

SYNTHESIS, STRUCTURE AND PROPERTIES OF ZIRCONIUM(IV) AND URANYL PERTECHNETATE AND PERRHENATE

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Formation of pertechnetate complexes with zirconium(IV) and uranium(VI) is believed to be the key point in Tc behavior in PUREX. Numerous attempts were undertaken for the determination of the structure of these compounds, but no data are available for Zr pertechnetate.

As for U(VI), Volk and Belikov [1] and Zaitseva and Slavinskiy [2] have shown that uranyl pertechnetate can form a dihydrate salt while crystallized from its aqueous solutions. This behavior is different from that of uranyl perchlorate forming crystal hydrates with much higher number of coordinated water (5 and 7). Such difference is very important, as smaller hydration numbers valid for TBP solvates could make the complexes lipophilic thus favorizing the extraction to organic phase (note that small hydration numbers correspond to high numbers of coordinated anions for actinyl compounds).

The hydrolysis studies and IR spectra have indicated that pertechnetate is able, to some extent, to complex the uranyl cation even in diluted solution [1]. According to IR spectra of in solid state, pertechnetate was acting as a strong bidentate ligand. In [2] it was shown that uranyl pertechnetate dihydrate, $\text{UO}_2(\text{TcO}_4)_2 \cdot 2\text{H}_2\text{O}$, is stepwise dehydrated to $\text{UO}_2(\text{TcO}_4)_2 \cdot 1.5\text{H}_2\text{O}$, $\text{UO}_2(\text{TcO}_4)_2 \cdot \text{H}_2\text{O}$ and finally to anhydrous $\text{UO}_2(\text{TcO}_4)_2$. No structural information was available.

The only structural study was dealing with Np(VI) pertechnetate [3] where X-ray single crystal analysis of Np(VI) dipertechnetate sesquihydrate has shown that its structure is presented by the formula $(\text{NpO}_2)_2(\text{TcO}_4)_4 \cdot 3\text{H}_2\text{O}$ crystallising in space group P_1 , $Z = 2$, $a = 5.322(2) \text{ \AA}$, $b = 13.034(4) \text{ \AA}$, $c = 15.460(4) \text{ \AA}$, $\alpha = 107.08(2)^\circ$, $\beta = 98.05(2)^\circ$, $\gamma = 93.86(2)^\circ$.

The ribbon structure of this compound was formed by two structure independent NpO_2^{2+} groups bonded one to another by bidentate bridging pertechnetate groups [3]. One NpO_2^{2+} group has all 5 equatorial positions occupied by coordinated TcO_4 groupings: four bidentate and one monodentate, while the other one also coordinates 3 water molecules.

Here we presents some new data on Zr pertechnetate and the indexation of powder diffraction pattern for U(VI) perrhenate.

$\text{Zr}(\text{TcO}_4)_4 \cdot 4\text{H}_2\text{O}$

The compound $\text{Zr}(\text{TcO}_4)_4 \cdot 4\text{H}_2\text{O}$ was prepared by reaction of $\text{ZrO}(\text{CO}_3)$ with 20% HTcO_4 followed by evaporation to dryness in an exsecator with P_2O_5 . The crystals were white coloured and plate by shape. Chemical analysis supported 1:4 ratio of Zr to Tc and 4 water molecules present. The X-ray pattern for $\text{Zr}(\text{TcO}_4)_4 \cdot 4\text{H}_2\text{O}$ is given at Fig. 1.

