

Cr(VI) Reduction by Natural Organic Matter in Cr(VI)-Doped Latosol Soil

The stable oxidation states of chromium in the environments are Cr(III) and Cr(VI). The toxicity of the soluble chromium species and their mobility in aquatic and terrestrial environments depend on their oxidation state. Cr(VI) can cause lung cancer and is more toxic and mobile than Cr(III). Over the past two decades, the lack of safe disposal has resulted in widespread water pollution and soil contamination problems throughout the world. Meanwhile, there have appeared many reports aimed to develop methods for in-situ remediation of chromium-containing soils by reducing Cr(VI) to Cr(III), thereby immobilizing and detoxifying chromium species. Cr(VI) has the highest oxidation state and is prone to reduction in soils via redox reactions carried out in different media. These media include aqueous inorganic species, mineral surfaces, nonhumic organic substances such as carbohydrates and proteins, and soil humic substances.

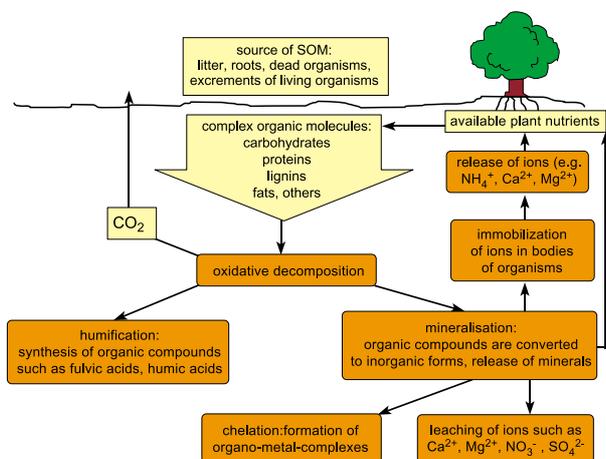


Fig. 1: Transformation of soil organic matters within soil. Courtesy of Prof. S. Grunwald, U. of Florida, at a website address of <http://grunwald.ifas.ufl.edu>.

Soils are formed from the weathering of rocks and exist in various forms such as alluvial, residual, siliceous, sand, clay, etc. Second only to clay in importance as a soil constituent is organic matter, which contributes significantly to soil sorbing capacity. Dead root and the residues from vegetation and crop fall and decay on the soil surfaces. All these residues are transformed by microorganisms into a mixture of organic substances called humus. Fig. 1 shows a schematic describing the transformation of soil organic matter (SOM) in the soils. These humic substances provide nutrients essential for plant growth and become an important part of food chain. Therefore, it is critically important that the soils need to be kept free from organic and inorganic contaminants generated from human activities. Moreover, the SOM offers several self-cleaning pathways in regard to contaminant removal: immobilization of metal ions in organisms, mineralization by converting organic into inorganic compounds, and fixation by forming organo-metal chelating complexes.

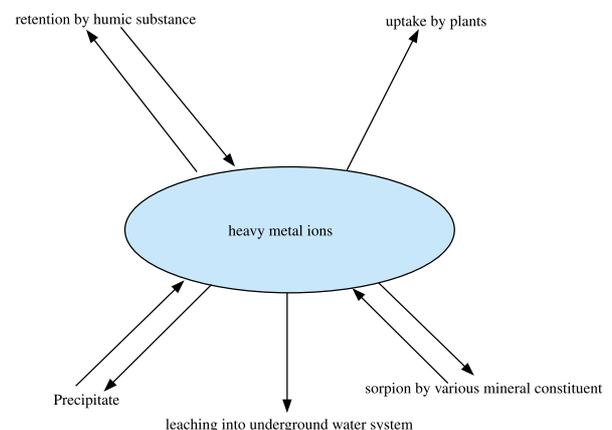


Fig. 2: Fate of heavy metal contaminants in soil system.

