to recombine with hydrogen and become unionized but they still remain inside the resin due to either lack of solubility or insufficient contact time, or both. This allows the fouled salt splitting site to be converted to its chloride form, which is then measured by the nitrate elution step.

The organics are not very soluble and diffuse slowly ([4], [8], [9], [10]), otherwise the acid treatment would be an easy way to remove fouling. In the salt splitting capacity test the resin is converted to the chloride form under alkaline conditions before the nitrate elution step so the organics remain ionically active and fixed to the salt splitting sites they are attached too. Therefore these sites cannot be converted to the chloride form so they are not measured by the nitrate elution step.

At ResinTech Inc. we have also developed simulation technology which is used with the "before" and "after" treatment test results to project comparative resin per-

formance. The results are useful in that they allow us to make an economic evaluation of whether or not to carry out a brine rejuvenation, rebed, or do nothing.

Figure 9 compares the known relative selectivity coefficients of various anions with the relative organic elution obtained by Wilson[12]. He used their sodium and potassium salts in otherwise identical batch equilibrium experiments. **Figure 9** shows that the correlation between the relative amount of organics eluted and the selectivity coefficient of the anion portion of the regenerants is quite good. **Figure 9** also confirms the importance of selectivity in regeneration effectiveness. Indirectly this shows the importance of proper concentration control in order to enhance the regeneration of the multivalent TOC substances (see **Figure 3** also).
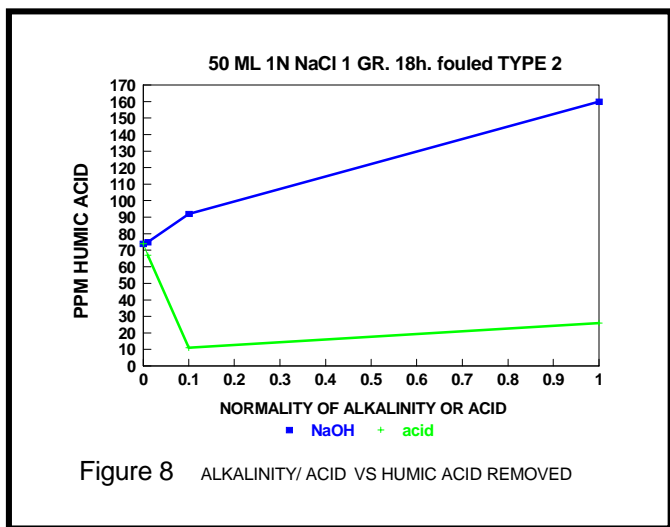

Figure 8   ALKALINITY/ ACID VS HUMIC ACID REMOVED

The Preuss factor, named after Albert F. Preuss who developed it, by co-worker, Sallie Fisher[3], was used to rate the relative fouling resistance of anion resins in the early 50's when researchers were looking for ways to define organic fouling and to rate fouling resistance in strong base anion resins. It was also applied to uranium recovery. The Preuss factor is the molar ratio of gel phase water to ion exchange capacity. It was found to be an excellent predictor of performance within resin types; i.e. Type 1 or Type 2.

At first, in attempts to quantify fouling and organic/resin interactions some researchers tried to equate ion exchange intermolecular distances to equivalent gel phase porosities([10]). It was frustrating to do that because of the wide variation in the shapes of the organic molecules, which can vary from the highly branched aromatics to long chain polymers or even simple alkanes. Therefore the molecular weight does not describe the physical shape. However, the Preuss factor described the relative size of the lake that the organics have to swim in as they move to and from the ion exchange sites, inside the gel phase of the resin.

Symons[11] listed the properties of each of the resins used in his study. I have used this data to calculate the Preuss