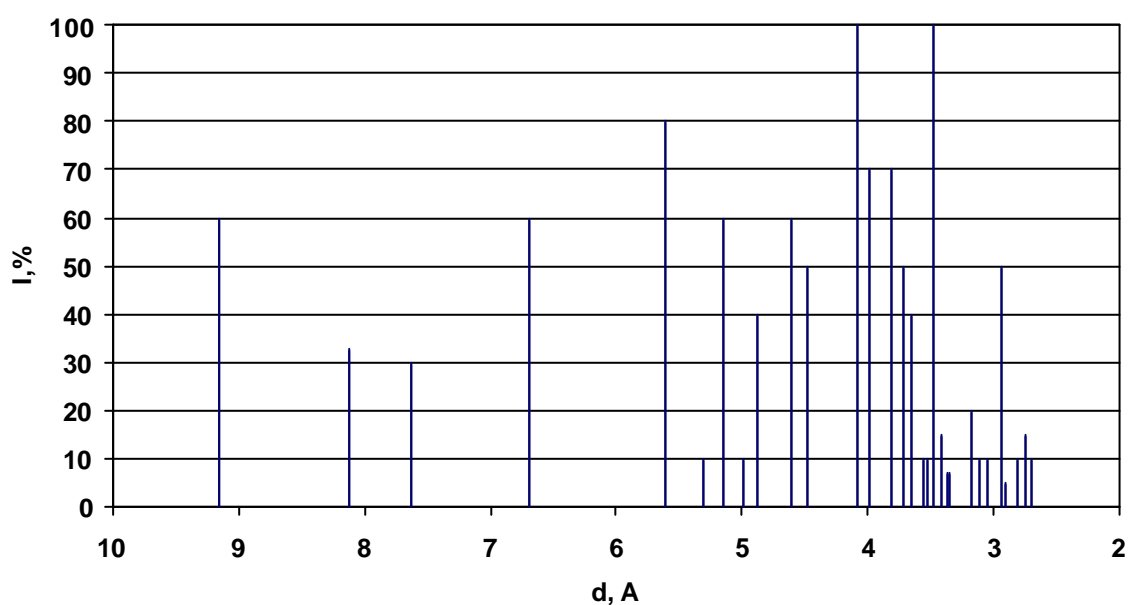


Fig. 1. Experimental X-ray diffraction pattern for $\text{Zr}(\text{TcO}_4)_4 \cdot 4\text{H}_2\text{O}$

The compound $\text{Zr}(\text{TcO}_4)_4 \cdot 4\text{H}_2\text{O}$ was hygroscopic and hydrolysed in excess water to form a new compound with smaller Zr:Tc ratio (~1:2) and partial release of HTcO_4 responsible for the red colour of the formed concentrated solution. This finding strongly supports the importance of hydrolytic studies for Zr(IV) even in highly acidic solutions and complicates the question of the forth of pertechnic acid in concentrated solutions.

$(\text{UO}_2)_2(\text{TcO}_4)_4 \cdot 3\text{H}_2\text{O}$, $(\text{UO}_2)_2(\text{ReO}_4)_4 \cdot 3\text{H}_2\text{O}$, $(\text{NpO}_2)_2(\text{ReO}_4)_4 \cdot 3\text{H}_2\text{O}$, and $(\text{NpO}_2)_2(\text{TcO}_4)_4 \cdot 3\text{H}_2\text{O}$

For indexing $(\text{UO}_2)(\text{ReO}_4)_2 \cdot 1.5\text{H}_2\text{O}$ we have generated the theoretical X-ray powder diffraction pattern for $(\text{NpO}_2)_2(\text{TcO}_4)_4 \cdot 3\text{H}_2\text{O}$ and $(\text{NpO}_2)_2(\text{ReO}_4)_4 \cdot 3\text{H}_2\text{O}$ (considering that Re and Tc salts should be isostructural, see Fig. 2).

