

UDC 546.78

## Sorptive Extraction of Tungsten from the Solution of Sodium Tungstate

S. N. CHEGRINTSEV, A. N. DYACHENKO and R. I. KRAIDENKO

*National Research Tomsk Polytechnical University,  
Pr. Lenina 30, Tomsk 634050 (Russia)**E-mail: chesen@tpu.ru*

(Received December 6, 2012)

### Abstract

Integrated studies of ion exchange extraction of tungsten was carried out in application to the carbonate solutions of autoclave leaching of raw material with low tungsten content. Anionite and desorbent for tungsten extraction were chosen. The integrated technology of processing tungsten-containing raw material was proposed, resulting in obtaining metal tungsten, with the possibility of regeneration of the treating reagent sodium carbonate.

**Key words:** tungsten, sorption, desorption, anionite, AV-17-8, Ambersep 920U, autoclave leaching

### INTRODUCTION

Tungsten content in the ores mined at the territory of Russia is 2–4 %; these ores are of difficult dressability, and the resulting concentrates have complicated composition and low tungsten content. Tungsten content in the wastes from tin production varies within the range 0.5–3.0 %. The data presented in literature [1] suggest the possibility of economically profitable processing of the raw material with low tungsten content basing on autoclave leaching of tungsten with sodium carbonate solution, resulting in the formation of sodium tungstate. In RF, sodium tungstate solution is processed through extraction thus obtaining the solution of ammonium tungstate and tungsten in the form of its oxide  $WO_3$  [2].

The goal of the present work was investigation of the processes and development of the technology of ammonium paratungstate on the basis of ion exchange. The studies were carried out in application to tungsten-containing soda solution from leaching industrial dumps of tin production in the autoclave regime.

### EXPERIMENTAL

The essence of the technology is the ion exchange recovery of tungsten in the sorption pressure column (SPC), followed by obtaining ammonium tungstate. The possibility to regenerate the reagent ( $Na_2CO_3$ ) for subsequent autoclave leaching of tungsten-containing raw material is provided, and the formation of wastes is minimized.

In general, the process includes the following stages: preliminary ion extraction of carbonate ion from the productive solution in the first SPC, subsequent extraction of tungstate ion in the second SPC with obtaining the final product – ammonium paratungstate. To choose the anionite and determine the optimal parameters of the process, the studies were carried out in the dynamic mode with the mixing rate of  $260 \text{ min}^{-1}$ . Tungsten sorption was studied using two widespread strongly basic anionites – Ambersep 920U and AV-17-8.

Productive solutions obtained from autoclave carbonate leaching of industrial dumps of the Novosibirsk Tin Plant were used in the work.

Tungsten concentration in the solution was 3.51 g/L, sodium carbonate 218 g/L, admixtures  $S^{2-}$ ,  $SiO_3^{2-}$ ,  $BO_3^{3-}$ ,  $PO_4^{3-}$  and  $AsO_4^{3-}$ . Tungsten in technological samples was determined by means of atomic absorption spectroscopy using an AAC iCE 3300 instrument.

In order to choose an optimal anionite, we studied the capacities of Ambersep 920U and AV-17-8 resins for tungstate ion. Artificial solutions with the same tungsten content as that in productive solutions (without carbonate ion) was used in experiments. It was established that the capacity with respect to tungsten is 32 kg/m<sup>3</sup> for Ambersep 920U and 42.5 kg/m<sup>3</sup> for AV-17-8 (Fig. 1). Subsequent studies were carried out using only AV-17-8 anionite.

## RESULTS AND DISCUSSION

It was found that the capacity of the anionite decreases almost by a factor of 2.7 during tungsten sorption from productive solutions: from 42.5 to 15.6 kg/m<sup>3</sup>. A decrease in tungsten sorption from productive solutions is connected with the precipitation of sulphides and elemental sulphur on the ionite surface, ionite charging ( $Cl^-$ ,  $SO_4^{2-}$ ,  $NO_3^-$ ,  $OH^-$ ), as well as with the competition between tungstate ions and carbonate ions in the solution.

After leaching and filtration, there is black-coloured, difficultly precipitable suspension in the solution. To determine the nature of the deposit, we carried out X-ray fluorescence analysis of the filtered suspension and the sorbent after its contact with the solution. Sorption is

hindered by sulphur which is present mainly in the form of iron (II) sulphides (FeS). It is proposed to carry out settling of productive solutions with the addition of a flocculant, for example VPK-402, before sorption. This flocculant also makes silicic acid precipitate from solution.