factors for each of them. **Figure 10** shows the relative order of TOC reduction abilities of those resins compared with their calculated Preuss factors for the 4 molecular
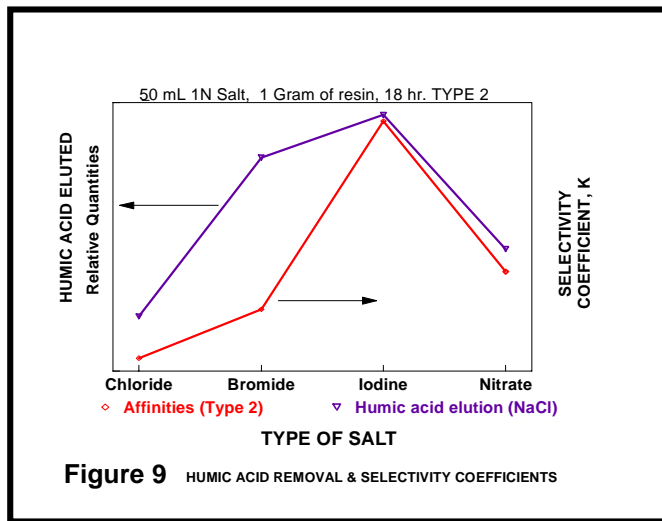

Figure 9   HUMIC ACID REMOVAL & SELECTIVITY COEFFICIENTS

weight ranges that were studied. **Figure 11** contains the data for all 4 ranges from **Figure 10** in a single graph.

The resins Symons[11] used included gel and macroporous types, styrenic and acrylics. **Figures 10 and 11** show that from below 1,000 to over 10,000 molecular weight, the Preuss factor provides an excellent correlation of increasing absorption capabilities (less leakage).The idea that the bigger the lake each ion exchange group has surrounding it, the more effective it was in removing the various ions holds up well.

It is commonly accepted that organic scavengers become fouled and performance suffers if they are overrun. There can be no doubt that organic substances are considerably larger than the common inorganic ions and can physically fill a resin, even before the ion exchange capacity is consumed.

If we consider the ratio of gel phase water per site the ion exchange lake, then when these substances fill that lake, diffusion becomes hindered and slowed. The bigger this lake, the more of the physical load it is able to handle.

Figure 12 shows water retention values of products meeting typical supplier specifications versus the ratio of moles of gel phase water to capacity; i.e. Preuss factor. Standard grade gel resins offered today, regardless of the supplier, have similar capacity and water retention values. The values used in **Figure 12** are calculated from midpoint values for typical gel resins plus ResinTech SIR-22P, which is a special purpose resin intended for organic removal. Interestingly, the Type 2 gel resin has the lowest and the acrylic resin has the highest Preuss factors of the standard gel resins.

Therefore you would expect the acrylic resins to be able to remove the most organics and the Type 2's to remove the least amount of organics of the common gel resins.
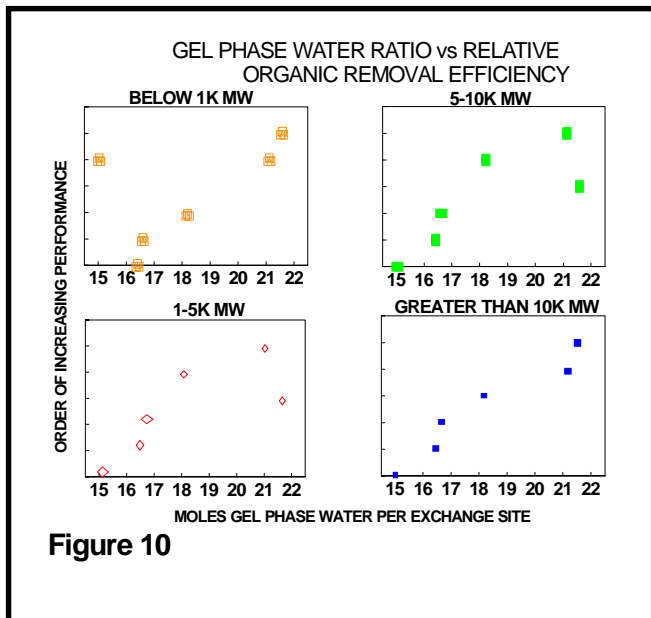
GEL PHASE WATER RATIO vs RELATIVE
ORGANIC REMOVAL EFFICIENCY