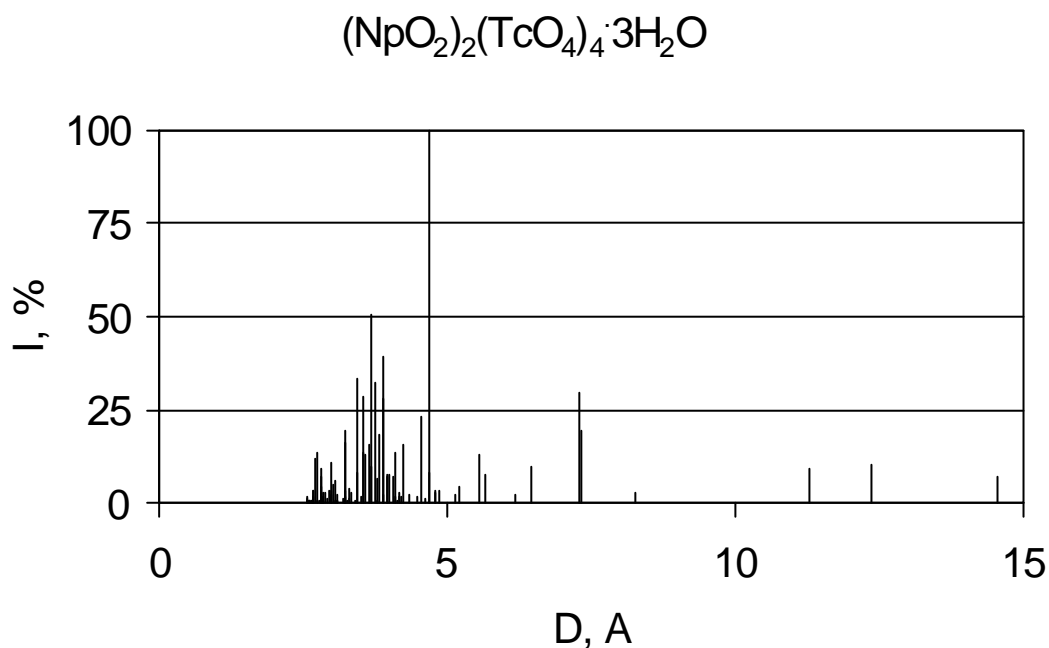


Fig. 2. Generated theoretical X-ray powder diffraction pattern for $(\text{NpO}_2)_2(\text{TcO}_4)_4 \cdot 3\text{H}_2\text{O}$

After the refinement we have indexed the X-ray powder pattern (firstly reported by Silvestre and Freundlich in [4], the corresponding X-ray pattern is given in Fig. 3.).

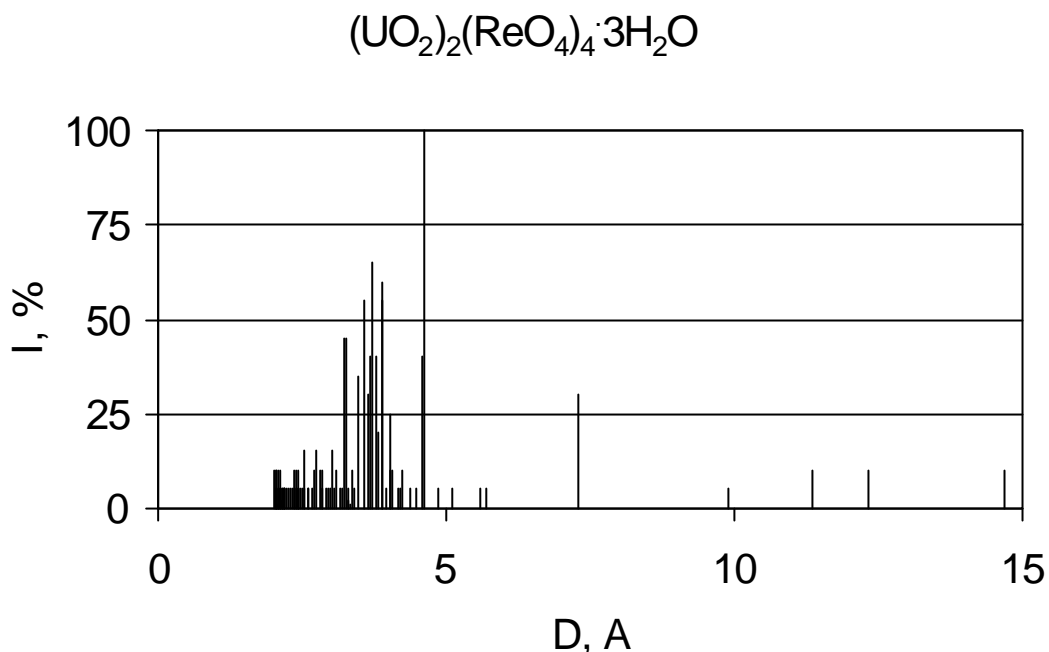
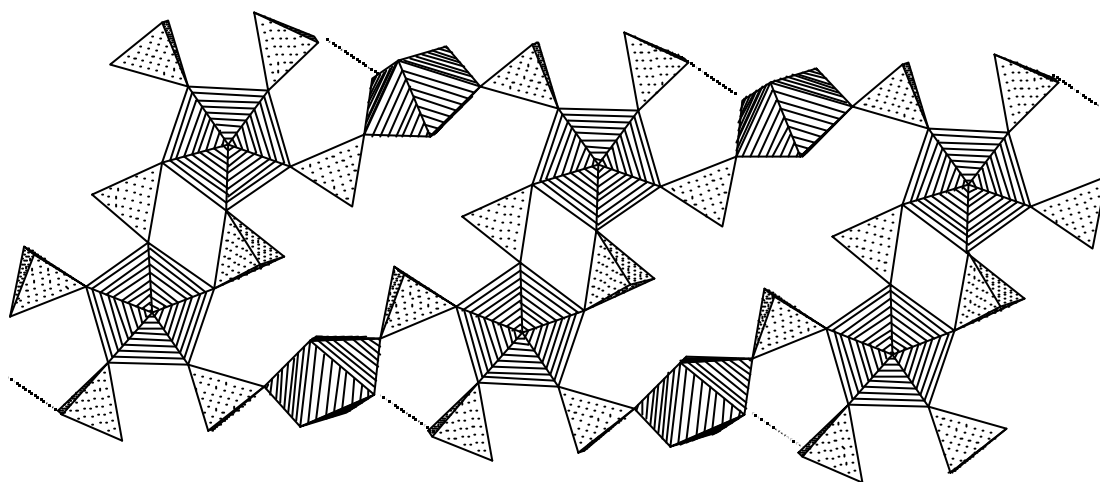


