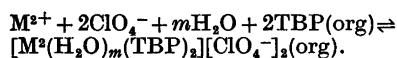


is likely that Pa(IV) is distributed in the form of monomeric aggregates of ion pairs. If the degree of complexation between TOPO and water is constant (or nearly constant), and the influence of the ionic strength on the distribution of Pa(IV) is small for the investigated perchlorate concentration range, then the ion pair must consist of two perchlorate and one Pa(IV) ion, which latter from the electro-neutrality criterium must be a doubly charged cation. Two cations,  $\text{PaO}^{2+}$  or  $\text{Pa}(\text{OH})_2^{2+}$ , are possible, which conclusion is in agreement with observations from other perchlorate media extraction systems.<sup>1,2</sup>

From the TOPO dependence of the distribution ( $\partial \log D / \partial \log [\text{TOPO}] = 2$ ) one concludes that the ion pair of Pa(IV) is solvated with two TOPO molecules. The extraction of Pa(IV) may then be formulated as  $\text{M}^{2+} + 2\text{ClO}_4^- + 2\text{TOPO}(\text{org}) \rightleftharpoons [\text{M}^{2+}(\text{TOPO})_2][\text{ClO}_4^-]_2(\text{org})$ . The possible participation of water in the extraction mechanism has not been studied due to experimental difficulties in determining the water content in the extracted complex when working at trace concentrations of Pa, and in evaluating the influence of the water activity on the extraction (one of the difficulties arises from the fact that TOPO itself extracts water). One notes that the number of TOPO solvates is still two at low acidities (1 M  $\text{HClO}_4$ ), which indicates that the extraction mechanism is uncharged although dehydrolyzation of Pa(IV) is expected.<sup>3</sup>

The distribution of Cr(II) and Zn(II) was found, from a preliminary investigation, like Pa(IV), to be dependent on the second power of the TOPO concentration. The extraction of the divalent ions with TOPO seems therefore to be similar to their extraction with TBP;<sup>7</sup>



The extraction constant for Pa(IV) has been calculated to be  $\log K_D = 4.41 \pm 0.10$  (the total TOPO concentration is used in the calculations, not free TOPO concentration). The thermodynamic constants corresponding to  $K_D$ , obtained from the temperature data, were  $\Delta H^\circ = -72 \pm 9 \text{ kJ mol}^{-1}$  and  $\Delta S^\circ = -157 \pm 31 \text{ J K}^{-1} \text{ mol}^{-1}$ .

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## A High Temperature Iron Telluride with Rhombohedral Structure

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A high temperature iron-tellurium phase has been found by DTA and X-ray high temperature investigations. This phase melts incongruently at about 920 °C, and transforms eutectoidally at 805 °C into the  $\text{Fe}_2\text{As}-\text{PbO}$  type phase with tetragonal structure and the phase with the hexagonal  $\text{NiAs}-\text{Cd}(\text{OH})_2$  type structure. The high temperature phase exists in a rather broad range of homogeneity from about  $\text{FeTe}_{0.80}$  to  $\text{FeTe}_{0.93}$  at 845 °C. This temperature corresponds to the peritectoid decomposition of the  $\text{Fe}_2\text{As}-\text{PbO}$  type phase. The corresponding composition of this phase is between  $\text{FeTe}_{0.75}$  and  $\text{FeTe}_{0.80}$ . By the peritectoid decomposition metallic iron and the high temperature phase are formed.

The X-ray high temperature patterns could be indexed according to a rhombohedral unit cell and the data are given in Table 1.

The lattice constants of  $\text{FeTe}_{0.90}$  were calculated for the temperatures 835 and 870 °C, and of a metal rich sample,  $\text{FeTe}_{0.75}$  at 850 °C. The latter is a two phase sample in which metallic iron exists in equilibrium with the high temperature phase of approximate composition  $\text{FeTe}_{0.80}$ . The following lattice constants refer to hexagonal setting:

$\text{FeTe}_{0.90}$ , 835 °C:  
 $a = 4.013 \pm 0.003 \text{ \AA}$ ,  $c = 20.96 \pm 0.02 \text{ \AA}$   
 $\text{FeTe}_{0.90}$ , 870 °C:

$$a = 4.030 \pm 0.003 \text{ \AA}, c = 21.09 \pm 0.02 \text{ \AA}$$

FeTe<sub>0.80</sub>, 850 °C:

$$a = 4.031 \pm 0.003 \text{ \AA}, c = 21.13 \pm 0.02 \text{ \AA}$$

Table 1. High temperature powder data of FeTe<sub>0.80</sub> at 835 °C. CuK $\alpha$  radiation. Hexagonal indexing.

$I_{\text{obs}}$	$h k l$	$d_{\text{obs}}$	$d_{\text{calc}}$
w	0 0 6	3.50	3.48
m	0 1 2	3.30	3.30
m	1 0 4	2.90	2.90
w	0 1 5	2.671	2.677
St	0 1 8	2.092	2.093
St	1 1 0	2.005	2.006
m	1 0 10	1.795	1.796
w	(1 1 6)	1.742	1.741
	(0 2 1)		1.739
w	2 0 2	1.716	1.715
w	2 0 8	1.450	1.449

The crystal structure appears to be similar to that of the ternary phase Ni<sub>1.5</sub>Fe<sub>1.5</sub>Te<sub>3</sub> found by Stevels.<sup>1</sup> According to Røst and Åkesson<sup>2</sup> the phase exists over a broad homogeneity range at 600 °C, and it seems therefore probable that the ternary phase exists within a range of homogeneity above 805 °C up to the binary composition FeTe<sub>0.8</sub>.

The crystal structure of a sample of the ternary phase having the composition Fe<sub>28</sub>Ni<sub>28</sub>Te<sub>44</sub> has been previously presented by Åkesson and Røst.<sup>3</sup> According to this determination there are partly occupied metal sites in the structure. Therefore, it seems reasonable that an increase of the metal/tellurium ratio will involve expansion of the lattice, as observed for the lattice constants referred above.

Further investigations of the iron-tellurium phases are in progress.

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