

Operating Experiences With A New Organic Trap Resin

By Peter Meyers. Presented at the 1995 International Water Conference.

SUMMARY: Strong Base anion exchange resins remove naturally-occurring organic acids. Unfortunately, the organics are not easily removed from the resin during regeneration and frequently cause anion resin to become organically fouled over time. Porous anion resins that have a high moisture content are resistant to organic fouling. A new ion exchange resin has extremely high moisture content and removes organics without fouling. The new resin has been successfully used as an organic trap, in front of ion exchange demineralizers. Because the organics can be removed by regeneration with brine, this resin is far more economical than activated carbon to protect demineralizer resins from fouling.

INTRODUCTION

Anion resins have the capability to remove naturally occurring organic acids from water. They do this by ion exchange of the organic acids onto the resin. The purpose of this paper is to discuss the operating results with a new type of anion resin -- ResinTech SIR-22P, that was specifically developed to exchange for organic acid ions. Field operating data from the Cape Hatteras Treatment System is presented. This plant operated successfully for a period of 2 years on a high organic bearing water and successfully reduced trihalomethane formation potential and organic color.

In addition to the Cape Hatteras data, we are presenting laboratory data from column studies performed at ResinTech. These studies were conducted with synthetic inlet analysis in order to study important variables that affect the operation of organic trap exchange systems.

What is an organic trap?

An organic trap is a strong base anion exchange unit generally operated in the chloride cycle and regenerated with sodium chloride. The purpose of an organic trap is either to remove color and/or to reduce TOC. The two most common applications are prior to chlorination of potable water supplies and ahead of an ion exchange demineralizer (to reduce THM formation potential and/or taste,

odor and color) to prevent resin fouling and/or to reduce organics in the effluent.

Although all strong base anion resins have the capability to function as organic traps, it has been proven that the more porous resins have higher capacity for organic acids, produce lower leakage of organics, and have less tendency to foul over time than resins with low porosity. Organic traps have an advantage over granular activated carbon in that they can be regenerated inexpensively. Organic traps have an advantage over membrane processes in capital cost, waste water production and in operating costs in cases where removal of inorganic ions is not necessary.

ORGANIC REMOVAL THEORY

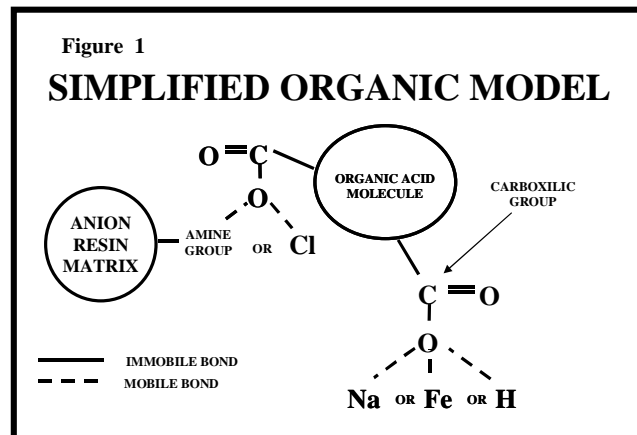
Ion Exchange Vs. Adsorption

The removal of organics by ion exchange resins has been shown to be accomplished by ion exchange and not by adsorption. This was documented in a paper given by James Symons, et al. Organics that are not ionized are not too well removed by ion exchange. There is a small amount of adsorption of hydrocarbons and other non-polar non-ionized organics by the styrene divinylbenzene skeleton of an ion exchange resin. There is little removal of polar organics such as alcohols, esters and ethers. Only organics that are substantially ionized can be removed by the mechanism of ion exchange.

Exchange for Organics

An anion exchange resin removes organics by exchanging the anionic portion of an organic molecule for an inorganic ion that is exchanged onto the resin. Anion resins are cationic in nature and, therefore, are attracted to anions. Size, charge and valence affect a particular resin's affinity for various anions. Low molecular weight organic acids such as acetic acid and formic acid are readily exchanged by anion resins. These acids are monovalent and do not have high selectivity coefficients. They are readily eluted from the resin during regeneration. The organics that we normally talk about in reference to organic traps are the naturally occurring carboxylic aromatic multivalent types of organics that are loosely grouped as Humic and Tannic materials. These organics are only partially soluble and are not always fully ionized. They have large and bulky structures, have relatively high molecular weight compared to most inorganic ions and often have more than one carboxylic group in each molecule. It is the portion of the organic molecule that is carboxylic that is attracted to the cationic exchange groups of anion exchange resins. The exchange occurs at the surface of the resin bead where chloride or some other inorganic anion is released and an organic carboxylic group exchanges onto the resin. The organic molecule then slowly exchanges in towards the center of the bead. As it does so, additional exchange sites at the surface of the bead become available for further organic removal. Organic acids that contain more than one carboxylic group can exchange for more than one counter ion. As a consequence, due to their divalent or multivalent nature, they can be very selectively held by anion exchange resin. **Figure 1** illustrates the basic mechanism of exchange for organic acids by anion resin.

