Current Insights on Reaction Kinetics and Mechanisms of PFAS Destruction during Hydrothermal Alkaline Treatment (HALT)

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Background/Objectives. The use of per- and polyfluoroalkyl substances (PFAS) in manufacturing processes, consumer goods, and firefighting foams has resulted in widespread need to remediate sites with PFAS-contaminated soil and groundwater. An additional need resulting from these remedial efforts is for safe disposal of PFAS-containing wastes generated during remedial actions or firefighting foam changeouts. Neither incineration nor landfilling of PFAS are attractive options, motivating a search for alternative PFAS destruction technologies. When coupled with suitable separation and volume reduction technology (e.g., soil washing, foam fractionation, reverse osmosis), emerging PFAS destruction technologies promise end-to-end treatment of PFAS-contaminated matrices.

Hydrothermal alkaline treatment (HALT), first investigated and developed at the Colorado School of Mines under SERDP Project ER18-1501, is an effective and efficient process for degrading halogenated compounds such as PFAS. High-pressure (10 to 30 MPa), high-temperature (200 to 350 °C), high-pH (>14) liquid water serves as an ideal reaction medium for promoting defluorination of PFAS in liquid matrices. Studies to-date have shown effective conversion of ultra-short-chain, short-chain, and long-chain PFAS, in a variety of matrices (e.g., AFFF, groundwater, IXR regeneration brines, foam fractionate, spent sorbent media) to inorganic fluoride, with high destruction and defluorination efficiencies. In this presentation, we summarize the insights gained from studies performed to-date investigating HALT, discussing currently hypothesized reaction mechanisms, reaction kinetics, end products, and matrix effects.

Approach/Activities. Several scales and configurations of HALT reactors were used to generate the data discussed here. Data from batch reactors, lab-scale continuous flow reactors, and a pilot-scale continuous flow reactor are synthesized to present the current state of understanding. A wide range of analytical tools and techniques have been leveraged in these studies, including LC-MS/MS, LC-QToF-MS, GC-MS, IC, ISE, ^{19}F-NMR, and HPLC.

Results/Lessons Learned. The currently held hypothesis is that PFAS are degraded under HALT conditions through nucleophilic substitution reactions (F <-> OH), driven by the high-pH environment. Destruction kinetics in continuous flow reactors appear to be significantly faster than in batch reactors, perhaps suggesting a physical mechanism for enhancing the initial reaction step, which may be tied to the surfactant / hydrophobic nature of the PFAS molecule. Production of inorganic fluoride in separate studies of PFOS, AFFF, TFA, and TFMS solutions confirms that C-F bonds are effectively cleaved under HALT conditions. Perfluorosulfonic acids (PFSAs) are more recalcitrant to reaction than perfluorocarboxylic acids (PFCAs). Extensive sampling and analysis of liquid products have indicated no production of stable intermediate species in the liquid phase. Efforts are ongoing to sample and analyze any gaseous products, to fully identify transient intermediate species and to robustly confirm the active reaction mechanism.