Figure 10

GEL Phase Water Ratio Vs
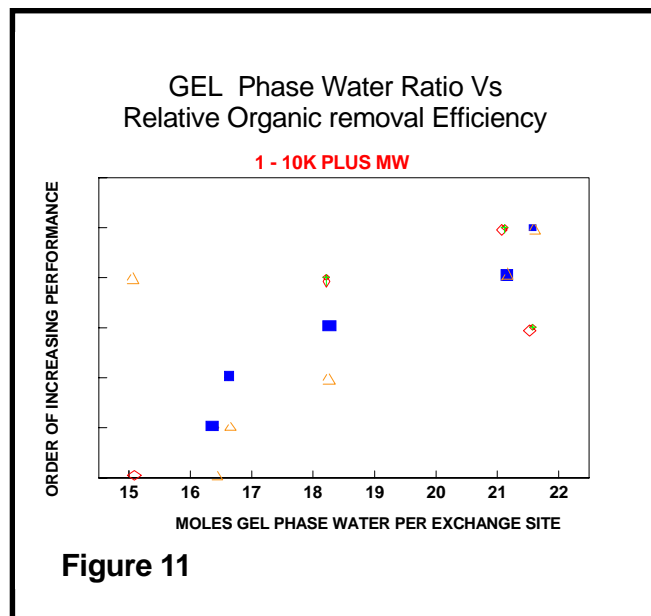Relative Organic removal Efficiency

1 - 10K PLUS MW

Figure 11

This is quite interesting since it is well known that both of these products are widely acclaimed for their excellent organic fouling resistance. However, since we are talking about organic fouling resistance rather than organic removal, regeneration efficiency is the key factor, not removal ability.

The strongly basic acrylic gel resins are indeed known to remove the most organics of all the common strong base gel anion resins. Likewise, it has long been recognized that one reason the Type 2's do not foul is because they let a significant portion of the organics slip by.

why Type 2's tend to foul less as the age than when they are brand new.

Let us look at inorganic ion regeneration to see the role that selectivity can play during regeneration. One example of the importance of the regeneration step is the regeneration of a calcium laden strong acid resin with sulfuric acid. Calcium is the most strongly absorbed ion of the common cations. Yet the higher the relative calcium content of the water, the lower the resin's operating capacity. This is because calcium is also the hardest ion to elute and in this case the operating capacity is determined by the regeneration cycle not the exhaustion cycle.

Figure 4, was calculated for the regeneration of lignosulfonate. It shows how the relative affinity between the regenerant compound and the substance being removed affects regeneration efficiency. Lignosulfonate is believed to behave in a similar manner to the humic substances. The Type 1 resin has the highest affinity for lignosulfate and, of course, it has the lowest regeneration efficiency. The Type 2 resin has the lowest selectivity for lignosulfinate and gives 3 times the **regenerable removal rate** at 10 pounds of NaOH regeneration than the standard Type 1 resin. This shows why Type 2 resins resist fouling better than the Type 1's.

The higher water retention Type 1 resins have lower se-

It is also well known that the Type 2 resins are the most efficiently regenerated resins. The acrylic resins, though more efficiently regenerated than styrene based Type 1's, are not as efficient as the Type 2's. Since the ability to elute the organics is a key factor in fouling resistance, so is regeneration efficiency.

As Type 2 resins age they become partially weakly basic. The weak base sites have a lower capacity for the weak organic acids. As I mentioned previously, we have found that when fouling occurs it is usually only the salt splitting groups that are affected. This explains lectivities, and higher Preuss factors, so they provide better overall performance than their lower water retention level Type 1 brothers. This is a major reason why the Type 1 porous gel resins are widely preferred over the standard porosity Type 1 gel resins (ResinTech SBG1P over ResinTech SBG1).
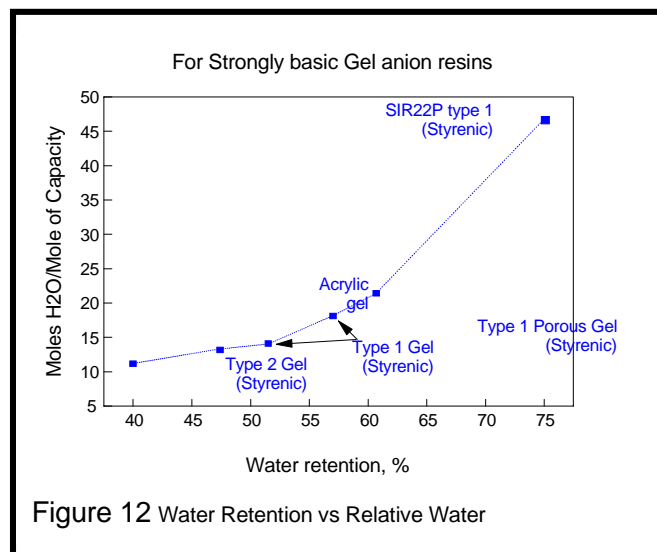