Fig.3. Experimental X-ray powder diffraction pattern for $(\text{UO}_2)_2(\text{ReO}_4)_4 \cdot 3\text{H}_2\text{O}$

We obtained for $(\text{UO}_2)_2(\text{ReO}_4)_4 \cdot 3\text{H}_2\text{O}$ the unit cell with the following parameters: $a = 5.324(2) \text{ \AA}$, $b = 13.073(8) \text{ \AA}$, $c = 15.495(4) \text{ \AA}$, $\alpha = 107.27(3)^\circ$, $\beta = 97.94(3)^\circ$, $\gamma = 94.04(2)^\circ$ (space group P_{-1} , $Z = 2$). So we concluded that it is completely isostructural to $(\text{NpO}_2)_2(\text{TcO}_4)_4 \cdot 3\text{H}_2\text{O}$ and therefore its formula should be duplicated compared to that proposed by Silvestre and Freundlich thus representing two U with different coordination.

This finding led us to conclusion that there is strong coordination between actinide(VI) and permetallate(VII) ions in solid and concentrated solutions (some about 2-5 M by pertechnetate) where these compounds are formed from (and most probably - also for organic solutions in TBP). It is quite typical not only for Np(VI) with pertechnetate but also is valid for U(VI) with perrhenate and should be favourable for U(VI) with pertechnetate.

Fig 4 . Coordination of pertechnetate and perrhenate with uranyl and neptunyl in $(\text{UO}_2)_2(\text{ReO}_4)_4 \cdot 3\text{H}_2\text{O}$ and $(\text{NpO}_2)_2(\text{TcO}_4)_4 \cdot 3\text{H}_2\text{O}$



REFERENCES

1. Volk V.I. and Belikov A.D., Sov. Radiochemistry . 1977, V. , No 6, pp. 811 - 816.
2. Zaytseva L.L. and Slavinsky A.V., Synthesis and physical chemical properties of uranyl pertechnetate. Russ. J. Inorg. Chem. 1976, V. 21, No. 3, pp. 645-1648 (Russ).
3. Fedoseev A.M., Krupa J.C., Budantseva N.A., Grigoriev M.S., Guerman K.E. Synthesis, properties and crystal structure of neptunium (VI) dipertechnetate sesquihydrate $(\text{NpO}_2)_2(\text{TcO}_4)_4 \cdot 3\text{H}_2\text{O}$. Journées des actinides, 1999, 15-17 april, Luso, Portugal. Abstracts.
4. Silvestre J.P. and Freundlich W. Compt. Rend. Acad. Sci. Paris, serie C., 1969, v. 268 C, p. 2098-2101.