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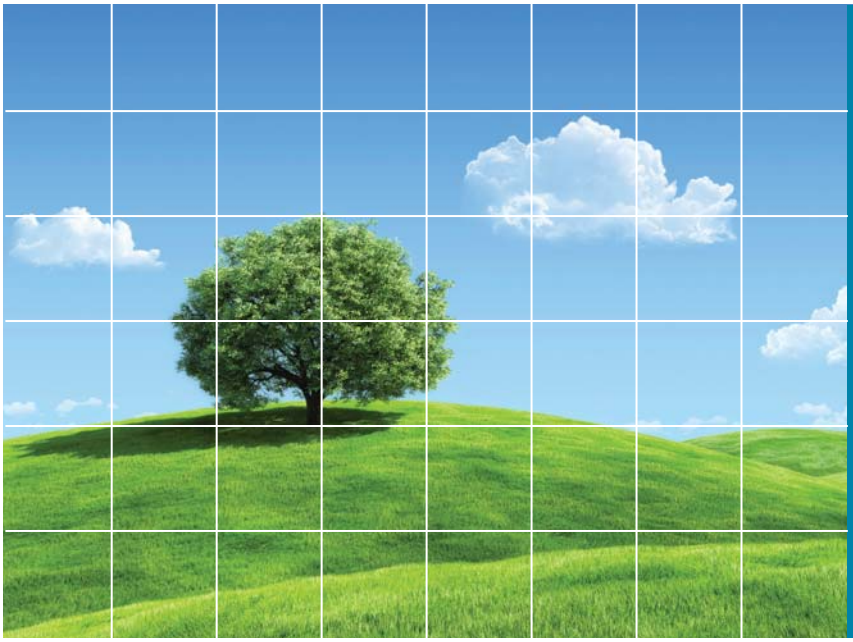

Remediation Technologies for Perfluorinated Compounds (PFCs), Including Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoic Acid (PFOA)

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ABSTRACT

Perfluorinated compounds (PFCs) are a family of compounds found in the environment as a legacy of manufacturing and use in a variety of applications over the past 50 years. Two PFCs of regulatory concern are perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA). Preliminary studies indicate that these compounds can bioaccumulate and pose human health concerns. Both are water soluble, nonvolatile, and persistent in the environment, making them difficult to treat using conventional remediation technologies. Groundwater extraction with inefficient carbon adsorption is currently the favored treatment technology for PFOS- or PFOA-impacted groundwater. For soil, excavation followed by landfill or incineration is required. Alternative treatment technologies are relatively experimental, expensive, and typically require groundwater extraction and ex-situ treatment. Examples include ion exchange, sonochemical treatment, reverse osmosis, and photolysis. However, more recent and ongoing study results indicate that chemical oxidation shows strong potential for its ability to destroy both PFOS and PFOA, making in-situ chemical oxidation a promising technology for full-scale demonstration.

INTRODUCTION

Because of their unique surface characteristics and resistance to degradation in the presence of heat or acids, perfluorinated compounds (PFCs) have been used extensively in a variety of products and industries. PFCs are present in aqueous film-forming foams that are commonly used as fire suppressants and are also used to manufacture Teflon and other non-stick consumer products. Other miscellaneous applications include the use of PFCs as a mist suppressant in hard chrome plating systems; in aviation hydraulic fluids; in etching aids that are used in the metal-working industry; in the print, food manufacturing, and photography industries; and in various consumer products. PFCs have been found at manufacturing sites and in landfills, and in particular, at airports, military sites and refineries where fire events and/or fire-fighting tests have occurred.

The adverse health effects of PFCs are not well understood; however, PFCs have been shown to bioaccumulate. Due to the strength of the highly polarized carbon-fluorine bond and their hydrophobic/lipophobic properties, PFCs are also very persistent in the environment. Toxicological studies suggest neurotoxic and immunotoxic effects (Johansson et al., 2009; Liu et al., 2010). The United States (U.S.) Environmental Protection Agency (EPA) has classified perfluorooctanoic acid (PFOA) as a "likely carcinogen." In January 2009, U.S. EPA established Provisional Health Advisories for PFOA (0.2 micrograms per liter [µg/L]) and perfluorooctane sulfonic acid (PFOS) (0.4 µg/L) (EPA, 2009). From an ecological risk perspective, threshold concentrations may be even lower. For example, the Netherlands National Institute for Public Health and the Environment (RIVM) has published a maximum permissible concentration of 0.65 nanograms per liter PFOS for freshwater (RIVM, 2010). Both PFOA and PFOS are listed on U.S. EPA Contaminant Candidate List 3 for future water quality regulations. PFOS production was voluntarily ceased in the U.S. in 2002, and its use is currently limited. The EU Environmental Ministry legislation has also banned PFOS production and use since June 27, 2011.

