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BRIEF COMMUNICATIONS

Extraction of Phosphorus(V), Molybdenum(VI), and Tungsten(VI) from Fluoride Solutions

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Abstract—The influence of titanim(IV) and silicon(IV) on the extraction of phosphorus(V), molybdenum (VI), and tungsten(VI) fluoride complexes by tributyl phosphate was studied.

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Development of effective and economic technologies of processing poor raw material with complicated composition makes urgent the study of the chemistry and technology of rare metals, since the number of consumers of rare metals grows. Industrially Ta(V) and Nb(V) are separated and purified by the extraction from fluoride solutions.

It is known that Ta(V) and Nb(V) are extracted from fluoride solutions as complexes of fluoroelemental acids $HTa(Nb)F_6$. An examination of the published data [1–4] allows us to conclude that many admixed elements, such as Ta(V) and Nb(V), are capable of forming fluoroelemental acids of the H_xMF_y type et al. These are strong acids, which readily dissociate to increase the hydrogen ion concentration (i.e. of the acidity of solutions) and, hence, to improve the Ta(V) and Nb(V) extraction. At the same time, as the acidity of solutions increases the extraction of admixtures also increases. It results in a severe competition between Ta(V) and Nb (V)fluoroelemental acids and macroadmixtures for a location in an organic phase that can impair the separation of Ta(V) and Nb(V) and their purification. Therefore, it is actual to study systematically the mutual influence of fluoride complexes of elements on their extraction in these systems with complicated composition.

It has been shown earlier that the addition of Ti(IV) and Si(IV) to the solutions considerably improves the extraction of Ti(IV), Nb(V), Ta(V), Mo(VI), and W(VI) [5–7].

In this work we have studied the effect of Ti(IV) and Si(IV) on the distribution P(V), Mo(VI), and W(VI) in more detail. The last-named elements are admixtures difficult to separate in the extraction technology of Ta(V) and Nb(V); Ti(IV) and Si(IV) are always present in the niobium-tantalum raw material [usually in considerable amounts, Ti(IV) in particular] [3, 4].

We used tributyl phosphate (TBP) as an extraction agent. The reagents were of analytical grade, TBP was of

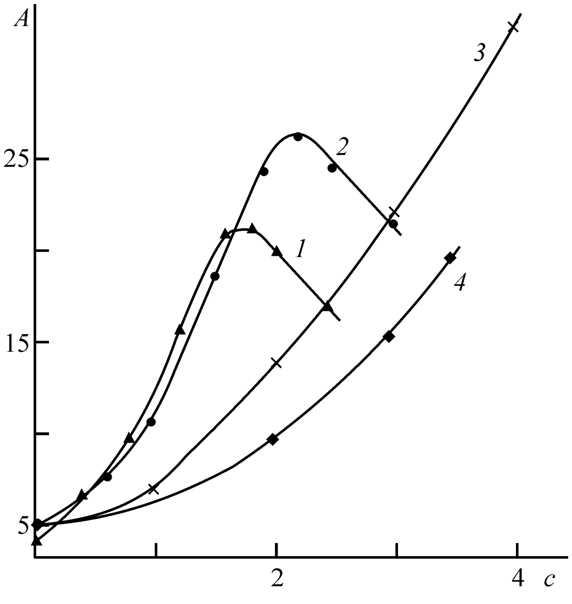

Fig. 1. Effect of (*1, 2*) Ti(IV), (*3*) Si(IV), and (*4*) H_2SO_4 on the extraction of (*1*) 0.1 and (*2–4*) 0.2 M P(V). (*A*) P(V) extraction (%); (*c*) Ti(IV), Si(IV), or H_2SO_4 content (M).

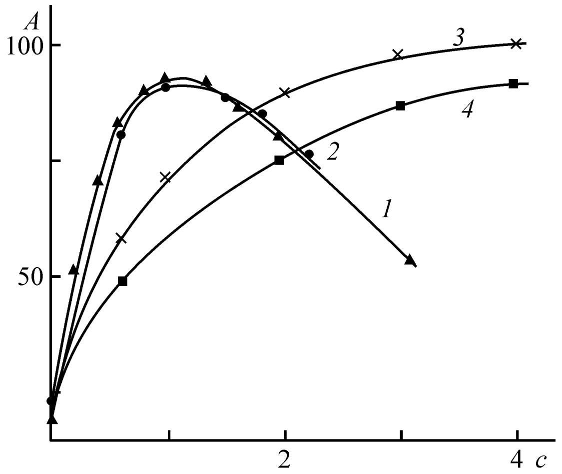

Fig. 2. Effect of (*1, 2*) Ti(IV), (*3*) Si(IV), and (*4*) H_2SO_4 on the extraction of (*1*) 0.03 and (*2–4*) 0.05 M Mo(VI). (*A*) Mo(VI) extraction (%);(*c*) Ti(IV), Si(IV), or H_2SO_4 content (M).