During regeneration, organic acids that have penetrated into the center of a resin bead must first be exchanged for an inorganic counter-ion and then again have time to diffuse from the inside of the bead to the surface where they can



escape the resin bead and leave the resin along with the spent regenerant. The effect of diffusion limited exchange is best illustrated by flow interruption tests where leakage significantly decreases after the flow is stopped for a period of time.

Naturally-occurring organic acids vary from region to region and no two are exactly identical. There are two commonly referred to types of natural organic acids. Humic acid comes from decayed leaves and other vegetation. Humus tends to be dark in color and has a very poorly defined chemical structure. The molecular weight of Humic acid can vary from as little as 200 to as much as 20,000. Humus is not very water soluble and is not well ionized. Humic acid is not as well removed by organic traps as is Tannic acid and has a greater tendency to foul anion resin. Tannic acid comes primarily from decayed trees and from certain types of plants such as tea. Tannins are light yellow, straw colored or even clear. They have a fairly well defined structure and a molecular weight around 2,000. They are readily water soluble and fairly well ionized. Tannic acid is easier to remove than Humic acid and has less tendency to foul anion resin. In summary, as the molecular weight increases, organic acids tend to be less and less well ionized, less soluble, less well exchanged by anion resin. Large organic acids are more difficult to regenerate off the resin once they have been exchanged. In general, Tannic acid is easier to remove than Humic acid.

Strong Base Vs. Weak Base Anion Resins

Weak base anion resins are only able to adsorb strong acids and, therefore, are ineffective at removing organic acids at pH greater than neutral. However, some of the older phenolic type weak base anion resins have adsorptive characteristics that allow them to remove some portion of the non-ionized organic material. Newer weak base anion resins may have a significant amount of strongly basic functionality. Weak base anion resins have some use in certain applications but, in general, only strongly basic anion resins that are capable of splitting salts are of use for removing organic acids.

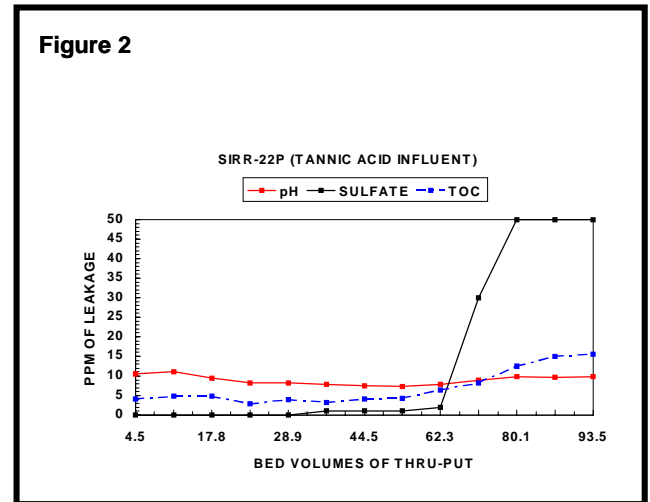
The Effect of a Resin's Porosity

We know that as moisture content in a resin increases, the internal porosity of the resin increases. As porosity increases, the rate at which organic acids can diffuse into and out of the resin increases. As a resin's porosity increases, it becomes more and more resistant to organic fouling and is more readily able to elute organics during regeneration. The best candidates for organic trap resins have always been the highly porous gel anion resins and the macroporous anion resins that have very high internal moisture content.

Sulfate Vs. Organic Selectivity

Sulfate competes with organics for exchange sites and the relative selectivity of anion resin for sulfate vs. organic acids is similar. This is documented in a paper given by James Symons (IWC-92-12). Only a fraction of a complex organic acid has a selectivity coefficient higher than that of sulfate. Therefore, as the resin exhausts into the sulfate form, some of the organic acid is concentrated into an organic rich band which moves in front of the sulfate exhaustion band. As the anion resin becomes exhausted to sulfate, those organics with the selectivity less than sulfate are displaced from the resin. In fact

