Seven Years of PFAS Planning and Removal: Lessons Learned for the Mining Community

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Abstract

Per- and polyfluoroalkyl substances (PFAS) are contaminants that have been detected in water supplies throughout the world. They have gained widespread public health attention and multiple regulatory agencies have implemented, or in the process of implementing, limits for using these compounds and releasing them into the environment. This presentation provides of overview of what PFAS are, where they can be present in mining environments, and how can they be treated. In addition, this presentation provides the lessons learned by the City of Issaquah, the first community to implement PFAS removal from groundwater. The City detected PFAS in 2015 at its 250 GPM (950 LPM) Well No. 4, the primary compound being PFOS but PFHxS, PFOA and other PFAS were also present. PFOS was detected at concentrations as high as 600 ng/L, 8.5-times higher than the USEPA Lifetime Advisory Level of 70 ng/L for PFOS+PFOA and 40-times higher than the State of Washington's action level of 15 ng/L. The City immediately reviewed the situation and selected wellhead treatment for PFAS removal. Granular activated carbon (GAC) vessels were installed in lead/lag configuration, with more vessels planned for future expansions. The system was designed, permitted, constructed, and started up in 77 days. The facility started operations in June 2016.

At the time of this presentation, the system has been in continuous use for six years and is one of the longest continuously operating PFAS removal systems in the world. This presentation discusses the operational surprises, challenges, and unintended consequences that the City has learned over this time. The lessons learned include much-longer than estimated media life and lower operational costs, PFOS contamination of an adjacent and much larger Well No. 5 (1,250 GPM / 4,730 LPM), the media becoming radioactive despite the water having non-detectable

radiation, ongoing bouts of biological growth, and ongoing issues with media disposal. Finally, additional PFAS have been detected due to transitioning to newer, more advanced analytical techniques.

Introduction

Per- and polyfluoroalkyl substances (PFAS) are contaminants that have been detected in water supplies throughout the world. They were developed decades ago and entered commercial use beginning in the late 1940s. These chemicals were incorporated into many products due to their unique chemical properties as lubricants and as water- and oil-repellents. Some of the industries using PFAS include mining production, automotive, aviation, aerospace and defense, biocides, cable and wiring, construction, electronics, energy, firefighting, food processing, household products, oil extraction, metal plating, medical articles, paper and packaging, semiconductors, textiles, leather goods, and apparel (OECD, 2013, UNEP, 2013).

There are thousands of PFAS compounds, most of which are highly persistent, bioaccumulative, and toxic and have been detected ubiquitously throughout the environment. PFAS are resistant to biological and thermal degradation. As a result, these human-made chemicals are expected to be detected for decades in the environment.

This paper describes what PFAS are and where PFAS can be found in the mining industry. In addition, this paper also presents the lessons learned from the City of Issaquah, Washington's seven years of experience in dealing with these contaminants in their water supplies. The City is one of the longest continuously operating PFAS removal systems in the world, and the longest one in operation along the North American Pacific Coast.

What is PFAS?

PFAS are synthetic chemicals consisting of molecules with carbon-fluorine chains. These compounds exhibit strong and persistent surfactant qualities that have been used in multiple industries, including mining, as firefighting foams, foaming/frothing agents, wetting agents, and mist suppressants (Gluge et al., 2020).

Figure 1 is the chemical structure of perfluorooctane sulfonic acid (PFOS), one of the most common PFAS compounds. Other common PFAS compounds are perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorohexane sulfonic acid (PFHxS), perfluoroheptanoic acid (PFHpA), and perfluorobutane sulfonic acid (PFBS). The common feature of all these compounds is the presence of multiple carbon-fluorine bonds that provide the chemicals with its durable surfactant qualities. The differences between the compounds are the number of carbon atoms (i.e., length of molecule) and the type and number of additional functional groups at the end of each chain to provide additional properties that were beneficial to mining and other industries.

