Perchlorate Facts

FOR TECHNOLOGY VENDORS

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A variety of resins are currently offered for perchlorate removal. Already a number of municipalities have installed treatment plants using either brine regenerable or disposable resins. For technology vendors, choosing the most cost effective approach is essential for maintaining competitiveness. Below we try answer questions that may be of interest to vendors, consultants, and advocates of this technology.

QUESTION 1: Why is ion exchange technology preferred for perchlorate removal?

Key reasons are:

(1) Ion exchange is an established technology for drinking water (e.g. softening, nitrate removal, tannin removal)
(2) Non-detect levels for perchlorate can be achieved in the treated water (e.g. <1 ppb)
(3) Resins utilized are ANSI / NSF-61 Certified for municipal applications
(4) Setup and operation is fast and simple - shortest lead time; minimum operator attention
(5) Other coincident contaminants (e.g. nitrate, uranium, chrome-6) can be simultaneously removed
(6) Ion exchange technology is particularly cost effective for removing trace levels of perchlorate in parts per billion range typically found in drinking water

QUESTION 2: What type of resins can remove perchlorate?

Strong base anions resins in the chloride form can all remove the perchlorate (ClO_4^-) ion to varying extents. These include SBA Type I acrylic and styrenic resins (e.g. Purolite A850E, A-600E), SBA Type II (A-300E), nitrate select resins (e.g. Purolite A-520E), and the perchlorate selective bifunctional resin, Purolite A-530E, developed in conjunction with Oak Ridge National Laboratory.

QUESTION 3: What resin properties determine perchlorate capacity?

Selectivity of the resin for perchlorate versus other competing anions is the key. A typical water will contain competing anions such as sulfate, nitrate, bicarbonate and chloride.
Table 1 shows that relative affinity of various resins for perchlorate versus these other anions.
All resins, except acrylic Type I, show higher selectivity for perchlorate than for sulfate or nitrate. This means that the resins will in general prefer to remove perchlorate from the water and release chloride or any ion for which it is less selective.

Table 1 – Affinity Relative to Chloride			
Resin Type	**Perchlorate**	**SO4**	**NO3**
Gel Acrylic Type I[4] (A-850E)	4 – 5	~ 11	2
Gel Styrenic Type I or II[9] (A-600E, A-300E)	100 – 150	~ 9.1	3.2
Nitrate Selective (A-520E)	>200	< 7	< 12
BiQuat (A-530E)*	>1000	< 6	< 12
* a perchlorate selective resin developed and licensed by Oak Ridge National Laboratories (ORNL).”BiQuat” is a trademark of ORNL			

The concentration of competing anions such as sulfate, nitrate, chloride and bicarbonate are typically about 1000 times higher than that for perchlorate (e.g. 50 ppm versus 50 ppb). So despite the higher selectivity for perchlorate, a significant fraction of the ion exchange sites on the resin beads will be occupied by these competing ions, leaving little left for perchlorate. A small change in the concentration of these competing anions can have a major impact on the resin’s capacity for perchlorate.

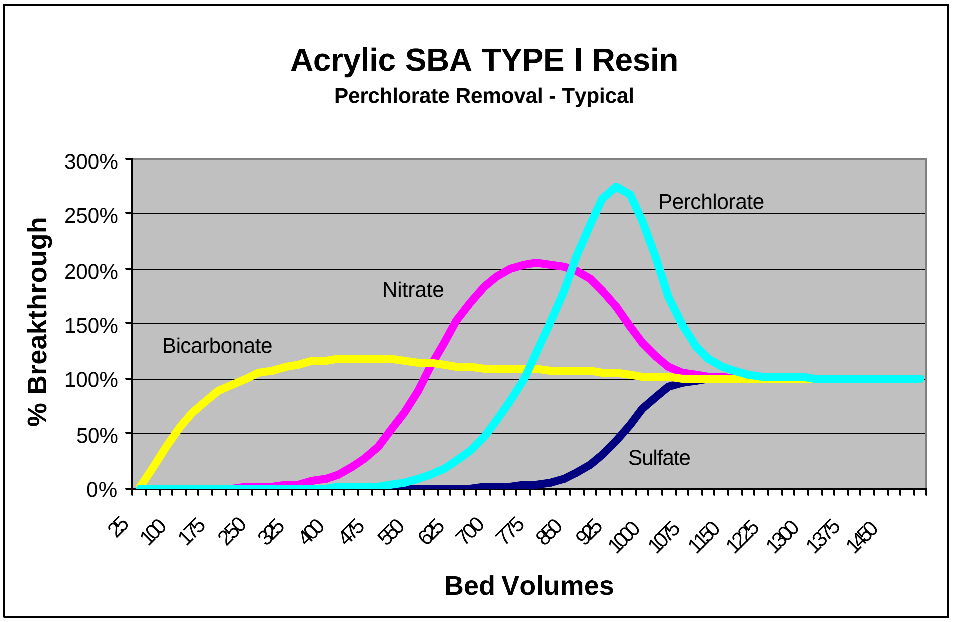
Therefore, it is critical to know the background water chemistry of the water if perchlorate capacity is to be assessed (see how to do this later on).