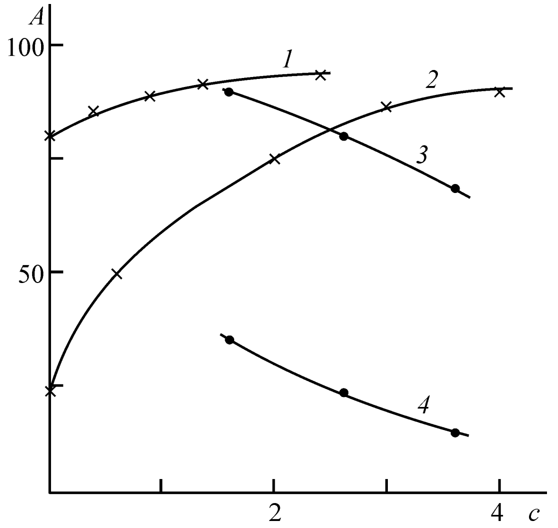

Fig. 3. Effect of (*1, 2*) H_2SO_4 and (*3, 4*) HF_{free} on the extraction of 0.05 M Mo(VI) from Ti(IV) solution. (*A*) Mo(VI) extraction (%);(*c*) H_2SO_4 or HF_{free} content (M). Concentration of Ti(IV) solution (M): (*2, 4*) 0, (*1, 3*) 0.6.

pure grade. The extraction was carried out at the volume ratio of organic and aqueous phases $V_o:V_{aq}=1:1$, the extraction duration was 30 min. To find P(V), Mo(VI), and W(VI) contents, we treated the extracts with a solution of 4 M HF at $V_o:V_{aq}=1:4$ with the subsequent determination of these elements in reextracts by the colorimetric method. Initial aqueous solutions for the extraction were prepared using concentrated HF and H_3PO_4 acids and fluoride solutions containing (M): (1) 5.76 Mo(VI), 20.0 HF; (2) 2.38 W(VI), 23.2 HF; (3) 7.02 Ti(IV) 35.6 HF; (4) 4.75 Si(IV), 28.5 HF. Other features of the technique of the work with aggressive fluoride solutions and of the analytical control are given in [5].

Extraction of W(VI) (0.03 M) from fluoride solutions

Composition of initial solution, M	Extracted, %
2.6 HF_{free}	0.6
2.6 HF_{free} + addition:	
1.2 Ti(IV)	49
2.0 Si(IV)	39
2.0 H_2SO_4	18

The experimental data are presented in Figs. 1–4 and in the table. The extraction of P(V) was carried out at the constant HF_{free} content of 2.0 M, the extraction of Mo(VI) and W(VI), at the 2.6 M content (HF_{free} is a conventional calculated HF content in excess of that required for the formation of H_2TiOF_4, H_2SiF_6, HPF_6, $HMoO_2F_3$, and $H_2WO_2F_4$ complexes, which dominate in the systems under study according to [1–4, 8]).

The addition of Ti(IV) and Si(IV) into solutions sharply improves the extraction of all the elements under study, in particular of W(VI). In the effect on the P(V), Mo(VI), and W(VI) distribution fluoroelemental acids of Ti(IV) and Si(IV) are close to H_2SO_4. Even at the Si(IV) concentration of 2 M the extraction of P(V), Mo(VI), and W(VI) increases from 5, 22, and 0.6 up to 25, 88.5, and 39%, respectively (the table and Figs. 1, 2).

