

## **The Rocky Hill Water Facility**

### **Section 9. The final analysis.**

The PFAS remediation problem for Rocky Hill has a practical and logical solution once the underlying issues are fully understood.

The underlying physics problem relates to the desired total and complete removal of PFAS molecular contaminants from the Rocky Hill water supply when they are already at very low trace levels of only a few dozen parts per million-million (parts per trillion) in the water volume, and barely detectable.

This becomes a difficult, almost impossible, task if there is a lot of other dissolved material in the water (and there generally is) and if there is no mechanism for identifying and isolating the PFAS contaminants.

Traditionally the approach to removing contaminants from drinking water was to adsorb everything possible using molecular adsorption, which is a surface interaction process based on the weak close-contact molecular attraction (Van der Waals) forces. The molecular adsorption process is one of the most important physical processes in nature, and is based on a fundamental interaction between any molecules or atoms.

The materials that have high levels of molecular adsorption in water are those that are insoluble, hydrophobic (water repellent), and that have very high surface area characteristics - since adsorption is a surface (contact) interaction.

The typical watershed aquifer has millions of tons of molecular adsorption materials (clays, sandstone, shale, fractured rock etc.) and therefore the aquifer is a massive source of molecular adsorption, removing molecular content from the water.

The molecular adsorption process applies to all molecules of all types, and is therefore not selective.

Also, as a limitation, molecules that have a significant solubility in water are not readily adsorbed by the weak molecular attraction forces, and remain in solution. Molecules that are highly soluble and those that dissolve and dissociate and ionize in solution do not undergo molecular adsorption.

The PFAS contaminants are soluble in water. Some of them are very soluble and therefore will never be fully adsorbed and eliminated with molecular adsorption. Molecular adsorption is therefore not a process that can ever totally remove all PFAS contaminants from the Rocky Hill water - which is the PFAS remediation goal. To totally eliminate PFAS it is required to have a process that is PFAS selective.

For those who might question why adding another ton or two of molecular adsorption material (such as GAC) in a filter would not remove the remaining trace levels of PFAS, the answer is that adding a few extra tons of adsorption medium to the already many thousands of tons of molecular adsorption material in the aquifer

is not going to change anything. The molecular adsorption in the aquifer has already reduced the contaminants to very low, trace, levels.

Consequently, in this situation, there are simply not enough of the trace level PFAS contaminants in the water volume to generate and establish the close molecular contact conditions that are required for a molecular adsorption process. Any close-contact interactions would be extremely rare, random, events. Molecular adsorption therefore would not work, and is simply not the answer. However, adding a filter with anion exchange resin is an entirely different story.

The PFAS molecule is basically a chain of from 4 to 8 carbon atoms that are each saturated with bonds to fluorine atoms.

The “per-fluoro” molecules have all the Carbon atoms fully bonded with Fluorine atoms, and are the major PFAS molecules. There are also “poly-fluoro” molecules that are not fully fluorinated, and there are many thousands of those.

The C–F (carbon–fluorine) bond is very strong. The “per-fluoros” are therefore chemically inert and can be considered chemically “bulletproof” in that they are not affected by acids or bases or any types of solvents and can even resist high temperature incineration. They have been referred to as “forever” chemicals.

PFAS chemicals have all the characteristics that people want. They are chemically inert for stain-proof and waterproof coatings for shoes, and clothing, and fabrics, sportswear, and household and commercial goods. Also, for application as flame retardants, and use in fire-fighting foams for high temperature jet fuel (and similar) fires. (PFOS).

Also, for use as pre-cursors in the production of low friction plastic products (Teflon) for high resistance electrical wiring insulation, non stick high temperature cooking ware, grease resistant wrapping paper and packaging ... etc. etc. (PFOA).

Taking PFOS as an example, along the body length of 8 Carbon atoms there are bonded fluorine atoms. There are no free bonding electrons and the strong C–F bonds are closed. The body of the PFOS molecule is chemically inert, and it is therefore totally hydrophobic (water repellent).