Fate of heavy metals in soils and the required cleanup methodology can be extremely complex. Fig. 2 shows a block diagram depicting this relationship. Being sorbed in soil system, heavy metals can associate themselves with more than one phase of the system. In the liquid phase, heavy metals exist either in suspended particulate forms or in hydrated forms depending on pH value. In contrast, in solid mineral phase, heavy metals can precipitate on the mineral surfaces. The sorbed form and the sorption mechanism are all dependent on pH value. Sometimes, the sorption interaction is not strong enough to prevent the ions from being leached into the underground water system. The bonding between the heavy metal ions and the humic substance is predominately via chemisorption. This strong interaction makes possible the retention of heavy metal ions by the humic substance and facilitates the redox reaction. Given the complexity of humic substance formed via humification processes as described in Fig. 1, the sorption of heavy metal ions to the humic substance can conceivably become rather complicated.

The schemes of reducing Cr(VI) to Cr(III) by natural organic matters (NOM) and other organic compounds have been proposed by several research groups. It has been reported that the compounds having oxygen-containing functional groups are capable of slowly reducing Cr(VI) at ~pH 7 with half-lives of several months to years. Jardine *et al.* demonstrated that in the dissolved NOM and Cr(VI) mixtures devoid of solid-phase substances, the Cr(VI) could be slowly reduced at a rate of 50% reduction in several months.

In this short report, we will demonstrate the unique advantage gained by applying XAS technique to the environmental study. Specifically, we would like (1) to establish a trend of the Cr(VI) reduction among varied Cr(VI)-doped Latosol soil samples and (2) to perform a speciation for the sample that is mostly reduced. X-ray absorption technique is a non-intrusive and powerful method to study the local environment of heavy metal. The speciation of chromium compound, determined via near-edge XAS analysis, can be rather involved due to the existence of multi-compounds in the complex samples like soils.

The top surface layer (0-15 cm depth) of "neat" Latosol soil was collected from the central area of Taiwan. It was dried, ground, and sieved to ± 50 mesh. The appropriate equivalent of the soil pedon is fine-silty, mixed, hyperthermic. Typic Kandudult and the soil pH value was determined by USEPA SW-846 Method 9045C to be 3.85 ± 0.01 . It was free of heavy metal contamination and thus termed "neat Latosol soil". The main inorganic composition (in oxide form) of the neat Latosol soil was: 64.3% SiO₂, 15.5% Al₂O₃, 3.2% Fe₂O₃, and 1.1% Na₂O. The soil also contained $8.35 \pm 0.47\%$ loss of ignition (LOI). The XRD-detectable crystalline species were silicon oxide and muscovite [KAl₂Si₃AlO₁₀(OH)₂]. The BET surface area of the neat Latosol soil was 6.47 m²/g via N₂-adsorption method. The soil sample was rich in NOM as indicated by the 3.11% carbon and 0.70% hydrogen determined from elemental analyzer.

To study the reduction capacity of the NOM-bearing Latosol soil, Cr(VI) was artificially doped into the neat Latosol soil to prepare a 40,000 mg Cr (kg soil)⁻¹ slurry. The slurry was then divided into two lots. The first lot of the slurry was wind-blown for 12 days at 30 °C to dryness and this sample is denoted as L-30. Three quarters of this L-30 sample were individually heated to 60 °C, 80 °C, and 105 °C for three days to study the effect of temperature on the extent of Cr(VI) reduction. As-treated samples are denoted as L-30-60, L-30-80, L-30-105, respectively. The second lot of the slurry was directly oven-heated at 80 °C for 2 days to dryness, and this dried sample was further heated at 105 °C for 1 day. This sample is denoted as L-80-105. The extent of Cr(VI) reduction was compared among the latter sample and the samples made from the first lot of the slurry to assess the effect of mild 80 °C heating of the liquid-state sample on Cr(VI) reduction.