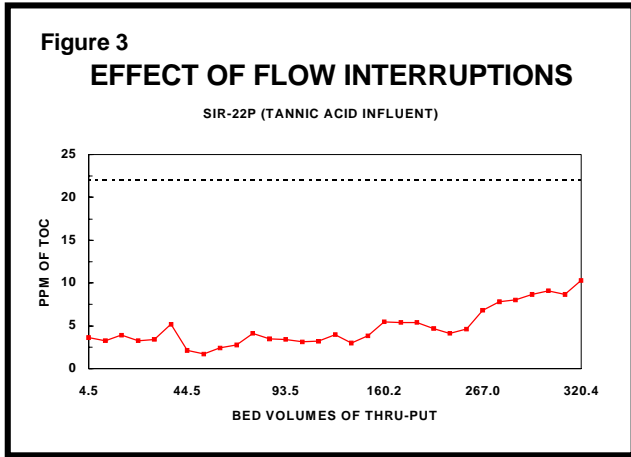
we see frequently several plateaus in the leakage curve from an organic removal resin. We see the first plateau when the chloride sites are depleted and the resin is converted to the bicarbonate form and then a second plateau when the resin goes into the sulfate form. This is shown in **Figure 2**.



Optimum removal occurs when the resin is operated as though it were a dealkalizer to bicarbonate breakthrough. However, significantly greater capacity can be obtained by operating the resin to or past sulfate break. Fortunately or unfortunately, as the case may be, the organics that have a selectivity coefficient higher than sulfate are the types of organics that are most difficult to remove from the resin and which result in the highest level of organic fouling. The fortunate part of all this is that if all we are interested in is protecting the anion resin in a demineralizer from fouling, we may be able to operate the organic trap to a substantially longer throughput and higher leakage endpoint but still capture the portion of the organics that will be most detrimental to the demineralizer resins.

Kinetics

The removal of organics is very kinetically sensitive. Organic acids are large bulky ions that, once exchanged onto the surface of the resin bead, diffuse very slowly in towards the center of the bead. **Figure 3** demonstrates this phenomenon by



means of what is called the flow interruption test. As the service run progresses leakage increases. If we stop the flow for a period of time, the exchange of organic ions away from the surface and in towards the center of the resin continues, freeing surface sites for further exchange. When the flow is resumed the leakage is substantially reduced for a short period of time. This means that there is a definite limit of the rate at which organic acids can be exchanged onto the resin during the service cycle. It also means that during regeneration, there must be sufficient time allowed for the organics that are exchanged off the resin to diffuse out of the resin bead and into the bulk regenerant solution. This is one of the keys to a successful organic trap and one of the reasons why the more highly porous anion resins out perform the standard porosity anion resins. A more porous resin is better able to diffuse organics through the looser skeleton of the ion exchange material.

Solubility of Organics

Naturally occurring organic acids tend to be sparingly soluble and not completely ionized, particularly at low pH. In this respect, we have found that Humic acid is far less soluble than Tannic acid. It is for this reason that it is advantageous to increase the pH of the regenerant solution. The high pH helps keep the organics soluble and prevents them from precipitating inside the resin bead. **Figure 4** illustrates the difference in the concentration of Humic acid

eluted from an anion resin with brine alone and with brine caustic as the regenerant.

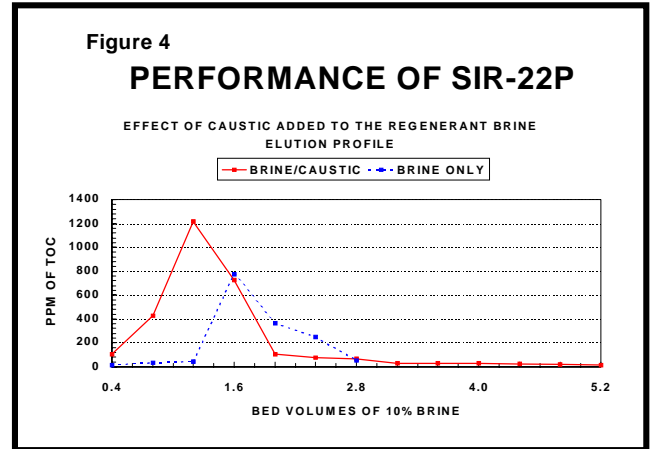


Figure 5 shows the effect of improved elution on the next service cycle.