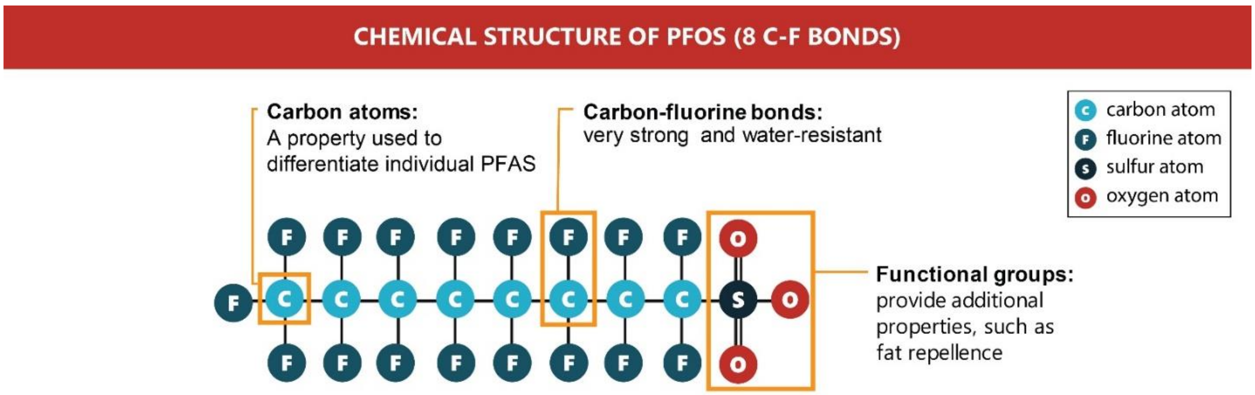


Figure 1: Chemical Structure of PFOS, a Common PFAS (Alito et al., 2020)

The durable physicochemical properties of PFAS that have made them useful and popular in industrial use has also resulted in negative impacts on the environmental and human health (ATSDR, 2019, AWWA 2020). Some PFAS either are, or degrade to, very persistent chemicals that accumulate in humans, animals, and the environment. Their resistance to degradation, and high mobility in the environment mean that PFAS are now throughout the world. Figure 2 is a conceptual diagram showing how these compounds move from various users and discharges to the environment and then back to urban areas.

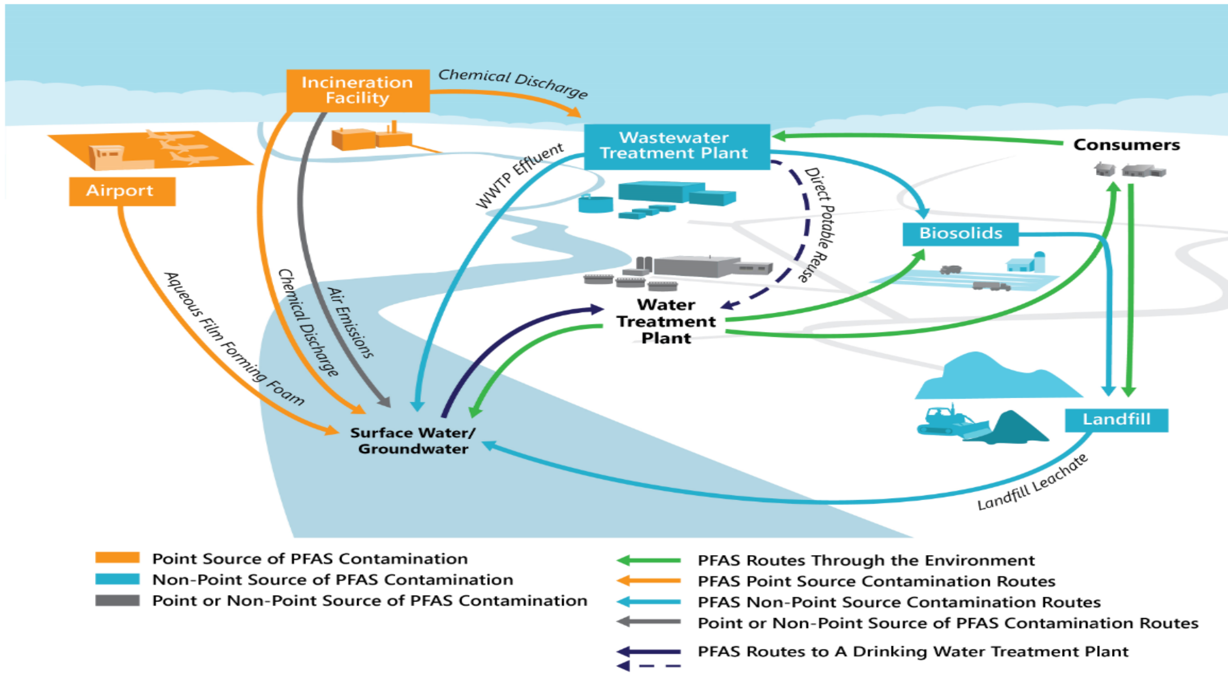


Figure 2: PFAS Migration Through the Environment (Alito et al., 2020)