Interesting results (well-pronounced maxima at the curves) were obtained for the extraction of the elements under study from fluoride-titanium solutions (Figs. 1, 2,

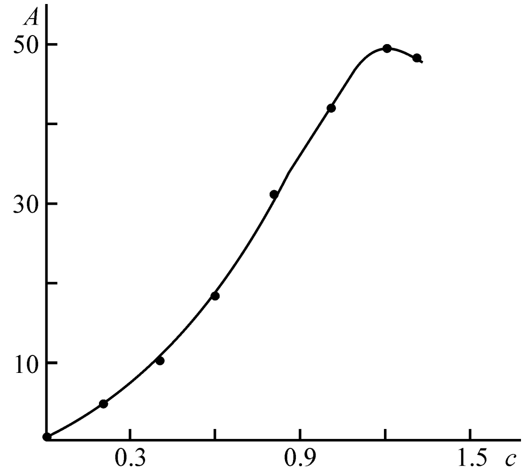

Fig. 4. Effect of Ti(IV) on the extraction of 0.03 M W(VI). (*A*) W(VI) extraction (%); (*c*) Ti(IV) content (M).

and 4). The extraction of P(V), Mo(VI), and W(VI) from H_2SiF_6 and H_2SO_4 solutions is carried out mainly in the form of fluoroelemental acids, a smooth growth of their extraction in these systems being caused by the increase in acidity of solutions due to added H_2SiF_6 or H_2SO_4. In the case of fluoride-titanium solutions we can assume that under the experimental conditions Ti(IV) is capable of forming mixed complex compounds with P(V), Mo(VI), and W(VI), for example heteropolyacids, which have a high extraction ability [9]. These latter are destroyed when a certain level of acidity is reached, that causes the presence of maxima at the corresponding curves. However there are no published data on the possibility of the formation and extraction of heteropolyacids in fluoride systems. More probable reasons of the abnormal course of curves for fluoride-titanium solutions can be the coextraction and suppression of the extraction of P(V), Mo(VI), and W(VI) admixtures in the presence of macroscopic concentrations of Ti(IV) and polymerization of extracted complexes in organic or aqueous phases [1, 2].

The study of the effect of P(V) and Mo(VI) concentrations on the dependence of their distribution on the Ti(IV) content (Figs. 1 and 2) has shown that the extraction in the point of a maximum increases as the P(V) concentration increases. It is attributable to the acidity growth in the system due to the increase in HPF_6 content from 0.1 up to 0.2 M. The concentration of Mo(VI) is much lower than that of P(V), and the variation of Mo(VI) content within the range of 0.03–0.05 M scarcely affects the system acidity, accordingly the curves for these concentration of Mo(VI) practically coincide.

Molybdenum(VI) is extracted most effectively from fluoride-titanium solutions (Fig. 2). At a fairly small Ti(IV) content of about 1 M Mo(VI) the extraction is 90% that points to a possibility of quantitative passing Mo(VI) in the organic phase under conditions of continuous counterflow extraction and realization of only three equilibrium steps. It can be expected that the addition of small amounts of Ti(IV) to the system will make it possible to separate Mo(VI) and W(VI) by the extraction from fluoride solutions (Figs. 1 and 4). The addition of H_2SO_4 to titanium-containing solutions further increases passing Mo(VI) in the organic phase. At the same time an attempt to lower Mo(VI) extraction by increasing HF concentration appeared ineffective (Fig. 3): Mo(VI) extraction for a solution of 3.6 M HF_{free} + 0.6 M Ti(IV) in one step still remains high, about 65%.

The extraction of W(VI) with the addition of Ti(IV) increases most sharply, almost by two orders of magnitude (Fig. 4). We failed to follow the effect of high Ti(IV) contents on the W(VI) distribution, as at Ti(IV) concentrations greater than or equal to 1.4 M, precipitates were formed in the initial solutions. According to preliminary data, these precipitates represent a mixture of tungstic acid and Ti(IV) and W(VI) complicated complex compounds.

As a whole the detected phenomenon (the presence of a maximum of admixture extraction at a certain composition of solutions) is of essential importance for technology. In processing rare-metal raw material of a complicated composition with a high content of admixtures such combination of solution compositions and mutual influence of elements on their extraction is possible when an abnormal high extraction of some admixtures will take place. This phenomenon should be taken into account in the extraction technology of Ta(V), Nb(V), and probably other elements.

CONCLUSIONS

(1) It was found that the extraction of P(V), Mo(VI), and W(VI) sharply increases in the presence of Ti(IV) and Si(IV) macro quantities. The maxima of the P(V), Mo(VI), and W (VI) extraction of 21–26, ~90, and 49%, respectively, were found for the dependence of the extraction degree on the Ti(IV) content.

(2) The data obtained are of interest for the extraction technology of Ta(V) and Nb(V) in the case of processing raw material with high admixture contents.

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