Nano-scale FeS_{x-1} as a key agent for pollutant transformations and redox buffering in suboxic systems

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Nano-particulate iron sulfide ($NP-Fe_{x-1}$) forms abiotically or biogenically under sulfate reducing conditions (SRC) when dissolved S(-II) is present and reacts with either dissolved or solid phase Fe(II). Such NP-FeS solid phases can subsequently serve as: an effective sink for aqueous phase toxic trace divalent metal cations (Hg, Cd, Ni)[1], a reducing agent for converting trace elements to more reduced and insoluble oxidation states (As(V) to As(III) or As(0))[2] or radionuclides (U(VI) to (U(IV))[3], or a facilitator of reductive transformation of carcenogenic chlorinated organic compounds like tricloroethylene (TCE) to benign end products [4], depending on pH and pe. When redox reactions between NP-FeS and trace quantities of redox active elements occur, as long as NP-FeS concentration is in great excess, NP-FeS can effectively maintain suboxic conditions through complete reduction of the trace oxidants, while forming relativley minor quantities of oxidized Fe and S solids (e.g., Fe_3S_4) from NP-FeS oxidation [5]. As the concentrations of oxidants increase relative to NP-FeS, NP-FeS will become more completely oxidized, leading to the potential remobilization of any solid phase associated trace elements originally sequestered by NP-FeS [6,7], or the diminishment of reducing properties of the NP-FeS for further effective redox conversion of organic trace pollutants. In this presentation, the mechanisms and impact of redox conversions of NP-FeS by trace elements pollutant oxidants or oxygen in suboxic systems will be discussed. The abilitiy of an NP-FeS system to serve as a redox buffer and the potential for NP-FeS to be regenerated by returning to SRCs will also be discussed. Examples from heterogenous aqueous/NP-FeS phase batch and flow-through reactor systems as function of pH and pe will be presented.

[1] Jeong et al. (2007), *ES&T* 41, 7699-7705.[2] Renock et al. (2009), *Chem Geol.,* 268, 116-125 [3] Hyun et al. (2012), *ES&T* 46, 3369-3376. [4] Butler and Hayes, *ES&T*, 33, 2021-2027. [5] Lan et al., *Environ. Sci.: Processes Impacts*, 2016, 18, 1266-1273. [6] Bi and Hayes, ES&T, 48, 632-640. [7] Jeong et al., *Geoch.et Cosmochim. Acta*, 74, 3182- 3198, 2010.