Mechanochemical Destruction as a Scalable Treatment Technology for Per- and Polyfluoroalkyl Substances (PFAS)

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Background/Objectives. The global environmental sector urgently requires innovative solutions to address the increasing prevalence of PFAS-related issues (e.g., contaminated soil, obsolete product stockpiles). Unlike more ‘conventional’ organic pollutants, PFAS exhibit extreme persistence and physicochemical properties that are resistant to targeted degradation. Treating such contaminants is a highly regulated and complex facet of the hazardous waste industry that considers efficacy, scalability, cost, safety, and treatment time, among other operational parameters. Mechanochemical destruction (MCD) is a novel treatment technology that utilizes high energy ball milling to initiate and propagate the destruction of PFASs. This technique has been shown to destroy organic contaminants without the need for hazardous oxidizing agents, extreme temperatures, harmful additives, or high pressures; however, the fundamental chemistry of the process was not well understood until recently. As an ex situ non-thermal process capable of high rates of PFAS destruction (>99.9%), MCD presents a compelling green solution for heavily contaminated land and obsolete product stockpiles. Comprehensive lines of evidence have been developed, with a focus on the determination of mechanistic degradation pathways, the kinetic progression of reactions, and the fate of mineralized substances.

Approach/Activities. In this work, a comprehensive analytical approach was undertaken to determine the fundamental underlying mechanisms of MCD reactions for PFAS spiked onto quartz sand as a grinding auxiliary. The overall process was characterized by conventional techniques, such as liquid chromatography-tandem mass spectroscopy, Fourier transform infrared, and surface area analysis. More novel techniques were also employed, including high resolution mass spectroscopy, solid-state nuclear magnetic resonance, and electron paramagnetic resonance. Subsequently, authentic samples of contaminated soil and firefighting foam concentrates were treated by MCD as proof-of-concept case studies to demonstrate the applicability of the technique to address ‘real-world’ problems.

Results/Lessons Learned. Quantitative analysis of ball milled samples revealed high destruction efficiencies ranging from 99.95% to 100% for five different perfluorosulfonic acids subjected to relatively mild MCD conditions at benchtop scale. Extensive non-targeted analysis of these time-resolved samples by high-resolution mass spectroscopy revealed the formation and ultimate destruction of intermediate degradation products. Solid-state nuclear magnetic resonance confirmed the mineralization of organic fluorine (C–F) in PFAS. At the culmination of the MCD process, the fluorine resides in a reservoir of stable Si–F bonds on the quartz sand surface, generating a benign solid end product. The mineralization of PFAS by MCD occurs via a complex collection of multiple mechanisms operating simultaneously. Based on the intermediates identified as part of the degradation product analysis, core mechanistic steps have been proposed which will be detailed in this presentation.

Finally, the MCD technique was applied to ‘real-world’ challenges, specifically for the destruction of PFAS in obsolete firefighting foam concentrates and PFAS-impacted soil. Upon mechanochemical treatment, PFAS were indiscriminately and effectively destroyed in foam concentrates as well as highly contaminated soil, despite the incredible complexity of these substrates. The observed destruction efficiencies ranged from 99.99% and 100% for a wide range of target PFAS present in these samples, demonstrating the capability of the MCD technique to address industrially-relevant pollution challenges.