QUESTION 4: Which type of resins can be regenerated with brine?

Strong base gel Acrylic Type I resins (e.g. Purolite A-850E) are economically regenerable with salt dosages ranging from 12 to 25 lbs per cubic foot of resin, depending on system design. It is difficult to economically regenerate other types of resins such as styrenic type I (e.g. Purolite A600E), type II (e.g. Purolite A300E) and nitrate select resins (e.g. Purolite A-520E) using brine.

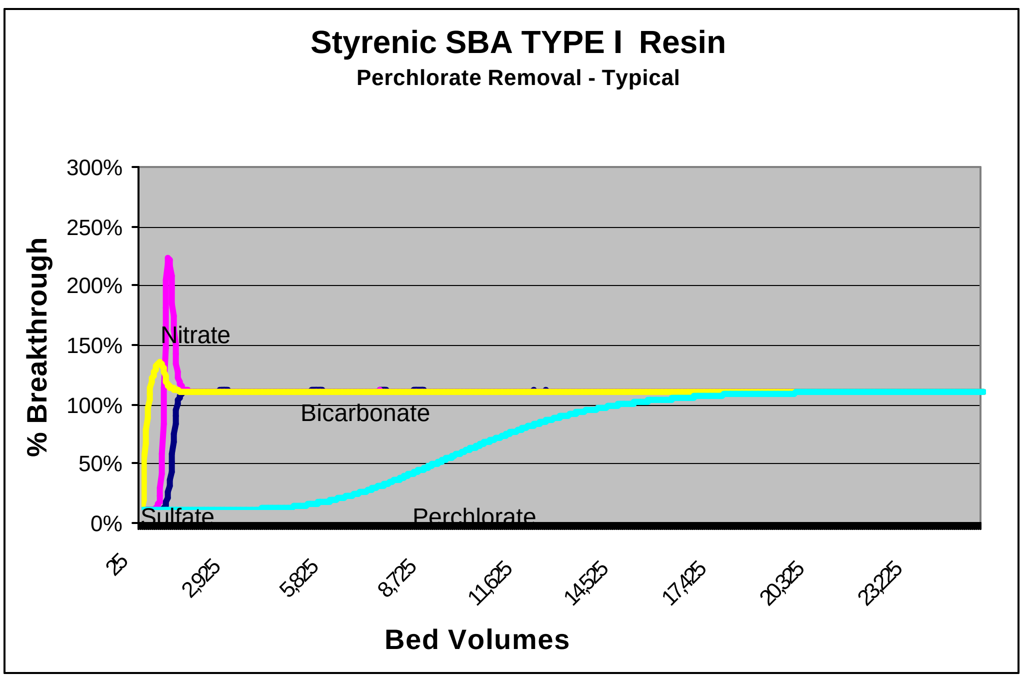
The reason should be clear from the affinity data in Table 1 – acrylic resins have a much lower selectivity for perchlorate than other resins, making it much easier to remove perchlorate from the resin with brine. Note that acrylic resins show higher selectivity for sulfate than for perchlorate (unlike other resins), which means that sulfate will displace or elute perchlorate from the resin as the ion exchange system operates. Thus the capacity of acrylic resins is largely determined by the amount of sulfate in the water and the point at which sulfate breaks from the ion exchange column. This can be seen in Graph 1 below. Sulfate pushes both nitrate and perchlorate of the ion exchange column.

In this case, perchlorate is the most selected of all anions considered and perchlorate breaks through in the effluent at about 5,000 bed volumes (note: 1 bed volume is approximately 7.5 gallons per cubic foot of resin). Effluent and influent levels of perchlorate equalize at about 15,000 BVs for this particular example.



Graph 1 – Typical Gel Acrylic SBA Type I breakthrough – sulfate elutes perchlorat

Graph 2 below is typical for styrenic type I resins



Graph 2 – Typical Styrenic SBA Type I breakthrough – perchlorate elutes last

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QUESTION 5: Is heating the brine helpful for regeneration?

Studies by the University of Houston have shown that no benefit is derived from heating the brine for acrylic type resins. In the case of styrenic Type I resins, some advantages apply when the brine is heated to about 60^{o}C. Even then the perchlorate is not completely removed from the resin. Despite this they have proposed using styrenics by limiting the perchlorate loading on the resin to the equivalent of about 1800 BVs. The expectation is that pilot studies will show that perchlorate leakage on subsequent cycles will be maintained below the current 4 ppb target. Since this procedure is not as yet proven, it is best to look at other alternatives at this time.

QUESTION 6: What other regenerants are available?

Oak Ridge National Laboratories have developed a proprietary tetrachloroferrate regeneration technique that is extremely effective in stripping the perchlorate from A-530E. Oak Ridge advises that the regenerant can be reused several times before the perchlorate must be destroyed. A catalytic destruct module is utilized for breakdown of the perchlorate into oxygen and chloride, allowing the regenerant to be reused at that point after regenerant top up.
Commercialization of the process is currently being sought by ORNL.
The ability to regenerate the resin, when it becomes available, should significantly impact the overall cost of perchlorate remediation.