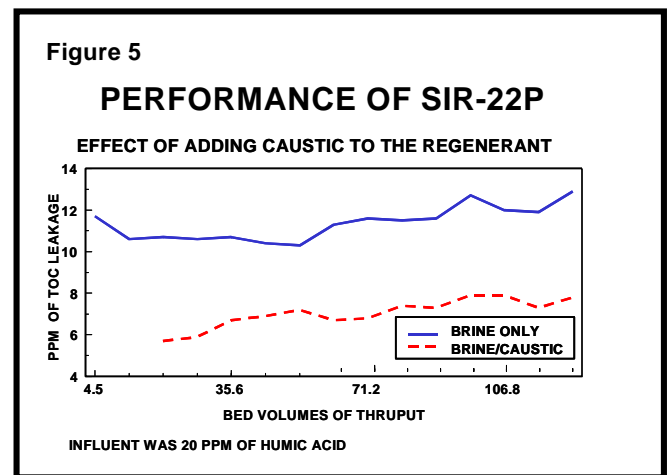
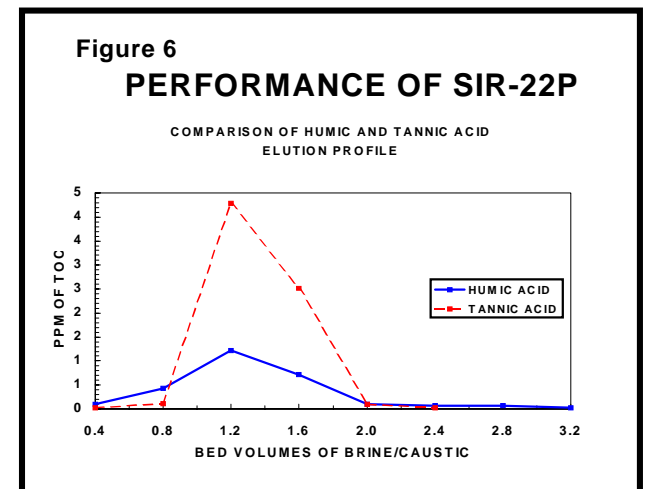


Figure 6 shows the difference between humic acid and tannic acid elutions under identical conditions of regeneration.



DEVELOPMENT OF SIR-22P

Based on the above theoretical data, ResinTech decided to produce a resin that would attempt to optimize the removal of organic acids. We did this in several different ways. First we elevated the moisture content to approximately 75% in the chloride form. This was done to make it easier for the organic acid to diffuse into and out of the resin bead and, hopefully, to reduce the selectivity difference between chloride and organic acids. Secondly, we reduced the particle size from a standard 16-40 mesh to a slightly smaller 30-50 mesh. This was done to increase the surface area of the resin and thereby have more of the exchange sites close to the surface and fewer exchange sites deep within the beads.

A consequence of increasing the moisture of an anion resin is that we decrease the selectivity coefficients for chlorides and sulfates making the resin less selective and, therefore, easier to regenerate. The net result is a unique strong base anion resin. It is not well suited for deionization because of the low selectivity for inorganic ions as compared to hydroxide. However, it still has enough selectivity to be efficient at removing organics and can be regenerated more readily than other types of strong base anion resins.

A comparison of SIR-22P against other types of strong base anion resins is given in **Figures 7 and 8**.

Figure 7
COMPARISON OF VARIOUS RESINS

Description	Standard Gel	Porous Gel	Macropore 2 nd Gen.	Extremely Porous Gel
	SBG1	SBG1P	SBMP1	SIR-22P
Capacity meq/ml	1.5	1.3	1.15	0.7
Moisture % Cl Form	40-43	50-53	55-60	75-80
Particle Size vs. Mesh	16-40	16-40	16-40	30-50

Figure 8
SELECTIVITY COEFFICIENTS OF VARIOUS ANION RESINS FOR CHLORIDE VS. HYDROXIDE

RESIN				SIR-22P
Type	Standard Gel	Porous Gel	2 nd Gen Macro*	Extremely Porous Gel
Moisture %	40-45	50-55	55-60	70-75
Selectivity Coefficient	25	11	35	1.5

* Gel phase porosity is about 40-50%

CAPE HATTERAS DATA

A small pilot plant of 1 cu.ft. of SIR-22P was installed at the Cape Hatteras Municipal Water Association in 1992 and showed such good promise for organic removal that a 70 gallon per minute plant was installed in 1993 and operated for approximately 11/2 years.

The Cape Hatteras water supply is from shallow wells. There are a number of wells having significantly different composition, primarily that of sodium chloride. The influent TOC varies from a low of 10 PPM to a high of perhaps 22 PPM. The organic color ranges from a high of 270 A.P.H.A. units to a low of 160 units. The water has a very high THM formation potential in excess of 1 milligram per liter and is not suitable for use as potable water as it comes out of the ground.

The Cape Hatteras treatment system consists of a media filter followed by ion exchange water softening followed by the SIR-22P organic trap.

Figure 9 (A, B, & C) shows the typical Cape Hatteras range of water analysis

Figure 9A

Cape Hatteras Raw Water Analysis

Mg/l (as CaCO ₃)	Low	High
Calcium	280	310
Magnesium	40	40
Sodium	50	220

Figure 9B

Cape Hatteras Raw Water Analysis

	Low	High
Bicarbonate (Mg/L as CaCO ₃)	270	320
Chloride (Mg/L as CaCO ₃)	45	275
Sulfate (Mg/L as CaCO ₃)	30	35
Silica (Mg/L as S ₁ O ₂)	9	16

Figure 9C

Cape Hatteras Raw Water Analysis

	Low	High
pH	7.1	7.4
Conductivity (mmho)	750	1200
Suspended Solids (mg/L)	4	7
Color (ALPHA)	160	270
TOC (mg/L as C)	10	22
Iron (mg/L as Fe)	3.8	4.0
TDS (mg/L)	440	770

Figure 10 shows the typical schematic diagram of the process flow.