The PFOS molecule also has to have a “head” and a “tail” as part of its structure. The “tail” has another Fluorine bonding.

Fortunately, the “head” of the PFOS sulphonic acid molecule is a functional group – in this case a sulphite ( $\text{SO}_3^-$ ) anion group – with a  $\text{H}^+$  which is quickly lost in solution to ( $\text{OH}^-$ ) bonding most likely. So the PFOS molecule has an anion group “head”. The PFOS salt is a sulphonate because the organic carbon chain group is linked to the main Sulphur atom of the anion group, which originates from the sulphonic acid.

The PFOS molecule therefore does not dissociate in water, it remains firmly intact as a fully fluorinated C8 molecule and is quite solidly linked to an anion ( $\text{SO}_3^-$ ) functional group at the PFOS “head” section.

One can therefore consider the PFOS sulphonate in water as being a fully mobile “PFOS anion”, or as being a sulphite anion dragging along a firmly attached PFOS C8 molecule body. This PFOS C8 body is of course totally fluorinated, is totally chemically inert, is totally hydrophobic, and there is nothing to impede its free mobility in water.

All PFAS molecules are water soluble, and all PFAS molecules have an anion functional group “head”.

This situation turns out to be the opportunity that is presented to us to be able to capture and totally remove all PFAS contaminants from the water.

They can all be captured with anion exchange. This is the PFAS selectivity we need.

Ion exchange is generally known from traditional commercial use as a water softener, based on removal of the Calcium ( $\text{Ca}^{++}$ ) and Magnesium ( $\text{Mg}^{++}$ ) ions with cation exchange resin. The technique can also be used to remove heavy metal contaminants. With cation exchange resins the Sodium  $\text{Na}^+$  cation is generally used as the mobile cation and is generated with brine saturation (which is also used in the generation of  $\text{Cl}^-$  mobile anions in the case of anion exchange resins). With cation exchange the  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  ions displace mobile  $\text{Na}^+$  cations from the resin.

The main technical challenge for ion exchange was always to increase the number of embedded fixed charge groups in the resin bead structures and, as the resin polymer technology progressed, many new and important applications emerged. Ion exchange has been used, for example, to separate Uranium isotopes in nuclear applications and is widely used in the purification of pharmaceuticals. The liquid chromatography technology with ion exchange resin columns is now widely used.

The application to trace PFAS contaminant removal in municipal water systems is very recent, and was waiting for the resin polymer technology to advance to the point of being able to embed massive numbers of fixed charges into the internal structures of the resin beads to the extent that the capacity of the ion exchange process might become comparable to, and competitive with, that of the molecular adsorption process.

That has been largely achieved, and was convincingly demonstrated in the Horsham pilot study on the removal of PFAS contamination from a municipal well for an extended period of almost 2 years, using a relatively small volume of Purolite anion exchange resin. This study was presented in **Section 2** and **Section 3** on this website and a system design for Rocky Hill, based on the results from the Horsham study, was presented in **Section 3** and has recently been further described and explained in detail in **Section 8**. ---- [www.rockyhillwater2020.com](http://www.rockyhillwater2020.com)

The Horsham study was very impressive in that it showed complete removal of PFAS contaminants by 20 cubic feet of ion exchange resin for an operating time of almost 2 years. The two GAC filters located before the ion exchange filter were both leaking PFAS contaminants almost immediately with total PFAS input levels that were relatively low (averaging around 100 ppt) and fluctuating up to 140 ppt.

By contrast, the PFAS contaminant level at the output from the ion exchange filter was at flat-line zero level for almost two years.

It was therefore perhaps natural to compare the excellent performance of the ion exchange filter to the GAC filters performance.

The volume of the ion exchange resin (20 cu ft = 150 gallons) and the Horsham flow rate (50 gpm) indicated an implied EBCT of 3 minutes for the ion exchange resin, compared to the typically accepted EBCT of 10 to 20 minutes for GAC.

The ion exchange resin was then being viewed as a super performing molecular adsorption material.