QUESTION 7: Why consider disposable resins at this time?

Although acrylic Type I resin, such as Purolite A-850E, can be regenerated with brine, economical use of this resin is constrained to waters with relatively low to medium sulfate levels. This is because the resin is more selective for sulfate than perchlorate and the breakpoint for sulfate determines the capacity for perchlorate. For higher sulfate waters, the capacity can typically fall to just a few hundred bed volumes (e.g. 150 to 300 BVs), requiring frequent regeneration and significantly increased levels of brine to be treated, making the economics unfavorable.

The alternative is to use higher capacity resins once and then incinerate it, referred to as "load and burn".
For this purpose, either A-600E (styrenic), A-520E (nitrate select), or A-530E perchlorate selective bifunctional resin can be utilized, depending on economics for each water quality. Each job must be evaluated on a case-by-case basis since the water has such a great impact on capacity.

End users enjoy a number of advantages:

(a) disposable resin treatment systems can be quickly installed to comply with regulations
(b) such plants are simple in design and require minimum operator attention
(c) non-detect perchlorate levels can be achieved in the treated water (e.g. < 1 ppb)
(d) long term liability for perchlorate removed is eliminated by incineration of the resin

QUESTION 8: Are there resin capacity and leakage curves for perchlorate?

Since the water quality in each case may be different and minor variations in concentrations of bulk anions can have a major impact on perchlorate capacity, there is no alternative but to evaluate waters on a case-by-case basis. Therefore no industry curves exist at this time.

Consequently, to evaluate the capacity of specific resin for perchlorate, the following standard alternatives can be considered:

(a) perform laboratory, pilot and scale up studies for the specific water and resins selected
(b) repeat the same for expected variations in the water quality during the treatment period.

As is well known, the procedures above can take a long time, especially if several types of resins must be evaluated. It is not inconceivable that several months can elapse before results can be obtained.

Therefore a good alternative toward dramatically shortening this process is the use of our ion simulation software which has been customized for perchlorate and similar trace ions.

QUESTION 9: What is Purolite Simulator Service?

We make use of proprietary modeling software to estimate perchlorate capacity of each of our Purolite resins for treating a specific water. While such modeling software cannot be expected to be 100% accurate, the advantages it offers allow us to quickly do the following:

(a) compare and cost out expected treatment cost for a variety of resins
(b) perform sensitivity analyses for anticipated changes in water quality
(c) evaluate changes that will occur to competing anions during service (e.g. bicarbonate, pH, nitrate)
(d) assess the simultaneous loading of other trace anions that may be present in the water (e.g. uranium, chrome-6, arsenic, selenium, etc.) for any peaking potential above MCLs.

(e) use output data to optimize equipment sizing and frequency of resin changeouts (in the case of disposable resins)
(f) use output data to compare brine and proprietary regeneration options

An example short form costing estimate is given below:

IX-SIMULATOR Projection Estimates

Medium Sulfate Water Example Only:		
Comparing Cost to Treat 1 Acre-Foot of Water (326,000 Gallons) to <4 ppb ClO4		
	A-530E	**A-600E**
Resin Capacity Estimate - Bed Volumes	75000	16000
Resin Volume to treat 1 Acre-Ft -ft3 or resin	0.58	2.72
Resin Cost - $ /ft3 of resin	400.00	125.00
Resin Cost to treat 1 Acre-Foot of Water - $/acre-ft	231.82	339.58
Disposal Cost - $ /ft3 of resin (estimate)	30	30
Disposal Cost for 1 Acre-Foot of Water - $/acre-ft	14.49	67.92
Total Resin & Disposal Cost per Acre-Foot of Water	**246.31**	**407.50**
Note: Capacities given are capacities to saturate the resin completely in lead-lag configuration These are best estimates only and no guarantee is given or implied		

Note: There may be charges associated with the cost of this service.

QUESTION 10: Will perchlorate removal impact other water parameters (e.g. pH)?

Perchlorate removal resins are typically operated in the chloride form. This means that chloride is exchanged for perchlorate as well as other anions present, such as sulfate, nitrate and bicarbonate (see graphs 1 and 2 in question 4 above for acrylic and styrenic resins respectively).

Decrease in bicarbonate, sulfate and nitrate will be evident in the early part of the cycle, with bicarbonate returning in short duration to close to the influent level. With acrylic and styrenic resins, nitrate tends to peak above the influent level and could possibly exceed the MCL of 45 ppm for nitrate. This will not occur with the nitrate select resins such as A-520E, or our bifunctional resin, A-530E.

Reduction in bicarbonate will result in a corresponding reduction in pH. It is not uncommon to see an initial reduction in pH of about 2 units, with the pH returning to influent level after about 200 bed volumes of water have been treated. For acrylic resins, which typically treat about 500 to 700 BVs of water per cycle, this can be a substantial part of the cycle. For the other resins with typical service cycles ranging from 10,000 to 100,000 BVs, this would be very minor fraction of the water treated.

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