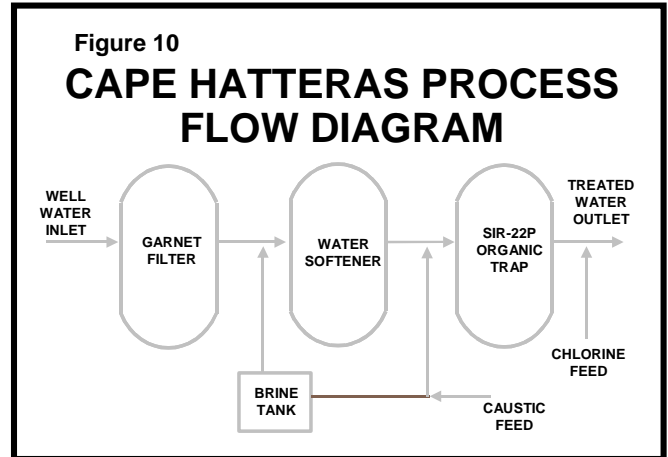
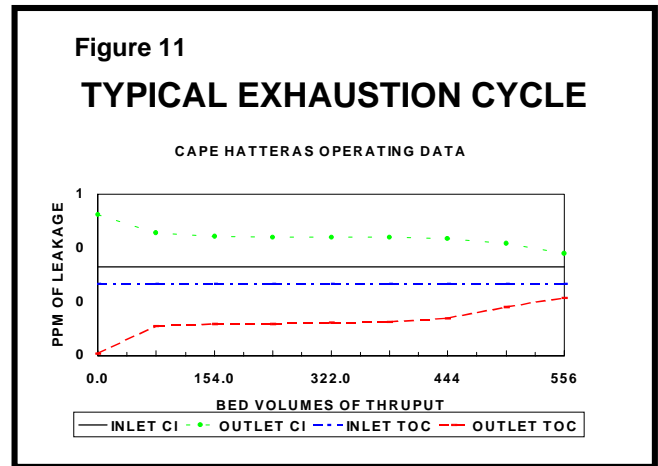


Figure 11 shows the typical analysis of the effluent from the organic trap during one run in early January 1994.



112 gallons per cu.ft. throughput represents the point at which the chloride exchange sites on the resin are exhausted and have been replaced by bicarbonate. There is a distinct change in pH and TOC leakage. The leakage then remains stable at the higher plateau level. This particular plant seldom tried to run to sulfate break but in this run was about 3,300 gallons per cu.ft. This thrupt volume represents about half of the total capacity of SIR-22P.

Figure 12 (A, B, & C) shows the iron and organic color profiles through several exhaustion cycles.

Figure 12A
Cape Hatteras Plant Data

Thruput Gal/cu.ft.	IRON mg/L (as Fe)			pH			COLOR APHA		
	Raw	Soft	SIR-22P	Raw	Soft	SIR-22P	Raw	Soft	SIR-22P
30	3.8	.7	.05	7.4	7.7	8.1	160	90	2
350	3.8	.9	.5	7.2	7.4	6.9	120	27	3
700	3.8	.2	.3	7.2	7.5	7.5	140	90	20

December 23, 1992

Figure 12B
Cape Hatteras Plant Data

Thruput Gal/cu.ft.	IRON mg/L (as Fe)			pH			COLOR APHA		
	Raw	Soft	SIR-22P	Raw	Soft	SIR-22P	Raw	Soft	SIR-22P
50	3.8	.4	.2	7.2	7.3	6.3	160	95	5
650	---	.3	.4	---	7.3	7.2	---	95	22

January 5, 1993

Figure 12C
Cape Hatteras Plant Data

Thruput Gal/cu.ft.	IRON mg/L (as Fe)			pH			COLOR APHA		
	Raw	Soft	SIR-22P	Raw	Soft	SIR-22P	Raw	Soft	SIR-22P
25	---	.03	.01	---	7.5	6.9	---	20	1
1300	---	.02	.02	---	7.9	7.6	---	18	1
1500	---	.01	.01	---	7.6	7.7	---	16	3

April 23, 1993

The raw water contains about 3.8 PPM of iron. About 80% of the iron is removed by the softener. A substantial amount of organic iron is removed

by the SIR-22P. pH drops as the resin is exhausted into the bicarbonate form. It rises back up as bicarbonates are displaced by sulfates and organics. When the resin is fully exhausted into the sulfate form, the outlet and inlet pH are approximately equal. Organic color is substantially reduced until the chloride sites are exhausted, then the color jumps up -- probably because of an increase in organic iron leakage when the pH rises and the change in resin composition occurs.

