

## TUNGSTEN PRODUCTION TECHNOLOGY FROM LOW-GRADE TUNGSTEN-CONTAINING MATERIALS

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### Annotation

Tungsten is a worldwide highly-consumed metal. As the tungsten price has increased substantially in the last decade there is an economic imperative to recycle it. It is suggested to involve tungsten-containing metallurgical slags and wastes in reprocessing. Extraction of 87 % of tungsten into solution was reached by autoclave pressure leaching with sodium carbonate (250 g/l) as a leaching agent. Temperature of the process is 220-230 °C, solid-to-liquid ratio – 1:5, stirring rate – 60 rpm, duration – 6 hours. After liquor purification from sulfur and silicon by flocculating agent VPK-402, ion-exchange extraction of tungstate-ion was carried out. Sorption properties of two anion-exchange resins – Amberjet 4200 and AV-17-8 – were studied in static conditions. It was revealed that strongly basic anion-exchange resin AV-17-8 in chloride-form is more capable of tungsten in comparison with Amberjet 4200: 42,5 kilos of W/m<sup>3</sup> against 32 kilos of W/m<sup>3</sup>. Carbonate-ions showed a greater affinity to the resin than tungstate-ions, therefore ion-exchange stage was performed in two steps: 1 – to remove CO<sub>3</sub><sup>2-</sup> from liquor, 2 – extract WO<sub>4</sub><sup>2-</sup>. Desorption was implemented by NH<sub>4</sub>Cl (50 g/l) with solid-to-liquid ratio 2,5:1 yielding ammonium paratungstate (NH<sub>4</sub>)<sub>2</sub>WO<sub>4</sub> (APT). Technology steps for production pure tungsten powder from APT through WO<sub>3</sub> are well-known and described briefly.

Key words: tungsten, market, wastes reprocessing, technology, autoclave leaching, ion-exchange, desorption, ammonium paratungstate, metallic powder.

Research field: chemical technology of rare elements.

Related sciences: chemistry, material sciences, Earth sciences.

### Introduction

Since 19-th century tungsten has been widely used in different fields of industry e. g. tungsten steels for panzer armor, torpedoes' shell, and airplanes' parts; its carbides and borides are known for their solidity and used as material for edge-tools; and of course tungsten is irreplaceable material for a glower of electrical lamp due to its incredibly high melting point 3422 °C. Another tungsten's important properties are very high density 19,25 kg/m<sup>3</sup>, extreme hardness 488 kg/mm<sup>2</sup>, high wear resistance, high tensile strength, low coefficient of expansion and high thermal and electrical conductivity. These unique parameters make tungsten strongly sought-for, therefore its consumption is showing relatively constant growth [1-3]. The metal's output almost doubled in almost 30 years from 25 000 tons per year in 1980 to slightly over 50 000 tons per year in 2008. In spite of steep drop in demand in 2008-2009 which affected every metal's market, output of tungsten is on its increase now with an average growth rate of 4,7 % per year [4].

Solutions that have been proposed to overcome the shortage of the metal consist in extensive enlargement of mining fields – development of new tungsten deposits – and intensive improvements of existing technologies – involve low-grade ores and wastes that were considered to be unreasonable to use. Generally, the first way (new deposits) is a lot more expensive than the second as it consists of mining works and technology development whereas intensive way includes only costs for researches in technology.

Existing technologies that are widely used in industry were designed to produce tungsten from ores with an average metal's concentration at least 5-10 %. The richest ones are situated in China, Republic of Korea, Burma, USA, Spain and Portugal [5]. Russia is represented by Caucasus, Ural and Trans-Baikal deposits containing as low as 4 % of tungsten [6, 7]. All the researches and technologies of tungsten processing have been carried out in sixties and don't meet contemporary issues, thus there is still a lot to be rediscovered.

A modern technology was suggested by a group of scientists from Tomsk Polytechnic University (fig. 1) [8]. The major steps of it are pressure soda leaching of tungsten scrap, extraction W from liquor to water by ion-exchange sorption and desorption yielding ammonium paratungstate (APT) with its, drying, heat-treatment with  $WO_3$  formation and its reduction to W powder by hydrogen.

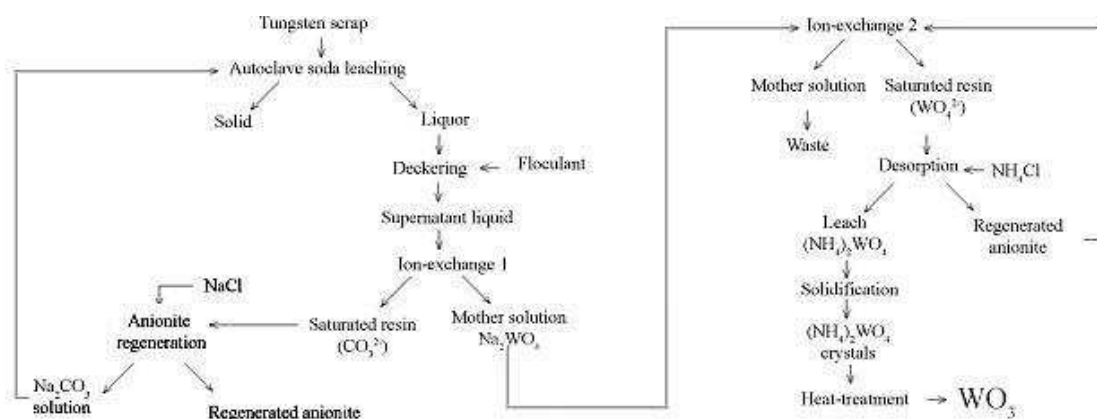


Fig. 1. Technology of tungsten production from low-grade ores and scrap.