There now seems to be a widespread replacing of GAC molecular adsorption medium with ion exchange resin as a better adsorption alternative, without fully understanding why. Anion exchange resin is now in high demand.

This however is making the serious mistake of directly equating anion exchange with the molecular adsorption process. They are fundamentally very different processes. There is no EBCT with ion exchange. It is not molecular adsorption. Ion exchange is a fast electrochemical process, and is not an adsorption process. This has all been presented in detail in **Section 8**.

The real point of the Horsham PFAS study was that a new player was now being introduced into the PFAS remediation game – namely the anion exchange process. This is not acknowledged specifically in the description of the Horsham study (**Section 2**) except for the observation that the study involved the ... “first permit issued by Pennsylvania for treating PFAS in drinking water using ix.”

The use of anion exchange for such PFAS contaminant removal is very new.

Another important point, that the PFAS contamination level and also the dissolved inorganic and organic content (measured at 200 ppb) were both indicative of very low contamination levels in the Horsham well #10, was not specifically mentioned – especially in regard to the significance of what that implied.

Although it was recognized that the dissolved organic content was acceptably low (200 parts per billion) it was not directly associated with the work of Boyer. et al (Univ. North Carolina 2008) in which the capture of DOM anions at low concentration levels with anion exchange resin had been shown to involve the release of Cl<sup>-</sup> mobile anions from the resin in accordance with the stoichiometric equation for electrostatic anion exchange, showing that the ion exchange process that was under way was therefore totally electrostatic, with no molecular adsorption involved at all.

Molecular adsorption would not have released mobile Cl<sup>-</sup> anions from the resin.

The later work by Dixit. et al. – which was published quite recently (2019, 2020) – showed that low level PFAS contamination was totally eliminated with the use of anion exchange, and also involved the stoichiometric release of Chloride (Cl<sup>-</sup>) indicating that the process was (again) entirely electrostatic anion exchange. This result was to be fully expected on the basis of the earlier Boyer. et al work.

At low contaminant levels there are simply not enough molecular contaminants to generate molecular close-contact conditions for molecular adsorption to occur. A “PFAS anion” in solution is not going to be entering into a resin bead as a result of any normal close-contact condition.

The PFAS anion is drawn into the resin bead by the electrostatic attraction of the positive charge cations that are deliberately embedded into the internal structure of the polymer resin beads.

It is this electrostatic attraction and the anion exchange process that is trapping the PFAS molecules inside the small resin beads. This has nothing to do with any molecular adsorption process.

That was the real situation at Horsham, and it is also the situation at Rocky Hill, where the contamination levels are even lower. The very impressive performance of PFAS elimination at Horsham was due to the massive number of embedded cations that they (Purolite) were now able to incorporate into their polymer resin beads – namely it was due to their new, advanced, anion exchange resin manufacturing technology.

The experimental data from the Horsham study provided a measurement of their resin capacity for PFAS capture, and permitted a simple performance calculation to be made for a similar Rocky Hill PFAS remediation system.

For Rocky Hill, the goal of remediation is total PFAS removal, not simply reduction of contaminant levels to obtain legal conformity to MCL numbers.

Conformity to MCL numbers only represents slight contaminant level reduction.

The anion exchange process is the only viable method of achieving total PFAS contaminant extraction from the water.

In the Rocky Hill Water Facility there is an aeration system that operates to remove volatile organic contaminants, and the proposed anion exchange filtration system would be added to remove PFAS contaminants (which cannot be removed by aeration).

The proposed PFAS remediation system uses two filter units loaded with Purolite PFA694E PFAS selective anion exchange resin. The design calls for 1000 liters of resin in each filter unit.

The filters are connected in series and located between the aeration stages of the Rocky Hill water facility to take advantage of the aeration system reducing the background anion load in the water that is due to dissolved organic and inorganic material. This background anion reduction is important and will extend the operational life of the anion exchange resin by extending the time before the anion saturation of the resin in the “lead” (first) filter. This is estimated to be around 4 years, and hopefully longer.

