

Distribution and Speciation of Tellurium in Contaminated Soils from Abandoned Mine Tailings: Comparison with Selenium

The distribution and speciation of tellurium (Te) and selenium (Se) in contaminated soil were studied by the μ -XRF, XRD and XAFS techniques. The results showed that the main host phase of both Te and Se was Fe(III) hydroxides in the soil, in which Te was present in the forms of both Te(VI) and Te(IV), while Se(IV) was the dominant Se species. The difference in the speciation and solubility of Se and Te can be ascribed to the structures of their surface complexes onto Fe(III) hydroxides in soil.

Tellurium (Te) has attracted increasing attention from a toxicological point of view, because the expanded industrial application of Te such as for new solar panel materials could lead to environmental pollution and induce Te poisoning in humans [1-3]. In addition, radio-tellurium may have been released into the environment by the Fukushima Daiichi Nuclear Power Plant accident, posing serious health risks [4, 5]. However, the distribution, chemical speciation, and biogeochemical behaviors of Te in the environment are still poorly understood, owing to challenging analytical methods for Te speciation. Although the XAFS method has been widely used to identify the speciation of metal(loid)s in solid samples [6-8], there has been little research on Te speciation in natural soil due to its low Te content and the high absorption energy of the K-edge of Te (31814 eV). In this study, we investigated Te speciation in soil from abandoned tailings in Kawazu Mine, Shimoda City, Shizuoka Prefecture, Japan, where the Te concentration in

soils was $15.2 \pm 2.7 \text{ mg kg}^{-1}$ ($n = 9$) [9, 10], by using the powerful μ -XRF-XAFS techniques at BL37XU, SPring-8 (Hyogo, Japan). Moreover, μ -XRD measurements for identifying the dominant minerals in soil particles were carried out at beamline BL-15A1, Photon Factory (Tsukuba, Japan).

As shown in Fig. 1(A), Te and Se were heterogeneously distributed in the thin section of soil by μ -XRF mapping, and elevated intensities of Te and Se were mainly observed in the iron-rich areas. The μ -XRD results suggested that the mineral compositions in the hotspots of Te and Se were goethite and a small amount of illite [Fig. 1(B)], which is consistent with the distribution of Te and Se in soil [Fig. 1(A)] and previous laboratory experiments [8]. Thus, the main host phases of Te and Se in soil are Fe(III) hydroxides and illite, although the association of Te and Se with amorphous or poorly-crystalline material that is not readily identified by the XRD method cannot be entirely ruled out.

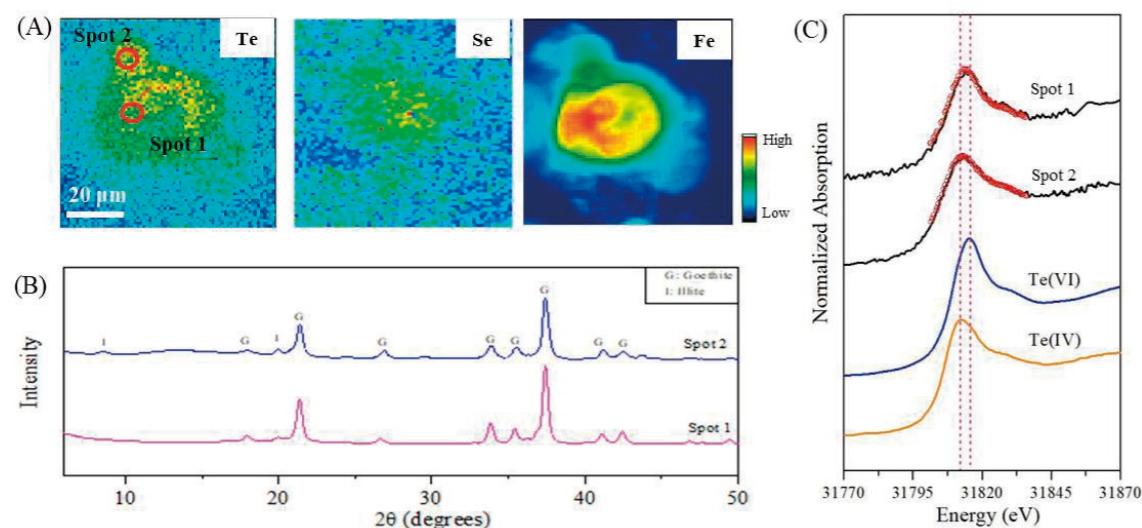


Figure 1: (A) μ -XRF maps of selected areas in the thin section sample of soil; (B) μ -XRD patterns of interesting hotspots in soil grains; and (C) Te K-edge μ -XANES spectra.