For Strongly basic Gel anion resins

Figure 12 Water Retention vs Relative Water

When resins become fouled they are usually rejuvenated using salt. As you can see in **Figure 4** the use of salt,

Table 2

Molecular weight distribution of T.O.C

	Lake Houston Texas (Symons et. al.)	Lake Anna Virginia (Wiser et. al.)
+		11.5
10 - 100K		10.1
10 +K	10.9	
5 - 10K	28.0	
1 - 10K		37.6
1 - 5K	9.5	
1K	51.6	
500 - <1K		17.0
150 - 500		23.8

instead of sodium hydroxide, quadruples the chemical efficiency of the regenerant. It is standard practice to use warm salt and extended contact time during injection,



Figure 13   TOC MOLECULAR WEIGHT DISTRIBUTION
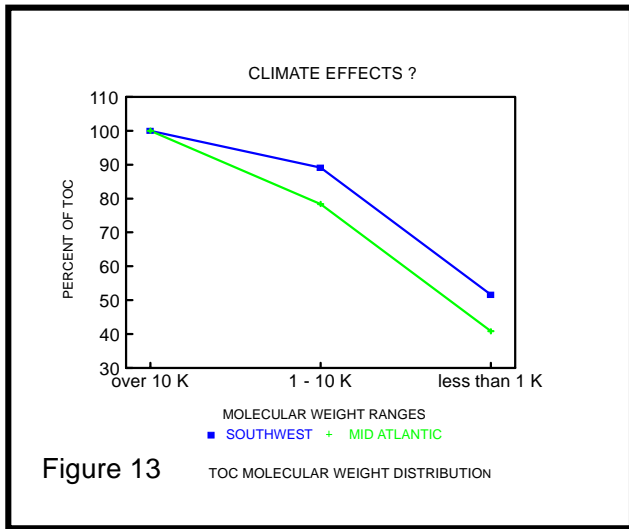
usually followed by a post soak before rinsing the salt out of the resin. A common rejuvenation procedure is to use 15 pounds of warm 10% NaCl with 1% NaOH injected over a one to three hour injection time followed up by an overnight soak before rinsing. Based on the information presented in **Figure 6**, we might expect that the injection step achieves 40% to 70% of the organic removal (regeneration) and the overnight post soak is responsible for the other 30% to 60%.

Compared to the normal sodium hydroxide regeneration this salt treatment can elute an order of magnitude more organics from a Type 1 resin. The importance of the post injection contact time has also been noted by others ([7], [14], [15]). This explains why "brine squeezes" for organic fouling treatments, when done properly, can be so effective.

Symons[11], and before him Wiser[13], determined the molecular weight distribution of the natural organics their results are shown in **Table 2** and **Figure 13**. **Figure 13** may also show something about the geographical or climatic influences on the molecular weight distribution. It is apparent that the more northern water (the Virginia water) has a higher molecular weight distribution than the water in Houston, Texas. Whether this is because of a higher residence time of the organics in the water, or longer sunlight hours to supply more UV or warmer temperature

and enhanced biological activity has not been determined. There is not enough information to say any more.

Symons'[11] determined the carboxylic acid content of the TOC Table **3** and **Figure 14** shows the calculated calcium carbonate to TOC ratio from the Symons data together with the theoretical values for various aromatic carboxylic acids. The higher molecular weight organics have a lower ratio of acidity. This is consistent with the theory of adding functional groups by oxidation and molecular weight reduction that was discussed earlier. The calcium carbonate equivalency ranged from .55 to 0.75 ppm of $CaCO_3$ per ppm of TOC as the molecular weight lowered from above 10,000 to 1,000. Values from molecular weights below 1,000 were not determined. However, the trend appears to not exceed the limiting value of a dicarboxylic acid of approximately 1.05. Therefore we can use these values to estimate the equivalent capacity load of TOC values in the same manner as for inorganic ions.

