

Uranium speciation in two Freital mine-tailing samples: SSE, μ -XRD, and μ -XRF results

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Introduction

- During the uranium ore extraction, uranium is converted from relatively insoluble U(IV) minerals to highly mobile U(VI) species.
- Contaminated mine waste piles and tailings and surrounding soils are usually covered by soil materials to reduce the Rn emission and radionuclide spreading by wind and water erosion.
- Little is known on the further fate of uranium at these sites. Only by determining the chemical forms of uranium, one will know if uranium remains mobile for extended time periods, or if it precipitates as secondary minerals.
- We investigated the uranium speciation in covered mine tailings by a combination of micro-spectroscopic and wet chemical approaches, which are fundamental to achieve reliable results.

Materials & Methods

Samples:

Samples:						
Uranium mine tailings Freital (former Wismut site, Saxony,		F1	F3		F1	F3
Germany)	рН/-	8.0	4.0			
Acidia are autraction from 1040 1060	Eh/mV	450	500	Co	45	37
Acidic ore extraction from 1949 - 1960	U	444	425	Ni	193	115
After 1968 covered with construction waste and tin-ore mining	Р	651	597	Cu	682	349
waste	s	25900	5433	Zn	876	294
Samples E1 and E2 collected from E and 12 m denth	Cl	52	127	As	254	177
samples FT and F3 collected from 5 and 12 m depth	K	27950	33500	Se	15	16
Large range in pH (4-8)	Ca	12390	1261	Hg	3	3
Oxic pore water conditions at sampling (1994)	Mn	71	135	Pb	1410	128
ono poro nator contantono at camping (1777)	Fe	21950	26800	Th	16	27
<u>μ-XRF and μ-XRD at ID-22 (ESRF):</u>						
u spot: 4*1.5 um ²	_					
= 1011 pb/s flux at E = 18 kol/						
		SI(LI)				
XRF data extraction with AXIL (Univ. of Antwerp)		,				
Pixel conversion with Fit2D (Hammersley, ESRF)						
Diffraction		· .				_
Dimaction	l _i (y,z)	- N				
	19	0° 1	P	KB foo	using	
				mir	ror	

Elemental Mapping (μ-XRF)

Distribution of U, K, S (left) and µ-XRF of selected microspots (right)



<u>Sample F1 (pH 8):</u>
U predominates
homogeneously distributed at

relatively low concentrations (mg/kg) in aggregates with a diameter of tens to hundreds of μ m, where it is associated with K and 3d metals

Distribution of U, Cu, V (left) and µ-XRF of selected microspots (right)



Sample F3 (pH 4): U is highly enriched in local spots (g/kg) with distinct elemental compositions suggesting a variety of Ucontaining minerals

Identification of crystalline phases (μ-XRD)



ample	Elements Z>18	identified phases
1-bulk		Qz, muscovite, (illite), kaolinite, gypsum
1-d1100	S, Fe, As, Pb, E	Bi,(Qz), muscovite, (jarosite)
	U, Y/Rb, Zr	
1-00	S, K, Fe, Ni, C	u,(Qz), kaolinite, muscovite, jarosite
	Zn, Pb, U	
1-01	like 00	(Qz), kaolinite, muscovite, jarosite
1-02	like 00 +Ti	kaolinite, muscovite, (illite), jarosite
1-03	like 00+Ti	(Qz), kaolinite, muscovite, jarosite
1-07	like 00+Ca +Ti	(Qz), kaolinite, muscovite, (illite) , gypsum,
		jarosite
1-08	like 00+Ca +Ti	(Qz), kaolinite, muscovite, (illite) , gypsum,
		jarosite
1-09	like 00+Ca +Ti	(Qz), kaolinite, muscovite, gypsum, jarosite
3-bulk		Qz, microcline, kaolinite, muscovite, (illite)
² 3-d040	K, V, Fe, U	Qz, muscovite, (illite), hematite, vanuralite
		(Al(UO ₂) ₂ V ₂ O ₈ (OH) x 11H ₂ O)
3-d044	K, Ca, Fe, U	Qz, muscovite , (uraninite), (uranyl hydrox-
		ide)
3-d048	K, Fe, As, U, Y	(Qz), hematite, uraninite, xenotime
3-d052	K, Fe, U	muscovite, (illite), uraninite, uranyl hydrox-
		ide
3-d056	Fe, Cu, Cr, U	(Qz), muscovite, (illite)
3-d060	K, Ca, Ti, V, F	e,(Qz), muscovite, (illite)
	Zn, As, Pb, U	
3-d064	K, Ca, Fe, Br, U	Qz, coffinite

Sample F1 (pH 8): U is associated with the layer silicates muscovite, illite and kaolinite.

Sample F3 (pH 4): U is hosted by a variety of U minerals, including coffinite, uraninite, uranyl hydroxide, and vanuralite, but also associated with layer silicates

Conclusions

Sample F1 (pH 8):

Identification of soluble phases (SSE)



Selective Sequential Extractions (SSE): Zeien, H.; Brümmer, G. W. *Mitt. Dtsch. Bodenkundl. Ges.* 1989, *59*, 505-510.

Sample F1: U is predominantly water soluble and/or ion exchangeable

Sample F3: U is predominantly hosted by recalcitrant solid phases, together with Th, Fe, Pb, and V The diffuse distribution of low U concentrations among aggregates of layer silicates, and the high extractability suggest that U is sorbed to layer silicate surfaces. The type of minerals (muscovite, illite and kaolinite) and the high pH are in line with inner-sphere sorption on edge sites of the minerals, while the extraction during SSE 1 suggest outer-sphere sorption (ion exchange).

Sample F3 (pH 4):

The combination of μ -XRF and μ -XRD enabled us to identify several U(IV) and U(VI) containing minerals like coffinite, uraninite, uranyl hydroxide, and vanuralite. Only a minor part of U is sorbed to layer silicates.

Geochemical implications:

At smaller depth (F1, 5 m), acidity from the ore extraction procedure was completely neutralized by the construction waste (jarosite, gypsum precipitation). Uranium remains highly mobile. At greater depth (F3, 12 m), the low pH was conserved. U(IV) minerals may have precipitated due to lower redox, and/or indicate a smaller ore processing efficiency for these older sediments. Uranium mobility is low.

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