PFAS in Mining

There are several uses of PFAS in the mining industry. These uses are summarized in Table 1 below. The surfactant qualities of PFAS have been utilized in ore processing (Gluge et al. 2020). It has been used to suppress sulfuric acid or cyanide misting when it is applied on leach piles to extract copper or gold. PFAS has also been added to sulfuric acid and cyanide to improve the wetting of ore piles for metal leaching. It used in ore floating to create a stable aqueous foam that improves metal salt separation. Finally, given its persistent throughout the environment, PFAS at a mine may not have originated from mining operations but could have been present as existing contamination in the mine's water supply. Use of this contaminated water has then spread PFAS throughout the operations.

Table 1: PFAS in Mining Operations

Ore Processing	Other Mining Operations
Mist suppressing agent	Fire fighting foam
Wetting agents	Hydraulic fluid additive
Flotation foaming agent	Biocide/herbicide
Existing contamination in supply water	Fire retardant clothing and fabric
	Oil/water repellant clothing and fabric
	Floor finishes and cleaning agents

PFAS is also found in other mining operations. Specifically, it is commonly used in fire fighting foams, specifically aqueous film forming foams (AFFFs) used to combat fuel fires. AFFFs is commonly stored at mines and used in actual fire fighting situations as well as in practice drills. PFAS-laden AFFFs are one of the largest sources of PFAS in the world, and whose production has since stopped in the United States and Canada. Other PFAS uses include equipment hydraulic fluids, site biocides/herbicides, various types of clothing and fabrics and even in cleaning materials used in indoor spaces.

Case Study: City of Issaquah, Washington

The City of Issaquah, Washington is a suburban community on the eastern outskirts of the Seattle metropolitan area. The City owns and operates their drinking water system and supplies water to approximately 43,000 people. Their water supplies consist of groundwater from four wells that the City's owns and augmented with regional drinking water purchased from another agency. In 2013, groundwater treatment consisted of sodium hypochlorite addition for disinfection purposes and fluoride addition to match the fluoride concentrations in the purchased regional water.

The 1996 amendments to the federal Safe Drinking Water Act required the Environmental Protection Agency (EPA) to regularly monitor unregulated contaminants for potential future regulation. The third round of monitoring, Third Unregulated Contaminant Monitoring Rule (UCMR3), was issued in 2012 and included several per- and polyfluoroalkyl substances (PFAS). The City was selected to sample their groundwaters and collected annual grab samples in 2013 to 2015. The sampling data submitted to EPA indicated that PFAS was found in high concentrations from water produced by the City's Gilman Well No. 4 (see Table 2).

Table 2: Gilman Well No. 4 PFAS Concentrations Reported for UCMR3

Year	PFOS (ng/L)	PFOA (ng/L)	PFNA (ng/L)	PFHxS (ng/L)	PFHpA (ng/L)	PFBS (ng/L)
2013	600	22	28	241	26	<9
2014	514	20	27	201	23	<9
2015	472	18	22	194	21	70

The EPA Provisional Health Advisory Limits were 200 ng/L for PFOS, 400 ng/L for PFOA, and no limits for the remaining compounds at the time of sampling. These advisory limits are voluntary and non-enforceable. In addition, data for UCMRs by definition are unregulated contaminants and EPA did not inform the City that any additional actions had to be completed. The State of Washington had no adopted limits for PFAS at this time and did not comment on these results.

Multiple options were evaluated to manage the PFAS. These options and issues were summarized in Table 3. Review of these options led the City to select treatment as the preferred PFAS management option.

Table 3: PFAS Management Options

Management Option	Advantages	Disadvantages
Abandon well	No capital costs.	Potential loss of water rights. Purchased water is more expensive than groundwater, even with treatment. PFAS remains.
Blend PFAS concentrations down with other wells	Already in use at the time. Maintains water rights. Depletes PFAS plume. No change in operations.	Unable to reach Council directive to achieve non-detect PFAS concentrations.
Pump water to adjacent Issaquah Creek	Maintains water rights. No capital costs – use existing valving and piping. Depletes PFAS plume. Water augments low summertime flows and provides beneficial cooling.	Permitting a PFAS-laden discharge to sensitive fish habitat would take a long time, with no certainty that a permit would be issued. Purchased water is more expensive than groundwater, even with treatment.
Treatment	Maintains water rights. Depletes PFAS plume. Treated water still cheaper than purchased regional water.	Incurs capital costs. Higher annual operating costs. Change in well operations.