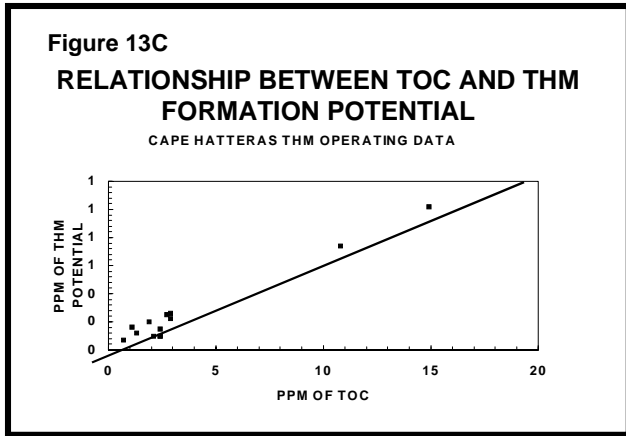
Figure 13 (A, B, & C) shows the relationship between TOC and THM formation potential. This clearly demonstrates the ability of the SIR-22P to substantially reduce TOC and thereby reduce THM formation potential. There is a linear relationship between TOC and THM potential.

Figure 13A
Cape Hatteras Data

DATE	INLET mg/L TOC	OUTLET mg/L TOC	OUTLET mg/L THM	COMMENTS
4/19/93	13.3 11.7	.65 1.51	.072	4,000 gals 23,000 gals
4/20/93	10.8	2.36	.148	48,000 gals
4/24/93	22	3.45		52,000 gals
4/25/93		5.27 4.16		80,000 gals 111,000 gals
5/17/93	14.9			Inlet THM = 1.024 mg/L
5/17/93	10.3	1.86 2.87	.199 .224	25,000 gals 35,000 gals

Figure 13B
Cape Hatteras Data

DATE	INLET mg/L TOC	OUTLET mg/L TOC	OUTLET mg/L THM	COMMENTS
6/28/93	19.0	1.06 1.34	.162 .123	12,000 gals 30,000 gals
8/24/93		2.37	.084 .099	0 gals 23,000 gals
12/12/93				Inlet THM = 0.740 mg/L
12/19/93	18 21	.87 1.25		300 gals 9,800 gals
1/10/94		2.1 2.4	.096 .098	(2nd Lab reported 0.046 mg/L THM)
1/11/94	22	2.7 2.9	.253 .259	



Higher TOC leads to the higher THM formation potential.

The Cape Hatteras plant operated for a period of 1 1/2 years without substantial resin fouling. The organic removal capability, both throughput and leakage, remained stable during the period of operation. There was one episode where the softener was not regenerated on time. Hard water got into the SIR-22P and hardness precipitants formed. The resin had to be cleaned with acid. This is not an uncommon experience with chloride cycle anion exchange systems. Another phenomenon that occurred in the Cape Hatteras plant was higher than expected pressure drop probably caused by 1) the use of the small bead resin and 2) the use slotted underdrain distributors that had very limited open area.

LAB DATA

Characteristics of Resin Fouling

When an anion exchange resin has become loaded with organic acids, there are changes in its ion exchange properties that cause it to behave differently than when it was new. The total capacity of the resin generally remains the same. A significant portion of the resin's salt splitting capacity becomes apparent weak base capacity. There is a corresponding increase in the amount of weak acid capacity. This is explained by the nature of the organic acids that are exchanged onto the resin. If we review the original organic

model, we see that the organic acids have carboxylic functionality. As the carboxylic acids are exchanged onto the resin, a portion of the carboxylic groups are available for exchange during regeneration with sodium hydroxide. These carboxylic groups are converted into the sodium form. In a demineralizer application, the sodium exchanged onto the weak acid groups gradually hydrolyzes of the resin during service. The carboxylic group returns to the hydrogen form, releasing sodium and causing the characteristically long rinse which is well associated with organic fouling. The tests that we have done at ResinTech indicate that the pick up of carboxylic functionality is approximately equal to the loss of salt splitting functionality. There is also a good correlation between cleaning the resin and reducing the amount of carboxylic functionality and restoring the amount of strong base functionality. This relationship is illustrated in **Figure 14**.