PFOS and PFOA can form when longer-chain PFCs partially degrade. Both PFOS and PFOA are long-lived in the environment, with little to no natural degradation (3M, 2000). ARCADIS is currently teaming with researchers at the University of California Los Angeles to more thoroughly evaluate the potential relevance of bioattenuation through laboratory studies to screen aerobic bacteria, anaerobic bacteria, and fungi. PFOS is thermally resistant at temperatures

below 1,100 degrees Celsius (Schultz et al., 2003; Yamada et al., 2005). PFCs therefore pose a significant treatment and remediation challenge. This paper provides an overview of the state of the art for the removal and treatment of PFOS and PFOA, with a focus on published reports and ongoing ARCADIS research regarding chemical oxidation methods.

CURRENT REMEDIATION TECHNOLOGIES FOR PFOS AND PFOA ARE LACKING

The most common remediation technology for groundwater impacted with PFOS and PFOA is groundwater extraction and treatment using granular activated carbon (GAC) for adsorption. Because treatment targets are typically low (sub- or low µg/L concentrations), it may be necessary to operate these pump-and-treat systems for many years to meet cleanup goals. For soil, excavation and disposal in a landfill is the standard approach. Both soil excavation and GAC removal are problematic because, rather than destroying the constituents, they merely transfer them to another medium (GAC) or location (landfill). In addition, landfills are becoming increasingly unwilling to accept PFOS-contaminated material due to the potential necessity of longer-term management and care. Regular thermal incinerators are operated at insufficient temperatures to degrade PFOS. High-temperature incineration or another destruction step is necessary to completely destroy PFOS and PFOA.

GAC consistently removes PFOS at µg/L concentrations with an efficiency of more than 90% (Ochoa-Herrera and Sierra-Alvarez, 2008). However, GAC can be inefficient at removing PFOA and other PFCs (Oliaei and Kessler, 2006). PFC sorption is lower than organics with similar molecular weights (Qui, 2007), and other co-contaminants will compete for, and preferentially utilize, the adsorptive potential of the GAC media. Sorption velocity is faster for longer-chained PFCs and smaller-diameter GAC particles; therefore, GAC that is optimized for PFOS removal will not optimally remove other PFCs (Qui, 2007). Other types of adsorbents that have been used for PFCs include powdered activated carbon, polymers, maize-straw-derived ash, alumina, and montmorillonite (Yu and Hu, 2011; Senevirathna et al., 2010; Hansen et al., 2010; Qu et al., 2009, Yu et al., 2009; Chen et al., 2011; Wang and Shih, 2011; Zhou et al., 2010). Spent adsorptive media typically must be incinerated, thereby adding to the overall management cost.

Other aboveground treatment technologies include ion exchange, nanofiltration (NF), and reverse osmosis (RO). These technologies are typically more costly than GAC, and a variety of resins containing different functional groups are available (e.g., Dowex products). A 3M-patented ion exchange resin will remove PFOS from water. A natural ion exchange substrate is zeolite, a hydrated alumina-silicate mineral, supplied by Sigma-Aldrich, Wako, and Zeolyst International. As with any type of ion exchange, the absorbing media (resin) is relatively expensive and will require resin regeneration, producing a low-volume concentrated waste stream that requires incineration (Ochoa-Herrera and Sierra-Alvanez, 2008). Ion exchange has not yet been used for PFC-contaminated water treatment on a large scale.

NF and RO are widely-accepted filtration techniques that have been tested for their effectiveness in removing PFCs. As expected, RO has higher removal efficiencies than NF due to the smaller pores and thicker rejection layers of RO. Removal rates for NF ranged from 90% to 99% (Tang et al., 2007; Schroder et al., 2010). An RO system with thin-film composite polyamide membranes removed 99% of PFOA at concentrations greater than 1 milligram per liter (mg/L) (Tang et al., 2007).

Several innovative and promising ex-situ technologies, including thermal treatment, sonochemistry, and photolysis, have been tested for their effectiveness in removing PFCs.