Table 4 is a review of the treatment options. Given these issues, the City selected granular activated carbon (GAC) as the treatment option to purchase and install. This information was presented to City Council in February 2016 and Council authorized staff on March 21, 2016 to reach full-scale treatment as fast as possible.

Table 4: PFAS Treatment Options

Treatment Option	Advantages	Disadvantages
Activated Carbon Absorption	No additional chemicals required. No repumping required. Effective PFAS removal. Compact outdoor design. Low capital costs.	Requires initial backwashing – wastewater management needed. Solid waste generation
Ion Exchange Resin Adsorption	No additional chemicals required. No repumping required. No initial backwashing required. Compact outdoor design. Low capital costs.	Very little published literature for PFAS removal at the time, and available data was inconclusive to achieving non-detectable concentrations. Solid waste generation.
Nanofiltration / Reverse Osmosis	Extensive literature demonstrating complete PFAS removal. Addresses other minor issues in groundwater quality (arsenic, manganese).	Requires repumping. Requires anti-scalant and cleaning chemicals. Requires building. Continuous liquid waste generation. Permeate requires post-treatment to minimize corrosion control issues. High capital costs.
Advanced UV/peroxide oxidation	Does not generate a liquid or solid waste residual.	Requires peroxide storage. Requires building. High capital costs. Published literature shows only partial PFAS destruction.

The facility was fully commissioned and put into production on July 16, 2020, 77 calendar days after City Council authorization to begin design and has been in daily operation since then. The only times the GAC system has not been in use are those hours in which the wells were offline due to lack of water demand and/or maintenance on the well pumps. Further investigations conducted after the system became operational determined that the PFAS were coming from a nearby firefighting training facility.

The PFAS concentrations in Well No. 4 groundwater have slowly decreased over time as the well continues withdrawing water from the aquifer (see Figure 3 for all the data and Figure 4 for PFAS compounds found at lower concentrations). All water samples from the GAC system have found non-detectable concentrations for all six PFAS from the lag vessel outlet. This is important as the EPA issued new guidance in November 2016, five months after the system became operational, that set the advisory limit to 70 ng/L for PFOS and PFOA combined. Similarly, the State of Washington has issued regulations in 2021 that sets individual PFOS and PFOA limits at 15 and 10 ng/L, respectively.

Figure 3: Gilman Well No. 4 Raw Water Quality (full-scale)