To determine the effect of counterion on the capacity of the resin with respect to tungstate ion, we carried out a series of experiments in which the ionite was charged before experiments to form nitrate, hydroxide, chloride and sulphate forms. It was established that the highest capacity is achieved in the case of sulphate counterion; the capacity of AV-17-8 anionite with respect to tungsten from pure solutions is 65 kg/m<sup>3</sup> of the resin.

Tungsten sorption is substantially dependent on the concentration of carbonate ions in the solution. It was found that the degree of tungsten recovery decreases with an increase in the concentration of carbonate ions in solution. During the contact between the resin saturated with tungstate ions and highly concentrated carbonate solutions, tungsten passes from the resin into the aqueous solution. It was concluded on the basis of the results obtained that it is necessary to carry out the sorption of tungsten from productive solutions in two stages: at the first stage, carbonate ions are extracted from solution, while at the second stage the recovery of tungstate ions is carried out.

The conduction of the process in two stages allows one to separate tungsten from carbonate ions and to desorb sodium carbonate obtaining carbonate solution that may be returned to the stage of treatment of tungsten-containing raw material.

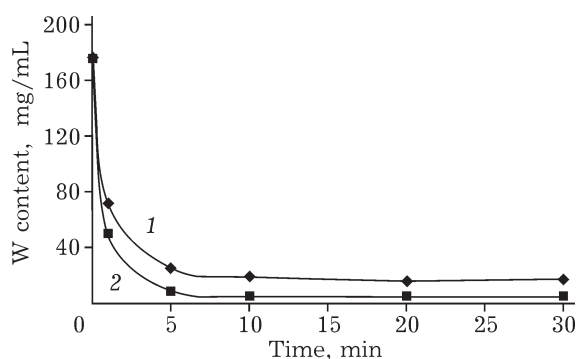


Fig. 1. Curves of tungsten sorption: 1 – Ambersep 920U anionite, 2 – AV-17-8 anionite.

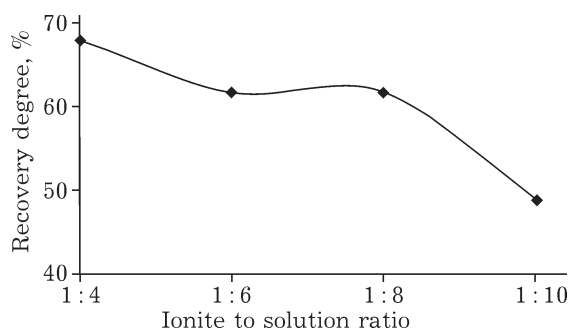


Fig. 2. Dependence of tungsten recovery degree on ionite to solution ratio.

In order to determine the optimal ratio between the ionite and solution, we carried out a series of experiments. It was established that the optimal recovery (60 %) during one step occurs with the ionite to solution ratio of 1 : 8 (Fig. 2).

The solutions of  $\text{NH}_4\text{OH}$  (250 g/L),  $\text{NH}_4\text{NO}_3$  (1000 g/L),  $(\text{NH}_4)_2\text{SO}_4$  (500 g/L) and  $\text{Na}_2\text{SO}_4$  (140 g/L), and a mixture of  $\text{Na}_2\text{SO}_4$  (50 g/L) with  $\text{NH}_4\text{OH}$  (200 g/L) were studied as desorbing agents. Results showed that the solutions

of  $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{NO}_3$  do not desorb tungsten from the resin; ammonium sulphate desorbs tungsten not completely because of the lack of ammonium ions for binding with tungstate. In this connection, the optimal desorbent is the mixture of ammonium sulphate and ammonium hydroxide. Sodium sulphate completely desorbs carbonate ion from the anionite with the formation of sodium carbonate solution. The use of desorbing agents in sul-