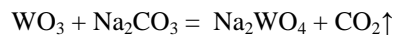
This paper is dedicated to explore optimal conditions under which soda leaching and sorption-desorption operations are about to be carried out with highest yield of W and the lowest costs. Therefore the objectives of this research are to determine:

1. Concentration of leaching agent –  $Na_2CO_3$ ;
2. Solid-to-liquid ratio in leaching process;
3. Duration of leaching process;
4. Stirring rate;
5. Type of ion-exchange resin;
6. Solid-to-liquid ratio in sorption process;
7. Form of mobile ion with the highest exchange capacity on W;
8. The effect of impurities;
9. Ability of ammonium chloride to desorb tungstate-ion from the resin;

10. Solid-to-liquid ratio in desorption process;

**Methodology**

Pressure leaching. The leaching was implemented in autoclave:



Under the temperature of 225 °C a series of experiments was carried out with the concentration of Na<sub>2</sub>CO<sub>3</sub> as a variable. The correspondence between sodium carbonate **m** and degree of extraction **α** is given in table 1.

Table 1. Concentration of leaching agent Na<sub>2</sub>CO<sub>3</sub> study.

<b>m (Na<sub>2</sub>CO<sub>3</sub>), g</b>	75	125	200	250
<b>α<sub>w</sub>, %</b>	40	55	76	84

It is clear that 250 g/l of leaching agent gives the best degree of tungsten's extraction.

The next parameter to identify is solid-to-liquid ratio. For that purposes three samples of leaching mixture were prepared with the ratio 1:2, 1:3 and 1:5. Reaction had been carried out for 8 hours under constant stirring (fig. 2).

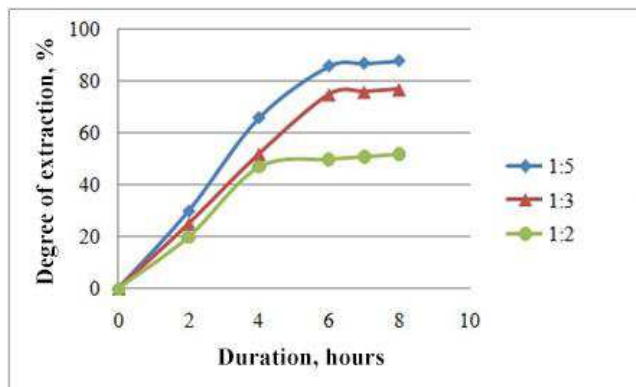
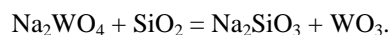


Fig. 2. Solid-to-liquid ratio in leaching process.

As it can be seen from the graph hereinbefore, 1:5 ratio results better extraction of tungsten than the other two options. Moreover implementing soda pressure leaching longer than 6 hours doesn't make sense as the curve achieves plateau and leaching inhibits.

Varying the stirring rate from 0 to 1500 it was revealed that degree of W extraction peaks at 60 rpm. Enhancement of stirring rate leads to contraction of tungsten leaching as it may be supposed that tungstate-ion exchanges with silicon oxide moving from liquor back to oxide form:



Finally, 60 rpm stirring was considered to be the most appropriate.

Ion-exchange. To extract WO<sub>4</sub><sup>2-</sup> from alkaline medium liquor by ion-exchange method two strongly basic anion-exchange resins were explored – Amberjet 4200 and AV-17-8 – as they are sustainable in alkaline medium and produced in large scale nowadays. AV-17-8 demonstrated larger W capacity than Amberjet 4200: 42,5 kg/m<sup>3</sup> in contrast to 32 kg/m<sup>3</sup> accordingly, consequently all the experiments were implemented with AV-17-8 resin.

Solid-to-liquid ratio in sorption process was determined with 1:2, 1:4, 1:6, 1:8, 1:10 samples under constant conditions with constant stirring of resin and liquor. The correspondence between solid-to-liquid ratio and extraction degree is shown in fig. 3.