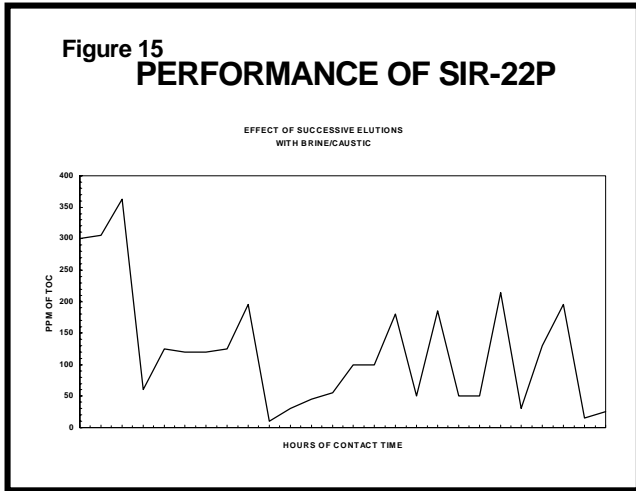
Figure 14
Relationship Between Resin Fouling & Changes in Ion Exchange Functionality

meq/mL of resin	Total Capacity	Weak Base Capacity	Weak Acid Capacity
New Resin	1.38	.02	.016
Fouled Resin	1.13	.15	.12
Fouled Resin after Cleaning	1.17	.10	.08

Regeneration Techniques

In a successful organic trap installation the amount of organics that are loaded onto the resin during the service cycle must be removed during the regeneration cycle. If the net mass of organic material loaded on the resin is greater than the net mass removed from the resin, then the resin will gradually foul and eventually the organic trap will crash. This has been one of the main operating problems with organic trap installations.

Figure 15 shows the results of successive elutions of SIR-22P with brine caustic over time.



The total amount of time required to remove all of the organic from the resin is several hundred hours. This means that the typical brine cycle of one hour or less is not nearly sufficient to completely regenerate the organics off the resin. It also means that the maximum operating capacity of the resin should be based on the net removal of from the resin during the preceding regeneration and that techniques for improving the efficiency of regeneration will improve the operating capacity of the resin. Another factor in the elution of the organics from the resin, is the solubility of the organics themselves. Humic acid is not very soluble, particularly at neutral or lower pH. What this means is that it is almost essential to raise the pH of the brine used in regeneration when the water contains a substantial fraction of Humic acid. This also explains why in some cases, cation resins are apparently able to remove a portion of the organics. The mechanism is by precipitation and filtration, not by ion exchange.

Lab Effluent Profiles

In our laboratory, we ran several different tests to characterize the difference between regular anion resins and SIR-22P.

Figure 16 shows the relationship between gel resins with increasing moisture content and

leakage of TOC. The only difference among the three resins is the moisture content. All are gel resins and all of the other variables that might be associated with organic traps have been eliminated.

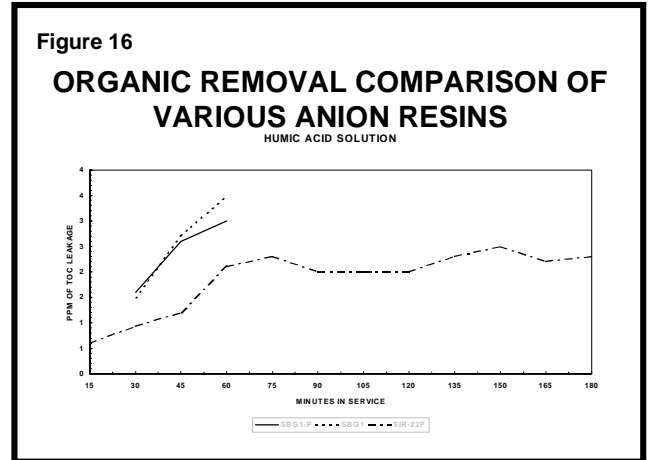
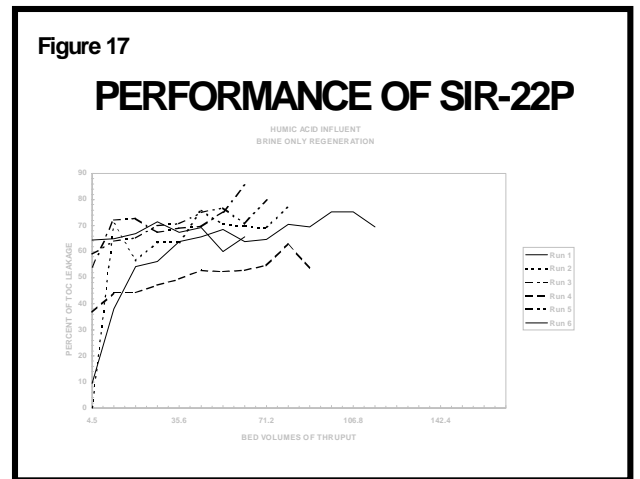


Figure 17 shows the effluent profile of SIR-22P on successive runs with Humic acid solution. This illustrates that the resin is reasonably stable in that the effluent characteristics are the same cycle after cycle after cycle.