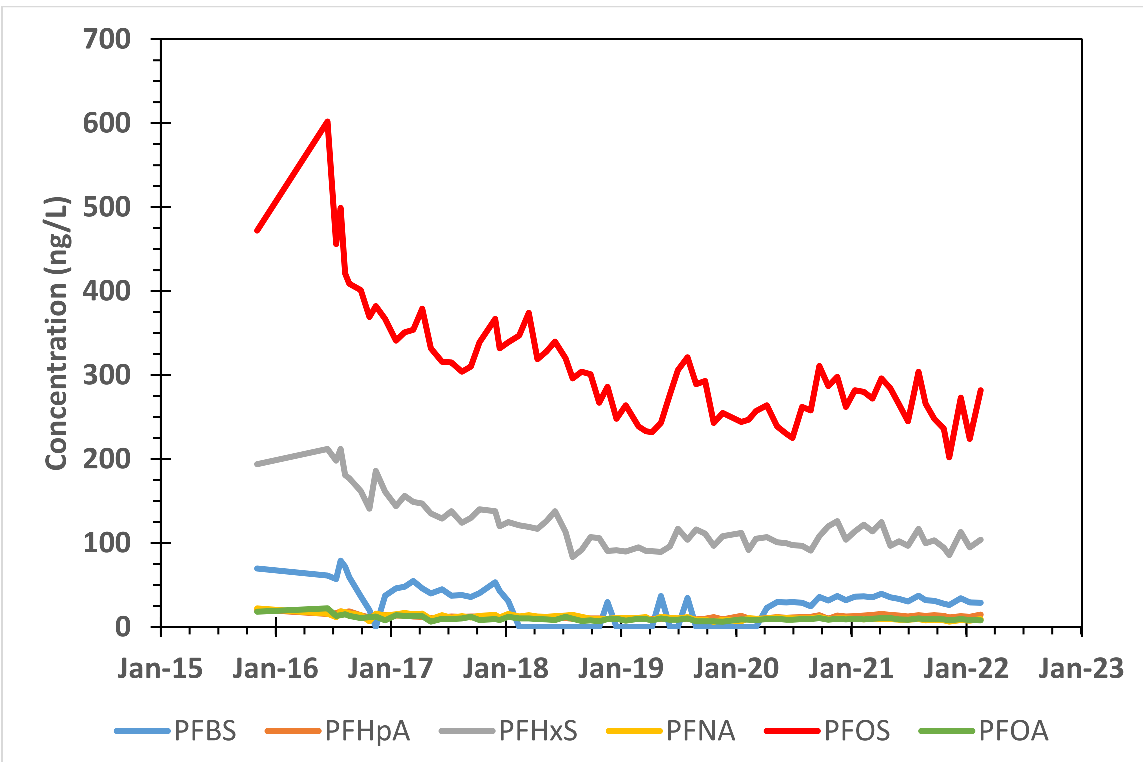
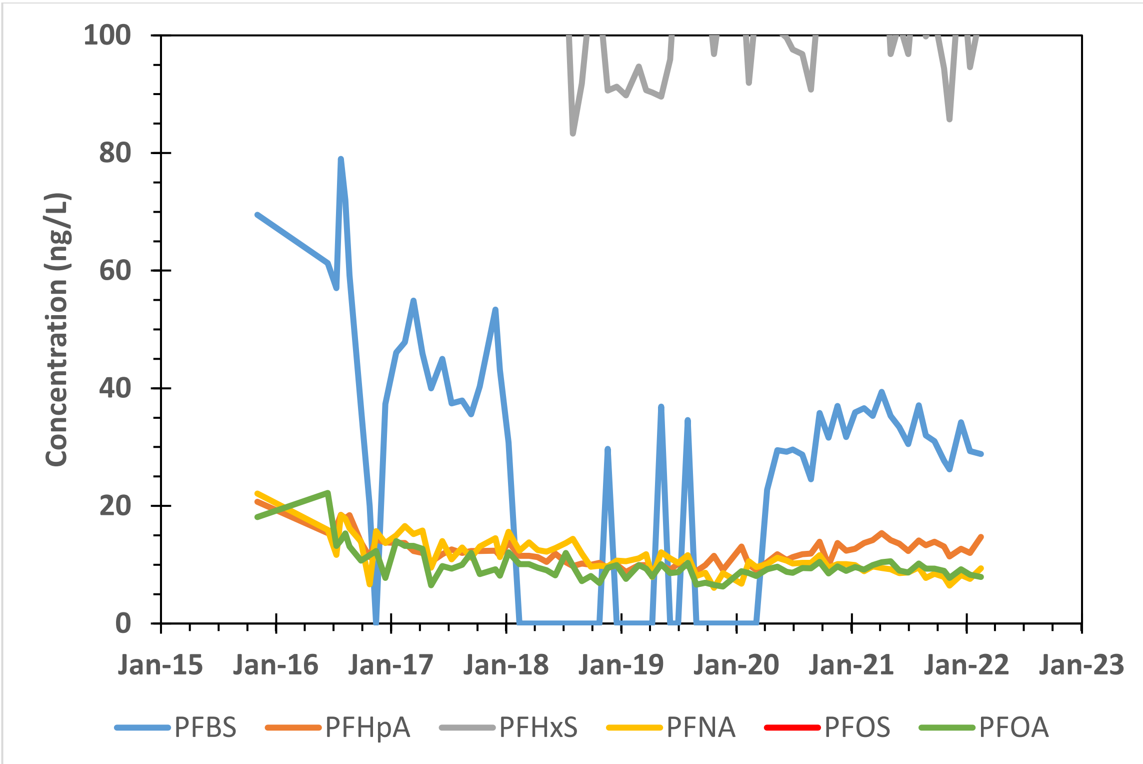


Figure 4: Gilman Well No. 4 Raw Water Quality (reduced-scale)



The GAC media has been changed out once. The coconut media has now been removed and both vessels are filled with the agglomerated bituminous coal media. Table 5 shows a comparison of the media performance. These results have led to the City selecting the bituminous coal as the media for all subsequent replacements.