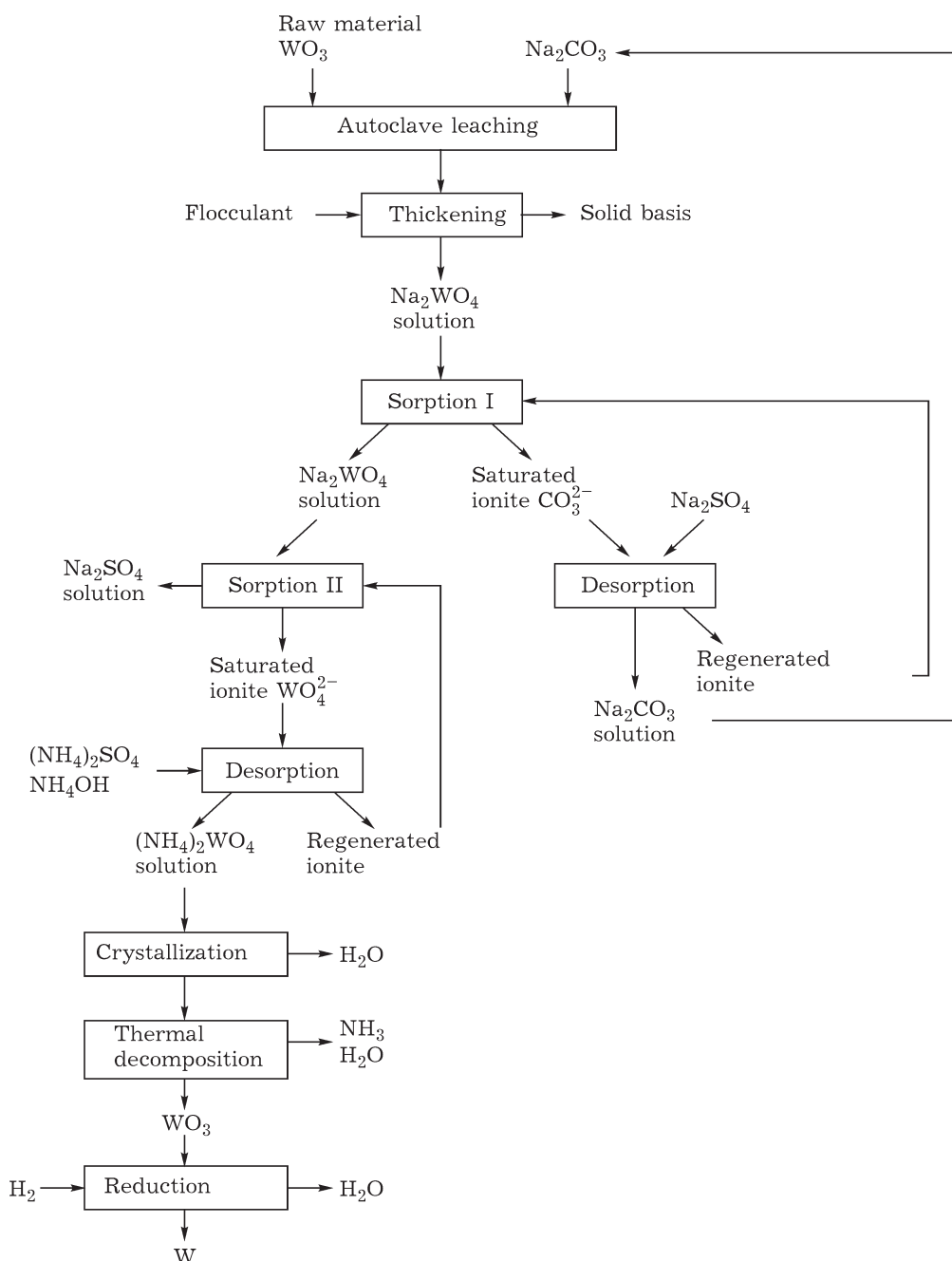


Fig. 3. Schematic of tungsten raw material processing into metal tungsten.

phate form allows recharging the anionite into the necessary state for further sorption.

The results of these studies were the basis for the technological scheme for processing tungsten-containing industrial dumps of tin production. The technology includes autoclave leaching, thickening, sorption recovery of carbonate ion and tungstate ion in two stages, crystallization of the resulting solution of ammonium paratungstate, thermal decomposition and reduction with hydrogen, resulting in metal tungsten as the final product (Fig. 3).

## CONCLUSION

1. Before sorption, in order to eliminate the negative effect of metal sulphides and silicic acid, it is necessary to remove these components through co-precipitation with flocculant (polyacrylamide).

2. The optimal anionite for tungsten sorption is AV-17-8 in the sulphate form with the ratio of ionite to solution equal to 1 : 8.

3. It is necessary to carry out the sorption in two stages: at first, it is necessary to remove carbonate ion from solution, and then tungstate ion. Optimal equipment for these processes is sorption pressure columns.

4. Desorption of  $\text{CO}_3^{2-}$  may be performed using  $\text{Na}_2\text{SO}_4$  solution with the concentration of 140 g/L, while desorption of  $\text{WO}_4^{2-}$  may be achieved with the solution containing  $(\text{NH}_4)_2\text{SO}_4$  50 g/L and  $\text{NH}_4\text{OH}$  200 g/L.

## REFERENCES

- 1 Bolzhakov K. A., Kindyakov P. S., Korshunov V. G., Fedorov P. I., Kislyakov I. P. (Eds.), *Khimiya i Tekhnologiya Redkikh i Rasseyannykh Elementov* (High School Textbook), Vyssh. Shkola, Moscow, 1976.
- 2 URL: <http://www.hidromet.ru>