Figure 14 $CaCO_3$ Equivalency to TOC
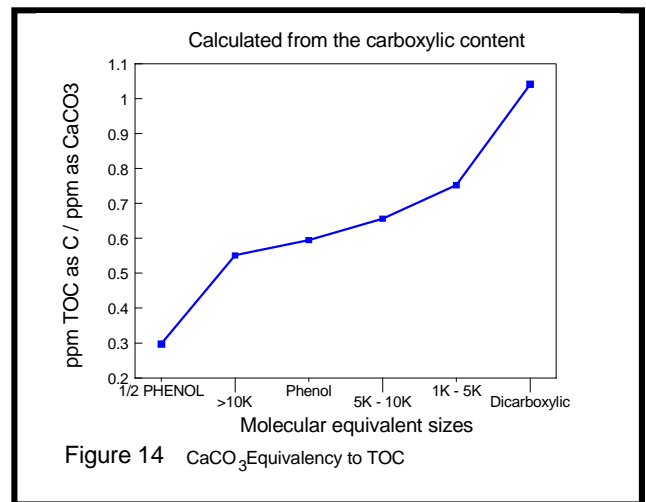
Of course, more work is needed to validate these ratios. However, we can use them now for generalized computational purposes. While, for more precise estimates, we can determine the TOC values and the organic acids ratio, or use direct measurements of the organic acids and convert them to calcium carbonate equivalents using 50 mg as $CaCO_3$ per meq of organic acids.

It has been shown that the lower molecular weight portion of the organic matter breaks through at the same time as the sulfates ([7], [11], [14], [15]). After the sulfate breakthrough, the net organic removal rate dropped by 70% during Symons' study. The sulfates at the bottom of the column were displacing some of the previously loaded TOC.

If the goal is reduction of the higher molecular weight TOC's, then the service cycle can extend past the sulfate break. For example, if you are trying to protect the working D.I. resin from fouling, you should be able to go well past the sulfate break. However, this should not be done if the resin is protecting a high purity water system and you want the maximum amount of TOC reduction. In this case, the system should have an activated carbon bed after the salt cycle strong base resin bed.

We have found that for maximum reduction of organics it is best to limit the service cycle to the sulfate breaks, and to polish with activated carbon to remove non-ionics. We compute the resins' throughput capacity based on the sulfate plus the TOC loading. We recommend a minimum one hour brine injection time and use a rating factor of 45% or less of the total capacity of the resin depending on the resin. The regenerant solution should be 10 pounds of salt in a 10% solution with an additional 2% of sodium hydroxide applied at a temperature of 120º F to a pre-warmed bed, not less than 70º F.

If only partial reduction or maximum throughput is desired, the service cycle can be run past the sulfate break. Once sulfate breakthrough occurs, the resin will continue to remove the higher molecular weight organics. However, all or most of the lower molecular weight organics, those with lower selectivities than sulfate, will be discharged as they are displaced by sulfates and the high molecular weight TOC's. During the later stage of the exhaustion cycle, the overall removal of organics may drop to as low as 30%, depending on the molecular weight distribution. After the sulfate breakthrough, TOC levels will rise and the concentration of the lower molecular weight TOC's may rise above their influent levels. This style of operation could be useful for using a scavenger resin ahead of or as a separate layer in the same vessel on top of a cation resin in a softener to remove or reduce color. However, unless the water is presoftened, the regenerant should not include sodium hydroxide, in order to avoid hardness precipitation. The operating capacity will be less than 20% of the total resin capacity.

Let us look at how the information presented here can be used to reclaim fouled resins. An organically fouled resin by definition is an anion resin that is no longer working well because it is loaded with too many organics for it to continue to be operated as an exchanger of inorganic ions in an efficient manner. The goal of the treatment is to remove enough organics to return the resin to successful operation. This requires sufficient dose, temperature, concentration, and contact time.

Time is the most important of these parameters, but all must be properly controlled. If the regenerant and resin are too cold it will decrease the kinetics to the point where the necessary contact time will increase significantly.

Therefore it is recommended that a minimum temperature of 120º F (not to exceed the design temperature of the vessel, internals or salt cycle temperature limit of the resin being treated) and a minimum dose level of 15 pounds of salt per cubic foot be used. The minimum injection time should be 2 hours followed by a minimum 10-hour soak before beginning the displacement rinse.