In **Figure 18**, we ran 3 tests with varying amounts of sulfate in the water. This test illustrates the difficulty of removing a fraction of the organics against high sulfates and demonstrates that the selectivity coefficient of SIR-22P for organic acids is about the same as that of sulfate because as the resin becomes exhausted into the sulfate form, the leakage of organics also increases.

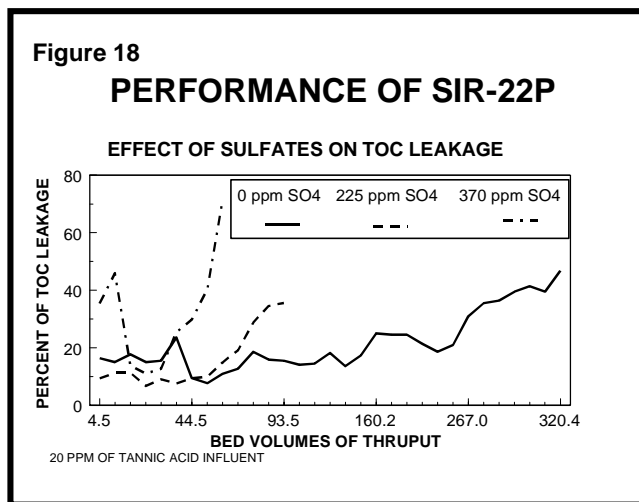
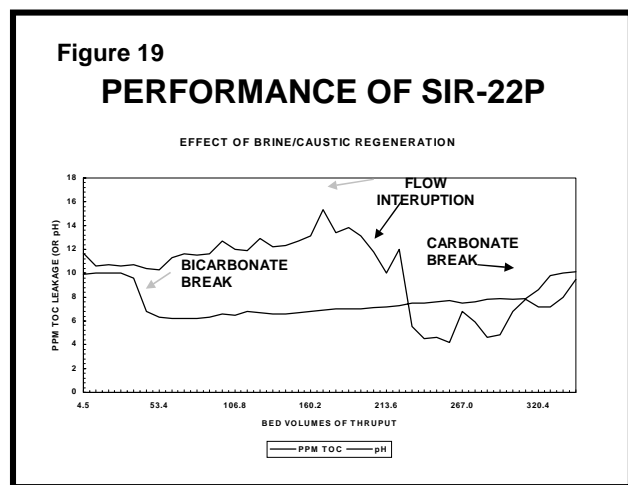


Figure 19 shows an exhaustion profile in the absence of sulfates. There are discrete pH changes in the effluent associated with alkalinity leakage that parallel changes in TOC leakage.



FUTURE WORK

Regeneration Techniques

There is still much work that needs to be accomplished in how to more effectively remove the organics from the resin. It is quite clear that adding caustic to the brine improves the regeneration and reduces leakage during the next cycle. This was illustrated in **Figure 5**.

We believe the caustic increases the solubility of the organic acids. This effect was illustrated by **Figure 4**.

Tannic acid is more soluble and easier to remove from the resin than is Humic acid. This was illustrated in **Figure 6**.

There is some promise to the possibility of reducing or replacing the carboxylic functionality of the organic acids. Perhaps by reducing the carboxylic group to an aldehyde thereby making the organic molecule non-ionized, will allow it to diffuse slowly out of the resin. This is one possible technique for getting the very, very difficult organics back off the resin. We know that increasing the brine contact time and increasing the brine temperature, improves the rate of elution of the organics which then in turn improves the operating capacity the next cycle. However, we do not have any quantifiable correlations that we are able to report at this time. We plan to explore the effect of different skeletal structures on organic removal. Acrylic anion resins may have advantages in some applications, particularly for waters with a high fraction of Humic acid. We plan a further look at porosity to see if a 75% moisture resin is optimum. Certainly it is better than a 55% - 60% moisture resin but we don't know if there's something in between 60% and 75% that is optimum.

CONCLUSIONS

SIR-22P is a good product that has been successfully used for organic removal and to reduce THM potential in a potable water supply. It is a better product for Tannic acid than it is for Humic acid. It has significant advantages over regular Type 1 and Type 1 porous anion resins and has been used successfully to treat waters that have caused other organic trapped resins to become fouled and fail to work.

BIBLIOGRAPHY

Gottlieb, M., "The Reversible Removal of Naturally Occurring Organics Using Sodium Chloride Regenerated Ion Exchange Resins". Presented at Watertech 11/10/93.

Symons, J.M., Fu, P.L-K and Kim, P.H-S, "The Use of Anion Exchange Resins for the Removal of Natural Organic Matter from Municipal Water". Presented at IWC, 10/19/92