Alteration of U(VI)-Phases Under Oxidizing Conditions

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INTRODUCTION

Uranium-(VI) phases are the primary alteration products of the UO_2 in spent nuclear fuel and the UO_{2+x} in natural uranium deposits. The U(VI)-phases generally form sheet structures of edge-sharing UO_2^{2+} polyhedra. The complexity of these structures offers numerous possibilities for coupled-substitutions of trace metals and radionuclides. The incorporation of radionuclides into U(VI)-structures provides a potential barrier to their release and transport in a geologic repository that experiences oxidizing conditions. In this study, we have used natural samples of UO_{2+x}, to study the U(VI)-phases that form during alteration and to determine the fate of the associated trace elements.

SAMPLE AND ANALYTICAL METHODS

Samples were obtained from the Marshall Pass deposit, Colorado, a unique locality because of the presence of Cu minerals; thus, this is also a potential analogue to canister interactions with spent nuclear fuel (SNF)[1] for programs considering such waste package materials. The uranium ore deposit is located close to the surface and has reacted both with ground and meteoritic waters. Primary uraninite formed under reducing conditions in veins controlled by faulting. The UO_{2+x} is intergrown with Cu, Zn, Pb, Sb, Ag, As sulfides and sulfosalts, such as tetrahedrite, covellite, chalcocite, chalcopyrite, galena and sphalerite[2]. Five samples of different degrees of alteration were analysed by optical petrography, scanning electron microscopy/energy dispersive X-ray spectrometry (SEM/EDS), electron microprobe analysis (EMPA) and transmission electron microscopy (TEM).

RESULTS AND DISCUSSION

The chemical composition of the uraninite by EMPA is 75.1-77.6 wt% U, 1.2-2.0 wt.% Ca 1.0-2.1 wt.% Pb, 0.98-1.7 wt.% W, 0.16-1.0 wt.% As, with minor amounts (<1 wt.%) of Zr, Ti, REE, Mo, Si, P and Fe.

The first stage of alteration was caused by penetration of oxidizing fluids with W and Mo. The oxidation of U may have caused the reduction in the uraninite unit cell parameter, creating microfractures, and providing additional pathways for the fluids. Uraninite grains show grain spallation, finally resulting in lost of cohesion and subsequent separation. Sulfides and sulfosalts are unstable under these conditions, liberating Pb, As, S, Cu, Zn, Sb, Ag. The presence of Mo in the fluids with liberated Pb resulted in precipitation of wulfenite ($PbMoO_4$). Acidic solutions derived from the dissolution of the sulfides caused the oxidation and dissolution of uraninite. In general, the sequence of uraninite alteration is consistent with that previously reported from the Nopal I deposit (Mexico) and the laboratory experiments: uraninite, uranyl oxide hydrates, uranyl silicates, and finally, alkali + alkali earth uranyl silicates[3,4].

In the present samples, the sequence of formation began with ianthinite, $U^{4+}(UO_2)O_4(OH)_6(H_2O)_9$, followed by schoepite-type minerals, e.g., $(UO_2)_8O_2(OH)_{12}(H_2O)_{12}$, with mainly preserved "dehydrated schoepite". Subsequently, two phases formed: (*i*) a rare Pb-uranyl oxide hydrate and (*ii*) mats of fine-grained platy crystals of a Ba-Mo-W uranyl phase with the composition of: 47.4-55.2 wt.% of U, 7.27-14.8 wt.% of W, 5.73-10.9 wt.% of Mo, 3.62-4.54 wt.% of Ba, 1.25-1.65 wt.% of Ti, 0.65-1.32 wt.% of Fe, and 0.26-0.61 wt.% of Ce. The latter phase is a uranotungstite-type[5] mineral, $(Ba,Pb,Fe^{2+})(UO_2)_2(WO_4)(OH)_4(H_2O)_{12}$, with possible substitution of Mo for W. A similar, but previously unknown, Cs-Ba-Mo uranyl oxide hydrate has been reported in the SNF corrosion experiments[6]. At the next stage of paragenesis, fluids with Si and Ca entered into the system leading to supersaturation for uranophane, $Ca(UO_2)_2(SiO_3OH)_2(H_2O)_5$, and then uranyl arsenates, (trogerite, $(UO_2)_3(AsO_4)_2(H_2O)_{12}$; metazeunerite, $Cu[(UO_2)(AsO_4)]_2(H_2O)_8$), precipitated partially replacing the previously formed phases.

A different alteration sequence was observed in the areas where uraninite is intergrown with sulfides and sulfosalts. The Cu-bearing minerals (tetrahedrite, covellite, chalcocite, chalcopyrite) show evidence of dissolution, such as corrosion rinds. The paragenesis of uranyl-minerals including Cu in the system may be applicable to the corrosion of Cu-based SNF containers[1]. In veinlets, (meta)zeunerite precipitated replacing uraninite and the Cu-minerals, as well. A thin layer (2-5μm) of a fine-grained unknown phase enriched in U (44.6-49.2 wt.%) and Sb (22.4-26.1 wt%) was found between uraninite, U-arsenate and tetrahedrite. This may be a new U-Sb mineral, a mixture of uranyl oxide hydrate and Sb oxide or antimonite containing U, which has been proposed as a phase that forms in the fission-product waste stream that results from the reprocessing of SNF, especially $^{90}Sr^{2+}$ and REE^{3+} in acidic waste streams[7].

The last stage of alteration is most likely caused by reaction with meteoric water of low ionic strength. U-arsenates and silicates were replaced by "dehydrated schoepite" (II). Finally, uranyl minerals were altered to swamboite, $U^{6+}(UO_2)_6(SiO_3OH)_6(H_2O)_{30}$.

CONCLUSIONS

In Marshall Pass, Colorado, oxidizing fluids of various compositions resulted in a complex sequence of alteration phases. The most common trace element is As, forming uranyl arsenates as a major phase. In case of supersaturation with W and Mo, an unknown U-W-Mo phase precipitated. Additionally, crystallization of a U-Sb phase reflects substantial local variability in Sb-concentration. This occurrence provides a good example of the complexity one may expect in anticipating the results of the corrosion of SNF in an open system under oxidizing conditions.

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