The operational protocol of the system is based around the required procedure for the anion exchange process. Each filter unit has a designated operation. They operate with one filter as the first “lead” filter and the second as the “lag” filter, and both filters are identically equipped with an output sampling port.

The active PFAS entrapment occurs in the “lead” filter. This will continue until the anion exchange resin is anion saturated. At this point the anion exchange process is depleted, and there will be PFAS contaminant “breakthrough” with detection of PFAS contaminant at the sampling port.

The output from the second (“lag”) filter is the output water source and the sampling port of the lag filter must indicate Zero PFAS contamination at all times.

At the detection of PFAS breakthrough in the “lead” filter, the filter is by-passed and closed off by manual valve operation. The water system is then running through the lag filter alone. The output from the lag filter remains at Zero PFAS contamination. The “lead” filter is then drained and decoupled and moved away to be re-loaded with new resin. When this has been done it is returned to be re-coupled into the system as the new “lag” filter, with the initial lag filter now wearing the captain’s hat and becoming the new “lead” filter of the PFAS remediation system.

This “Texas Tango” filter swap routine is repeated every 4 years, hopefully longer, when there is detected PFAS breakthrough in the system’s “lead” (first) filter.

This described operational procedure is important and has to be maintained.

There is replacement of 1000 liters of resin every 4 years for one filter only (the lead filter) although both filters are in active use in the PFAS removal.

This is the only recurring cost for the remediation system, and can be scheduled.

It is seen that this operational procedure always keeps the output water supply from the PFAS remediation system at Zero (ND) PFAS level, and uses two system filters but with the main anion exchange operation and PFAS capture, and detected PFAS breakthrough, only based in one (the lead filter).

Also, it allows ample time to unload the spent resin and recharge that filter since the “lag” filter (which is now operating as the main “lead” filter) was essentially unused. This “lead-lag” form of operation is used in many types of systems to permit needed line replacements without shutting down system operation, and it fits perfectly with the required anion exchange operation of the water facility as described.

The Rocky Hill water facility operation is not disrupted, and resin replacement can be handled on site.

In the Horsham study, where they only used one anion exchange filter, they inserted an extra sampling port at the 2/3 level of the filter to configure it as a dual unit and detected PFAS breakthrough in the top section – although of course there was no replacement routine.

From the above description it is seen that the extension building (or filter shed) described in **Section 8** is more than just a place to store the filters, but is a location where the filters can be moved around and easily configured into the system. This requires some working space as well as some practical engineering approaches in planning how to handle the loaded filters, either involving the use of dollies or perhaps using tracks.

Although the filter switching routine is only expected to be performed every 4 or so years it ideally should be made into a simple routine that is easily manageable.

The extension building therefore turns out to be a critical component in the PFAS remediation system – in addition to being the most expensive part. The remediation system is otherwise relatively inexpensive, using commercially available components.

This scientific analysis has indicated that we do not need large volumes of expensive anion exchange resin – such as advocated in recent outside contractor proposals for Rocky Hill that were erroneously based on treating anion exchange resin as a molecular adsorption material, having an associated EBCT parameter. In the Rocky Hill situation of low contaminant levels there is no molecular adsorption, and only the electrostatic anion exchange process applies. It is all about the process, and there is no EBCT with electrostatic anion exchange. We only have to use the volume of anion exchange resin that is needed to give the operating time that we desire before resin replacement.

We are very fortunate in having the very low PFAS contaminant levels and low background anion levels and the other low contaminant levels of the Rocky Hill aquifer that enable us to take full advantage of what the electrostatic anion exchange process offers.

This is due entirely to the aquifer and the enormous level of molecular adsorption that is being used in the aquifer in generating the overall excellent water quality. The aquifer and the Rocky Hill Water Facility comprise a very valuable community asset, and a resource that will be increasingly important in the future.

This analysis has been presented to outline some of the PFAS remediation issues, and explain some of the reasoning behind the design of the proposed Rocky Hill PFAS remediation system that was described in **Section 8**.

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