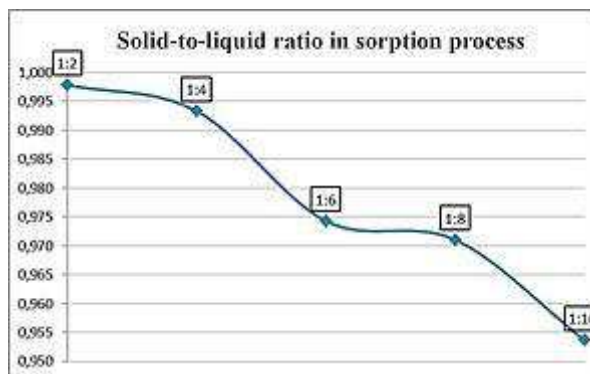


Fig. 3. Solid-to-liquid ratio in sorption process.

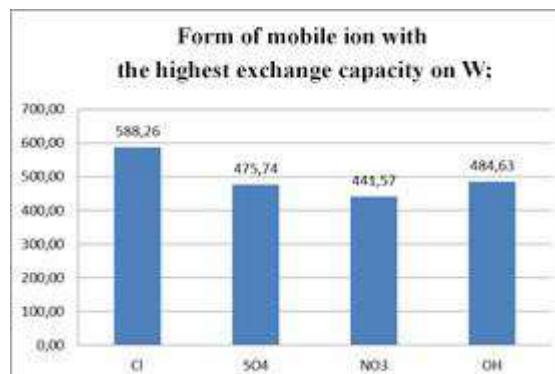
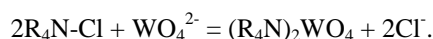


Fig 4. Form of mobile ion.

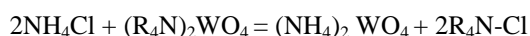
Though 1:2 ratio achieves the best result, it was decided to choose 1:8 ratio for next steps since difference in extraction degree is insignificant but the costs of 1:2 option exceed ones of 1:8.

Investigation in form of mobile ion with the highest exchange capacity on W was performed on resin charged Cl<sup>-</sup>, OH<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> ions. As far as it was predicted by the theory of ion-exchange affinity, chlorine-ion reached the highest W capacity – 588,26 kg/m<sup>3</sup> of the resin – among others (fig. 4) reacting:



It was determined that carbonate-ion suppresses tungstate-ion sorption as it has more affinity to AV-17-8 resin. Solution lays in two-stage sorption: firstly, CO<sub>3</sub><sup>2-</sup> ions are removed and secondly, with no interference action, WO<sub>4</sub><sup>2-</sup> ions are easily extracted. Being sorbed and purified, WO<sub>4</sub><sup>2-</sup> is ready to be moved to liquid form.

Study of desorption was carried out in static conditions with constant stirring. The first and the very needed desorbent NH<sub>4</sub>Cl as it yields ammonium paratungstate and regenerates ion-exchange resin simultaneously:



Research resulted that ammonium chloride (50 g/l) removes WO<sub>4</sub><sup>2-</sup> in great extent, thus it can be used as a desorbing agent in this technology in solid-to-liquid ratio 2,5:1.

## Results

1	Concentration of leaching agent – Na <sub>2</sub> CO <sub>3</sub>	250 g/l
2	Solid-to-liquid ratio in leaching process	1:5
3	Duration of leaching process	6 hours
4	Stirring rate	60 rpm
5	Type of ion-exchange resin	AV-17-8
6	Solid-to-liquid ratio in sorption process	1:8
7	Form of mobile ion with the highest exchange capacity on W	Cl <sup>-</sup> (588,26 kg/m <sup>3</sup> of the resin)

8	The effect of impurities	CO <sub>3</sub> <sup>2-</sup> negatively affects sorption of WO <sub>4</sub> <sup>2-</sup> ; two-stage sorption was proposed
9	Ability of ammonium chloride to desorb tungstate-ion	possible
10	Solid-to-liquid ratio in desorption process	2,5:1

### Conclusion

Conditions under which soda leaching and sorption-desorption operations are about to be carried out with highest benefits and yield were determined. Research has shown that extraction of 87 % of tungsten into solution can be reached by autoclave pressure leaching with sodium carbonate as a leaching agent. Temperature of the process is 220-230 °C, solid-to-liquid ratio – 1:5, stirring rate – 60 rpm, duration – 6 hours. After liquor purification from sulfur and silicon by flocculating agent VPK-402, ion-exchange extraction of tungstate-ion was carried out. Sorption properties of two anion-exchange resins – Amberjet 4200 and AV-17-8 – were studied in static conditions. It was revealed that strongly basic anion-exchange resin AV-17-8 in chloride-form is more capable of tungsten in comparison with Amberjet 4200: 42,5 kilos of W/m<sup>3</sup> against 32 kilos of W/m<sup>3</sup>. Carbonate-ions showed a greater affinity to the resin than tungstate-ions, therefore ion-exchange stage was performed in two steps: 1 – to remove CO<sub>3</sub><sup>2-</sup> from liquor, 2 – extract WO<sub>4</sub><sup>2-</sup>. Desorption was implemented by NH<sub>4</sub>Cl (50 g/l) with solid-to-liquid ratio 2,5:1 yielding ammonium paratungstate (NH<sub>4</sub>)<sub>2</sub>WO<sub>4</sub> (APT).

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