

Oxidation of non-crystalline U(IV): role of reduced sulfur

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Uranium is a contaminant of concern in subsurface environments impacted by mining or ore processing or in areas of naturally occurring uranium-bearing rocks. Hexavalent uranium is soluble and highly mobile, and represents a threat to water quality. Remediation approaches aim at immobilizing uranium, preferably *in situ*. Reductive precipitation is one such strategy and relies on microbial processes to reduce hexavalent uranium to its tetravalent state, which is largely insoluble. Two major types of U(IV) precipitates have been identified: crystalline U(IV) such as uraninite (UO₂) and non-crystalline forms in which U(IV) is associated with a solid phase but coordinated with functional groups such as carboxylic or phosphato groups [1,2]. The latter, referred to as non-crystalline U(IV) (NCU4), is not well characterized, its reactivity is not well constrained and the role of iron sulfide precipitates in its stability poorly understood [3]. In this work, we seek to compare NCU4 stability under oxic conditions in the presence and absence of iron sulfide species. Non-crystalline U(IV) was produced through the reduction of U(VI) in a flow-through column packed with sediment from the Old Rifle CO (USA), experimental site and receiving a cocktail of electron donors in the presence and absence of sulfate (and thus, iron sulfide precipitates). After accumulation of U(IV) in the sediment, it was characterized and found to harbor approximately ~85-95% NCU4. Each sediment type (with or without sulfate) was then placed in continuously stirred tank reactors through which oxic or anoxic water was flowing. The water contained either 1 or 10 mM sodium bicarbonate. The leaching of uranium was monitored and the speciation of the sediment post-leaching characterized. We observed that, under oxic conditions, about ~90% of the NCU4 was oxidized both both conditions (sulfate and no sulfate) while UO₂ largely remained constant. In contrast, batch experiments revealed that, surprisingly, the presence of reduced sulfur in the sediment enhanced the rate of oxidation of NCU4. Further investigation showed that reactive oxygen species play an important role in NCU4 oxidation under fully oxic conditions. The work presented offers a more definitive view of the fate of NCU4 under environmentally relevant conditions.

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