

Mössbauer evidence of rapid pyrite formation during the interaction between dissolved sulfide and lepidocrocite

M. WAN^{1*}, C. SCHRÖDER^{1,2} AND S. PEIFFER¹,

¹Department of Hydrology, University of Bayreuth, Bayreuth Germany, moli.wan@uni-bayreuth.de (* presenting author); s.peiffer@uni-bayreuth.de

²Center for Applied Geoscience, Eberhard Karls University, Tübingen, Germany, christian.schroeder@ifg.uni-tuebingen.de

Mössbauer spectroscopy has been applied to study mineral transformation during the interaction between lepidocrocite and dissolved sulphide with two different initial concentration ratios. Synthetic lepidocrocite enriched with the Mössbauer sensitive isotope Fe-57 was reacted with dissolved sulphide at neutral pH in an anoxic glove box, the initial molar ratios of iron and sulphide being 3.125 and 0.5, respectively. Solid samples for Mössbauer analysis were collected by filtration at different time steps after 15 min, 2hrs, 48hrs, 72hrs and 1 week for the 3.125 iron-sulphide ratio; and after 72h and 1 week for the 0.5 iron-sulphide ratio. Dissolved and solid phase ferrous iron, dissolved sulphide and elemental sulphur were measured with wet chemistry analysis techniques in parallel runs.

Mössbauer spectra provide evidence for rapid pyrite formation within 48hrs during the reaction at an initial molar ratio of 3.125. Pyrite formation was accompanied by a decrease of elemental sulphur and mackinawite, which is the main iron intermediate product with minor pyrrhotite and magnetite. At the ratio of 3.125, excess lepidocrocite existed and dissolved sulphide was completely consumed after 15min. Acid extractable Fe(II) concentration was in excess of that of Fe(II) bonded as FeS, which has been reported before^[1,2] and the difference of the two iron species was defined as excess Fe(II)^[2]. In the experiment with an initial ratio of 0.5, lepidocrocite was completely transferred to mackinawite. In this system dissolved sulphide was not completely consumed even after 1 week. No pyrite could be detected. Species including elemental sulphur and mackinawite were stable in 1 week without any further transformation. The long term preservation of unstable iron sulphide minerals at a low concentration of dissolved sulphide is consistent with the observation in marine sediment^[3].

These experiments show an important linkage between rapid pyrite formation and surplus lepidocrocite and/or the excess Fe(II) formed during reaction. Together with wet chemistry analysis results we propose that some of the electrons donated by sulphide oxidation are preserved temporally in the lepidocrocite bulk and lead to formation of the excess Fe(II) fraction and ultimately rapid pyrite formation.

[1] Poulton *et al.* (2004) *Geochim. Cosmochim. Acta* **68**, 3703–3715.

[2] Hellige *et al.* (2011) *Geochim. Cosmochim. Acta* **81**, 69–81

[3] Gognon *et al.* (1995) *Geochim. Cosmochim. Acta* **59**, 2663–2675.

The characterization and evaluation of different biochars as reactive materials for Mercury (II) stabilization

ALANA O. WANG^{1*}, PENG LIU¹, CAROL J. PTACEK¹,
DAVID W. BLOWES¹, RICHARD C. LANDIS²,
WILLIAM R. BERTI², JAMES A. DYER²

¹Department of Earth and Environmental Sciences, University of Waterloo, Waterloo, Canada

*o3wang@uwaterloo.ca

²E. I. du Pont de Nemours and Company, Wilmington, USA

Introduction and Objectives:

Biochars, produced through low-temperature pyrolysis of environmental biomass, have considerable potential for stabilizing heavy metal in aquatic and sediment systems through surface adsorption reactions. Recent advancements in the uses of biochars to remediate heavy metals, such as Pb, Cd, and Cu, have not been extended to Hg. The complex properties of biochars can also limit the understanding about the leaching potential for nutrients and trace elements. The objectives of this study are to characterize and evaluate different types of biochars for their potentials for Hg treatment and soluble elements releasing. In this study, three biochars produced from different raw materials were evaluated, including spent mushroom soil, pine bark, and fresh mushroom soil containing poultry manure. These biochars were first characterized by surface area, total sulphur and total carbon content, scanning electron microscope/energy dispersion X-ray spectroscopy (SEM/EDX), and Fourier transform infrared spectroscopy (FT-IR). These biochars were then evaluated through a series of laboratory batch studies using Hg-spiked river water or natural river water as the equilibrating solution within 2 days and 14 days reaction time. Subsequent washing experiments were conducted to evaluate the sustained reactivity of biochars.

Results and Discussions:

The mushroom soil-based biochars (spent, and fresh mushroom soil) were observed to have higher surface area than the wood-based biochar, which are consistent with their irregular distorted porous structures as observed by SEM. The surfaces of all three biochars were also observed to have various functional groups as indicated through FT-IR analyses, which might stabilize Hg and release nutrients and trace elements. In batch studies with all three biochars using Hg-spiked river water, greater than 80% and greater than 95% of Hg was removed from the Hg-spiked river water with an initial concentration of 8000 ng L⁻¹ within 2 days and 14 days reaction time, respectively. When compare these batch tests, the mushroom soil-based biochars were found to reduce greater amount of Hg from the Hg-spiked river water than the wood-base biochar, indicating better surface adsorptions. In batch studies using natural river water, the alkalinity and concentrations of nutrients (NH₃-N, PO₄-P, DOC), anions (SO₄²⁻, Cl⁻), and trace elements (As, Pb, and Cu) were observed to increase especially in the river water containing the mushroom soil-based biochars. The effective Hg removal and the soluble constituents releasing were all consistent with the presence of functional groups observed by FTIR. Step-wise washing of these biochars resulted in substantial decrease in the release of nutrients and anions with minor decrease in the Hg removal rates. In fact, greater than 85% Hg removal rates were observed in all batch equilibrating solutions after using these washed biochars. These results suggest that, of all biochars evaluated, both the unwashed biochars and the washed biochars have the potential to immobilize Hg without the addition of soluble constituents as mentioned above.