Thermal treatment of a fluorotelomer-based acrylic polymer was successful (99% destruction at 950 degrees Celcius) (Yamada et al., 2005). For example, laboratory-scale studies have shown greater than 99% destruction of PFOS at 600 degrees Celsius, although total destruction of the fluorinated chain was not documented in the Yamada group's study. High-temperature incineration is used to destroy highly concentrated aqueous solutions and contaminated soils (Vecitis et al., 2009).

Sonochemistry refers to the use of an acoustic field to generate chemical reactions in a solution. Sound waves collapse the bubbles in the solution, generating high vapor temperatures. PFCs then pyrolytically decompose at the bubble-water interface (Moriwaki et al., 2005).

Finally, a number of photolytic oxidation (advanced oxidation) processes have been tested for PFCs. These includeultraviolet (UV) light in combination with iodide, aqueous periodate, iron, and titanium dioxide (Park et al., 2011; Caoet al., 2010; Hozumi et al,, 2002; Wang et al., 2008; Hori et al, 2007; and Estrellan et al., 2010). PFOA removal efficiencies ranged from 70% to 96%, however, removal efficiencies were lower for other types of PFCs. Tests using zerovalent iron in 350-degree-Celsius subcritical water partially degraded PFOS (Hori et al., 2006).

Over the past five years, ARCADIS and its partners have conducted PFC characterization and remediation projects in The Netherlands, Germany, the U.S., and the United Kingdom. At this time, we are unaware of any full-scale in-situ remediation projects for PFOS and PFOA in the U.S. or Europe. There are currently no proven, in-situ-demonstrated technologies for PFC remediation. Most of the studies relevant to in-situ remediation are immature. For example, ARCADIS is currently working with the University of California at Los Angeles to conduct basic research studies to identify whether anaerobic or aerobic bacteria or fungi can degrade PFOS and other PFCs. However, there is an urgency in Europe to develop effective treatment methods to address PFC-contaminated sites. Although the European Union (EU) has not yet established remediation goals for PFOS and PFOA, these compounds are regulated under EU regulations (e.g., remediation is required in The Netherlands for more-recent releases [post-1987]).

RECENT REMEDIAL TECHNOLOGY DEVELOPMENTS: CHEMICAL OXIDATION

ARCADIS and its partners have conducted studies to shed light on the promising potential of chemical oxidation for PFC treatment. Chemical oxidation has the potential to destroy PFOS and PFOA in situ rather than transferring contamination to another waste stream or area. An in-situ chemical oxidation (ISCO) approach directed at source areas could greatly reduce life-cycle costs and treatment timeframes, thereby providing significant reduction in the overall remedial life cycle. Unlike ex-situ treatment and landfilling, ISCO eliminates the need for long-term management of waste residuals.

Several laboratory studies attest to the feasibility and varying degrees of effectiveness of chemical oxidation and chemical reduction for PFOS and PFOA destruction (Hori et al., 2005; 2008; Kingshott, 2008). Activated persulfate has been shown to partially destroy PFOA, mainly under conditions that are difficult to apply in a full-scale in-situ remediation project. Advanced oxidation processes using activated persulfate are characterized by the high reactivity of the sulfate and hydroxyl radicals driving the oxidation process. Several variations of oxidation processes using persulfate show promising results for degrading PFOA (Hori et al., 2005, 2008).

Hori et al. (2005) found that persulfate produced highly oxidative sulfate radicals that efficiently degraded PFOA to fluoride ions and carbon dioxide. Only minor amounts of shorter-chain perfluorocarboxylic acids formed, indicating that complete mineralization may be possible with further oxidation. Up to 56 mg/L of PFOA was completely destroyed using light-activated persulfate (12 grams per liter [g/L] of persulfate and 4 hours of irradiation). Further testing showed that heat-activated persulfate could also effectively decompose PFOA (Hori et al., 2008). An aqueous solution containing 155 mg/L PFOA and 12 g/L persulfate was heated at 80 degrees Celsius. After six hours, aqueous-phase PFOA concentrations were less than 0.6 mg/L (the detection limit). Fluoride ions and carbon dioxide (molar ratios of 77.5% and 70.2%, respectively) were measured, demonstrating significant PFOA mineralization. Similarly, Lee et al. (2010) demonstrated that persulfate could be activated using iron and heat to decompose PFOA. Recent results from the University of California at Berkeley demonstrate that iron-containing minerals in aquifers slowly catalyze persulfate activation on time scales of days to weeks. Similar findings were published by Watts (2011) and Ahmad et al. (2010). Furthermore, persulfate can react through reductive mechanisms, making persulfate a very versatile oxidant (Furman et al., 2010).

