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Redox oscillation impact on natural and engineered biogeochemical systems: chemical resilience and implications for contaminant mobility

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Abstract

Many geochemical systems fluctuate regularly from oxic to anoxic conditions (flooded soils and nuclear waste surface repositories, for instance). In these conditions many inorganic contaminants including Sb, Se, Cr, As, and U are highly sensitive to changes in redox conditions. These oscillations may result in changes to their speciation, toxicity, and mobility. We demonstrate through the combination of redox-stat batch-reactor experiments that periodic and cumulative changes to matrix mineralogy, contaminant speciation, and mineral surface properties occur following periodic cycles of reduction and oxidation. These changes result in both short-term (intra-cycle) and long-term (inter-cycle) changes to K_d values for a range of redox sensitive contaminants. These results demonstrate that naturally occurring redox oscillations may result in long-term immobilization of contaminants in the solid phase in addition to short-term variations in mobility.

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1. Introduction

Many geochemical systems fluctuate regularly from oxic to anoxic conditions. Systems becoming seasonally anoxic include macrophyte water treatment plant, and engineered low activity nuclear waste disposal. The period of these redox oscillations may vary from minutes (respiration in mud), to hours (macrophyte water treatment plants), to days (wetland plant rhizosphere; and urban wastewater pipes), weeks (irrigated rice field; oxygenated water injection in Fe rich GW), to years (phreatic- or engineered-flooded soils, floodplain, riparian and hyporheic zones, seasonally stratified lakes, and groundwater abstracted aquifers, artificial surface recharge aquifers), to decades (lake “sediments”, swamps and peat-bogs becoming oxic “soils” upon urbanization, desertification or agriculture expansion; anoxic sedimentary formation and aquifers turn oxic upon groundwater over-abstraction or fracking fluid intrusion) to million years (banded iron formations). Reactions in these systems often do not reach thermodynamic equilibrium and physical/chemical diffusion, electron transfer kinetics, and solid phase nucleation (e.g. carbonate, sulphide, metallic), together with microorganisms, control the transient states of these systems.

In such systems, the mineralogical composition is often considered to be static, and therefore, that interactions with contaminants and nutrients may be well constrained. Typically, solid/aqueous partition coefficients (K_d values) are obtained empirically to determine the proportion of contaminant immobilised by the solid phase for individual barrier material/contaminant combinations at defined contaminant loadings and pH. These values may then be used as indicators of potential contaminant mobility around waste storage facilities following the possible failure of engineered barriers [1]. While K_d values are a useful tool to modellers estimating contaminant mobility through porous media at thermodynamic equilibrium, matrix mineralogy, and therefore K_d values, are liable to change over time and under dynamic biogeochemical conditions [2].

In the present paper we shall discuss the chemistry, biology and mineralogy of near surface environments implicated in back-filled or excavated storage solutions, currently proposed for low-level long-lived waste (LL-LLW). These systems may be implicated to groundwater level variations, which will result in more dynamic redox conditions than those predicted in e.g. deep, anoxic geological storage conditions [2]. To conduct experimental, analytical or spectroscopic investigation on these systems is a challenge which will be discussed, together with the “natural attenuation”- or release - of toxic elements (such as As, Sb, Se, Cr, U) [3-5]. Dynamic conditions are similar to those experienced in pluvial, fluvial or phreatic influenced soils and are likely to be far from thermodynamic equilibrium [6]. (Bio)chemical models of such redox oscillatory systems should be included in risk assessment and system management of former military or mine sites, waste storage facilities, “green” waste water treatment, floodplains and urban development.

2. Material and Methods

During a series of laboratory experiments argillaceous substrates were subjected to successive cycles of oxidizing and reducing conditions with Eh oscillating between -215 and +340 mV induced via both abiotic and microbial methods. Chemically induced cycles of oxidation and reduction were achieved via a combination of gas sparging (nitrogen vs. compressed air) and the addition of a synthetic reduced humic substance analogue (AH_2DS^{2-}). Microbially induced cycles of oxidation and reduction were achieved using gas sparging (nitrogen gas vs. compressed air) to stimulate different metabolic pathways of a natively present microbial community.

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