Multiple treatments can be used as a preventative measure when performed on a regular basis. A 5 pound minimum dose level with 1 hour injection time and a combined displacement rinse and soak time of 1 hour is recommended. The frequency of this treatment depends on the percent of TOC of the anion load. It is suggested that for standard resins the TOC loading factor be kept to a small fraction, probably less than 25% of the total resin capacity. We intend to provide more specific information in the future.

SUMMARY and FUTURE WORK

I have shown, through historical developments, how we come to know that naturally occurring organic substances are best dealt with by ion exchange resins. In this paper these substances were examined only as ions. We have reviewed recent and historical work to demonstrate that equilibrium and kinetic factors, especially time, are as important in defining regeneration (desorption) effectiveness as the dose level of the regenerant. It has been shown that the naturally occurring organic substances have affinities for the resin similar in degree to sulfate.

From the information presented in this paper, we can describe the properties of what would make an efficient organic scavenger:
- A. It must have sufficient gel phase water to physically accommodate the organic matter.
- B. It must have sufficient ion exchange functionality to provide acceptable capacity.

- C. It must have excellent osmotic shock characteristics to withstand the internal stresses during loading and regeneration.

ResinTech SIR-22P is an example of such a product. It has a gel phase water retention of approximately 75% and a total capacity over 10 Kgrs. per cubic foot. ResinTech SIR-22P has a Preuss factor of over two and one half times the standard resins, including the acrylic types. In an ongoing trial it has already demonstrated its ability to run to complete organic breakthrough without fouling and provide consistently high TOC reduction while operated in the chloride cycle. Its detailed performance characteristics will be the topic in a future chapter of this work.

This then concludes the first portion of this endeavor. ResinTech Inc. is continuing the study of ways to further quantify the kinetic and equilibrium factors discussed here. Our studies include an ongoing full-scale trial of SIR-22P.

Bibliography

1. Anderson, Robert E., **Estimation of Ion Exchange Process Limits by Selectivity Calculations**, Journal of Chromatography, 201 (1980)

2. Abrams, I.M., **Removal of Organics from Water by Synthetic Resinous Adsobents**, Chemical Engineering Progress Symposium Series, 106-112 (1969)

3. Fisher, S., **personal communication**, August, 1993

4. Gjessing, E.T., **Gel- and Ultramembrane Filtration of Aquatic Humus; A Comparison of the Two Methods**, Schw. Z. Hydrol, 286-293, (1973)

5. Kressman, T.R., and J.A. Kitchener, **J. Chem. Soc.**, 1201 (1949)

6. Kunin, R., and R.J. Myers, **Discussions Faradya Soc.**, 114 (1949)

7. Kunin, R.F., Suffet, I., **Activated Carbon Adsorption of Organics from the Aqueous Phase**, Ann Arbor Science: Ann Arbor, Vol. 2, 425. (1980)

8. Kunin, Robert, **The Role of Organics in Water Treatment**, Amber-hi-lites, 168 (Autum, 1968)

9. Kunin, Robert, **The Role of Organic Matter in Water Treatment - A Universal Theory**, Amber-hi-Lites, 179 (Spring, 1986)

10. Kunin, Robert, **Ion Exchange Resin**, Robert Krieger Publishing Co. (1972)

11. Symons, J.M., Fu, P.L-K, Kim, P. H-S, **The Use of Anion Exchange Resins for the Removal of Natural Organic Mater from Municipal Water**, Interanation Water Conference Proceedings Book, 92-120 (Pittsburgh, PA, October, 1992)

12. Wilson, A.L., **Organic Fouling of Strongly Basic Anion Exchange Resin**, J. Applied Chemicstry, Vol. 9, 352-359 (1959)

13. Wiser, S.L., Lee, Y.H., Stroh, C.R., O'Brien, Mr. **Removal of Organics from Secondary Makeup Water -- Case Study,** International Water Conference Proceedings Book, 1-17 (Pittsburgh, PA, November, 1985)

14. Wolff, J.J., **Strong Base Anion Exchangers and Organic Matters**, Dia-prosium Bulletin, 68.C.2 (1968)

15. Wolff, J.J., **Organic Matters Scavengers**, Dia-prosium Bulletin, 68.C.3.A (1968)