Table 5: Summary of GAC Media Performance

Parameter	Coconut Media	Bituminous Coal Media
Dates in Lead Service		
Time in Lead Service (months)	11	54 and counting
Water processed (millions of gallons)	102	>463
Estimated PFAS sorbed (kg)	0.24	>1.18
Bed volumes to change-out	19,092	>86,600

Three operational challenges have arisen since this system started operations. The first is that bacterial growth was found on the GAC after six months of operation. This growth caused rapid headloss development. This issue was not identified earlier as the City had never experienced problems with bacteria due to the chlorine addition. However, the GAC system was installed prior to the chlorine addition feed point. GAC is frequently used as an engineered substrate for various purposefully designed and operated biofiltration processes, and the Gilman GAC system wound up being an inadvertent biological process. Laboratory analyses found that the bacteria were native iron bacteria that was using the GAC as substrate for which to grow and utilizing the naturally occurring iron in the water. An evaluation was conducted to identify methods to manage this growth. Conversations with TIGG and Calgon Carbon indicated that suppression can be achieved by applying up to 1 mg/L chlorine onto the GAC. Further engineering analysis determined that the cost of purchasing additional equipment and repiping the system to provide chlorine prior to the GAC was prohibitive.

Instead, the City is backwashing the lead GAC vessel once per month to remove excess biological growth and reduce the system headloss. This process is not recommended by GAC vendors as it disrupts the mass transfer zone of the media and it causes fully saturated GAC at the top of the media bed to intermix with GAC at the bottom of the bed that would be PFAS-free. The result is often early PFAS leakage from the GAC vessels. However, the City's experience after five continuous years of operation has not found such leakage occurring.

The second issue relates to the biogrowth-induced headloss development. The water main that Gilman Well No. 4 discharges into has an operating pressure of 110 psi. The clean filter headloss was 10 psi so the pressure at inlet side of the GAC is 120 psi. The original system was shipped with 125 psi rupture disks to protect the vessels with over-pressurization. These disks are the standard feature for these vessels. The biogrowth resulted an additional headloss of up to 10 psi, resulting in feed pressures reaching 130 psi. The inlet rupture disk blew out at this pressure, causing water to pour out onto to the surrounding areas and causing a system shutdown so that staff can replace the disk. After the disk ruptured a second time, staff replaced the device with a pressure relief valve and began closely monitoring headloss development. The lead vessel is backwashed just before the pressure relief valve would open.

The final issue relates to the disposal of the spent coconut GAC. The media vendor arranged final disposal of the spent media in California. During transit, the hauler entered a California Highway Patrol truck inspection station by the Oregon-California state line for routine inspection. The inspection indicated that the media was radioactive, and the shipment had to be stopped for further analysis. This issue caused City staff to exert considerable effort to make necessary arrangements for subsequent testing and verifications. The re-testing determined that the radioactivity was below regulated limits and the media could continue its transit to the final disposal site. The hauler was delayed for four days but the City was not fined.

The aftermath of the episode was an in-depth analysis for potential sources of radioactivity and how to manage it in the future. A sample of the groundwater and the bituminous coal media in the lead vessel were sent to analysis. The data found that the groundwater had non-detectable concentrations of radionuclides and radiation. However, the media was found to contain appreciable amount of various radioactive elements.

The hypothesis is that non-detectable concentrations are not the same as zero concentrations. These potentially very low concentrations can add up to an appreciable total mass when there is a lot of water involved, such as it the case with the Gilman GAC system. In addition, conversations with Calgon Carbon have indicated that all types of GAC have demonstrated absorptive capacities for radionuclides. At the time of this paper, the author has sampled the existing media to determine its potential radionuclide content and its impact on final disposal options. This is a serious consideration as the bituminous coal in the lead vessel has now treated nearly four times the water of the coconut GAC that caused the initial concerns.

Conclusion

PFAS has become a ubiquitous contaminant that is present throughout the economy, including the mining sector. PFAS's surfactant qualities provide multiple benefits in ore processing, fire fighting, and other mine operations. However, this contaminant's persistence means that some mines may have potentially large PFAS concentrations.

There are several options to manage PFAS such as abandoning the contaminated water supply, blending down the contamination, and treatment. The City of Issaquah explored these options and chose treatment. Treatment has successfully removed the PFAS for the past several years. We have gained considerable experience from it, including learning that:

- The GAC media has proven to capable of reducing up to 600 ng/L of PFOS down to non-detectable concentrations.
- Bituminous coal carbon has a significantly larger sorption capacity for PFAS than coconut GAC.

- Unforeseen biological fouling caused excessive system headloss that resulted in equipment changes.
- The fouling also resulted in the City backwashing monthly, which is contrary to vendor recommendations. However, this action has not caused an issue with performance.
- The long operations have resulted in the media accumulating radionuclides, which is now an issue being reviewed to determine its impact on media disposal options, logistics, and ultimately costs.

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