The speciation and local structure around chromium in all Cr(VI)-doped Latosol soil samples as well as reference compounds such as CrO₃, Cr₂O₃, Cr metal, Cr(OH)₃, and CrO₃ solution (i.e., denoted as HCrO₄⁻) were investigated at the wiggler beamline BL17C1 of SRRRC. The Cr K-edge (5,989 eV) XAS spectra for the Cr(VI)-doped Latosol soil samples were



collected in the fluorescence mode at room temperature, whereas the spectra for chromium reference compounds were collected in transmission mode. Data analysis was performed using a commercial WinXAS software.

It is known that the relative height of the Cr pre-edge peak is proportional to the percentage of chromium(VI) in total chromium. A glance at the pre-edge feature already reveals the degree of Cr(VI) reduction qualitatively. Fig. 3 compiles all the XANES results for the samples. The effect on the Cr(VI) reduction by the wind-blowing alone is the least (L-30). Additional heat application at 65, 80, and 105 °C for 3 days to the L-30 sample reduces the Cr pre-edge peak and higher temperature treatment reduces Cr(VI) more, but not that dramatically. It can be deduced that heating the dry sample L-30 to 65-105 °C for 3 days has limited effect on enhancing Cr(VI) reduction. Note that the DOL-80-105 sample shown in Fig. 3 was prepared by first destroying and/or removing the LOI from neat Latosol soil at 900 °C for 2 hours prior to Cr(VI) doping. As-treated DOL-80-105 sample contained only 0.04% carbon, as compared to 3.11% carbon in neat Latosol soil. The de-LOI process removed ~99% of the carbon from Latosol soil and thus the DOL-80-105 sample was considered as free from humic substance. Fig. 3 clearly shows that the pre-edge peak for the DOL-80-105 sample is much greater than all other samples, indicating the least Cr(VI) reduction due to the lack of humic substance.

Furthermore, a comparison of the pre-edge

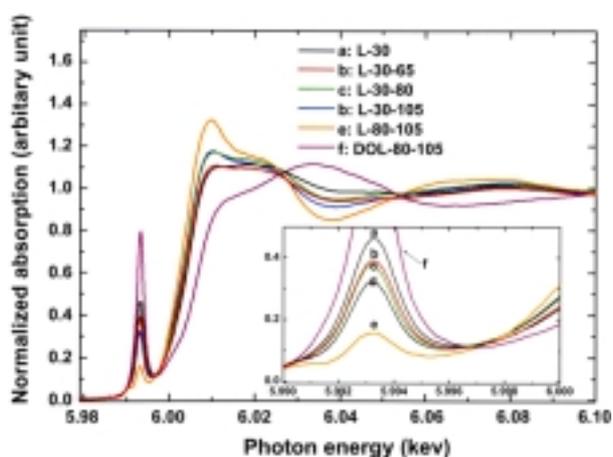


Fig. 3: Cr XANES spectra for mildly heated samples. The pre-edge features have been magnified in the inset for clarity.

peaks among L-80-105 and all other various samples immediately reveals that the rate of Cr(VI) reduction by NOM was greatly enhanced for the redox reaction carried out in a water medium of 80 °C than for that executed at 30 °C. The enhancement of Cr(VI) reduction for the L-80-105 sample is probably due to the increased diffusion rate for reactants and the increased redox reaction rate. We also noted that Cr(OH)₃, undetected with X-ray diffraction (XRD) technique perhaps owing to small crystallinity, was readily detected by X-ray absorption spectroscopy (XAS) and identified to be a key chromium species after ~90% Cr(VI) reduction. The present heat treatment temperature of no more than 105 °C was considered low. This low heat requirement suggests an energy-saving strategy of tapping into the waste heat generated from industrial flue gas to achieve Cr(VI) reduction in NOM-bearing or -amended soils, sediments, sludges, and wastes.

Beamline:

17C1 Wiggler beamline

Experimental Station:

EXAFS end station

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Publications:

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