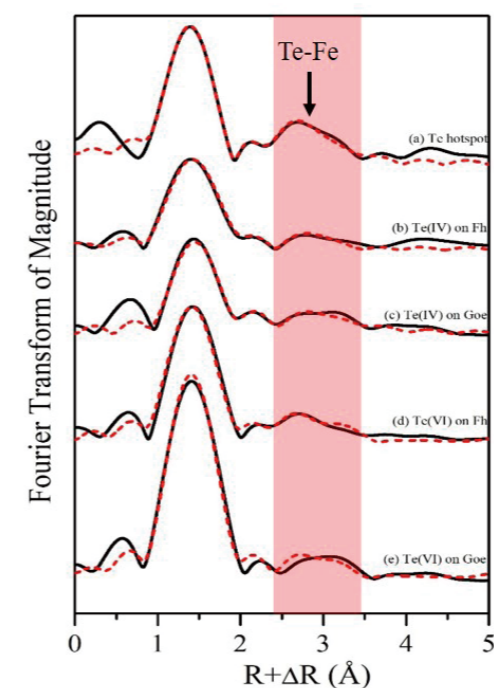


Figure 2: Te K-edge EXAFS spectra of the hotspot in soil grains and adsorbed samples. (Fh: ferrihydrite; Goe: goethite)

Tellurium K-edge μ -XANES spectra for Te hotspots and reference materials are shown in Fig. 1(C). It was observed that Te was present as a mixture of Te(IV) and Te(VI) species in the contaminated soil. Although Te(VI) is prevalent under neutral pH and oxic conditions from the Eh-pH diagram of Te [8], dominant Te(IV) species can also be observed in some hotspots [e.g., Spot 1 in Fig. 1(C)]. In contrast, Se(IV) was the predominant form in the same soil particles [9]. Interestingly, the hotspot with a high ratio of Te(IV) contained more illite mineral than others based on their μ -XRD patterns [Fig. 1(B)], possibly implying that Te(IV) could be retained by illite in addition to goethite in soil. Furthermore, Te K-edge EXAFS spectra showed that a prominent peak (Te-O shell) and further distant peaks corresponding to Te-Fe shells were present in the radial structure function (RSF) of goethite, ferrihydrite, and the Te hotspot in soil (Fig. 2). The presence of Te-Fe shells indicates that inner-sphere surface complexes are formed in the surface of Fe(III) hydroxides and natural soil [7-9]. It has been documented that the formation of inner-sphere or outer-sphere complexes during the adsorption of oxyanions on ferrihydrite can be clearly predicted by the

average value of $\text{p}K_{a1}$ and $\text{p}K_{a2}$ [9]. Based on the two $\text{p}K_a$ mode, the inner-sphere complexation would be the main attachment mode for Te(IV), Te(VI), and Se(IV) species, while Se(VI) prefers to form outer-sphere complexes on ferrihydrite. These theoretical predictions are consistent with EXAFS spectroscopic observations here and previous studies [7, 8].

In addition, a leaching experiment showed that approximately 0.1% of Se and less than 0.001% of Te in the same soil sample were leached by water. This significant difference in the solubility of Te and Se can be ascribed to a larger affinity of Te, because both Te(IV) and Te(VI) can be strongly retained by Fe(III) hydroxides in soil particles via inner-sphere complexation, while Se(VI) is readily distributed to water due to the formation of weaker outer-sphere complexes. Therefore, this study clarified the chemical speciation and host phases of Te and Se in the contaminated soil by the μ -XRF, XRD and XAFS techniques. These findings provide important insights into the solubility, mobility, and bioavailability of Te and Se in surface environments.

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