Testing of chemical oxidation pathways for PFOS destruction was previously conducted by an ARCADIS/Imperial College London team (Kingshott, 2008). This research assessed different methods for activating persulfate to more easily treat PFOS-contaminated soils, sediments, and groundwater. Treatments that successfully destroyed PFOS (>97.5% destruction) included Fenton's reagent, activated persulfate, peroxide-activated persulfate, and heat-activated persulfate. The study also conducted an initial evaluation of strong reductants for PFC treatment, including sodium dithionite and sodium hypophosphate. However, these reactions generally required extreme chemical environments and doses and still only partially degraded PFOS (Kingshott, 2008).

ARCADIS conducted laboratory studies in 2011 to degrade PFOS under less-extreme conditions. The results demonstrated that common oxidants and types of activation showed incomplete degradation of PFOS and PFOA under conditions that are achievable in the field. Nevertheless, using a very specific combination of reagents, ARCADIS demonstrated an efficient degradation method with significant promise for destroying PFOS and PFOA in soil and groundwater using soluble reagents and doses that are easily achievable in the field under ambient conditions (ARCADIS patent pending). These data provide a solid foundation for conducting site-specific treatability tests and field-scale demonstration of ISCO for PFOS and PFOA destruction.

SUMMARY AND CONCLUSIONS

PFCs such as PFOS and PFOA pose new remediation challenges because they are persistent and recalcitrant to degradation under natural environmental conditions. Technologies currently used to address these compounds include groundwater extraction and various methods of ex-situ treatment, and excavation and off-site disposal of contaminated soils. These technologies can be expensive, and they are inefficient because they transfer PFCs to new media/locations.

A review of available studies shows that oxidation-based treatment technologies, such as activated persulfate, have significant potential to treat soil and groundwater impacted by PFOS and PFOA. Chemical oxidation technologies represent a giant leap forward in managing the risks posed by PFCs, including PFOS and PFOA. The next step is to conduct in-depth pilot-scale testing to provide key parameters for assessing the feasibility, design, cost, and performance under field conditions and to demonstrate PFC destruction in a full-scale setting.

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ABOUT THE AUTHORS

Elisabeth L. Hawley, P.E. is a Senior Environmental Engineer at ARCADIS U.S., Inc. in Emeryville, California. She leads ARCADIS' Technical Knowledge and Innovation (TKI) network on emerging contaminants and is sharing technical information and lessons learned on perfluorinated compounds; 1,4-dioxane; N-nitrosodimethylamine; 1,2,3-trichloropropane; and more to benefit federal, industrial, and municipal clients. She is currently delineating the extent of PFCs in soil and groundwater at four sites and is analyzing other historical PFC usage areas for PFC presence.

Tessa Pancras is an in-situ chemical oxidation remediation specialist and Research and Development Leader for ARCADIS Netherlands. An environmental chemist by background, she has developed new, combined, and innovative technologies for in-situ remediation projects in a number of countries and regulatory environments. She has evaluated and implemented in-situ remediation technologies for several emerging contaminants, including 1,4-dioxane; tetrahydrofuran; and PFOS. Her recent work testing various oxidants has helped to verify the effectiveness of ISCO for PFCs.

Jeff Burdick is a hydrogeologist and Associate Vice President at ARCADIS U.S., Inc. n Philadelphia and serves as the Remedial Strategies Discipline Director within the TKI group. Jeff focuses on in-situ biological and chemical oxidation methods of groundwater remediation and works with ARCADIS U.S. and European treatability teams to develop approaches for more-recalcitrant compounds.

ABOUT ARCADIS

ARCADIS is an international company providing consultancy, design, engineering and management services in infrastructure, water, environment and buildings. We enhance mobility, sustainability and quality of life by creating balance in the built and natural environments. ARCADIS develops, designs, implements, maintains and operates projects for companies and governments. With 19,000 employees and more than $3.2 billion in revenues, the company has an extensive international network supported by strong local market positions. ARCADIS supports UN-HABITAT with knowledge and expertise to improve the quality of life in rapidly growing cities around the world.

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