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State and prospects of processing tin-containing raw materials in Kazakhstan

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ABSTRACT

The article discusses the current state-of-the-art in the tin industry and the prospects of the Republic of Kazakhstan. The evaluation is performed in terms of the development of domestic tin production for the growing global demand and the development of the domestic high-tech industry. The study includes the main domestic sources of the raw material base of the tin, which includes mineral raw materials, anthropogenic and secondary waste. Since the most important for the contemporary tin industry are mineral raw materials, the possibility of complex processing of ore from the Syrymbet deposit was studied. Based on the results of the studies performed, it was found that the mineral tin-containing raw materials of the Syrymbet deposit, in addition to cassiterite, also contain acid-soluble tin-containing minerals (stannin, etc.). At the stage of gravity concentration, the most efficient extraction performance of tin into concentrate was found for the gravity separator – amounting to 34.2%. At the leaching stage, the most efficient extraction of tin (1,543 µg/L) showed an aqueous solution of sulfuric acid with a concentration of 100 g/L, at a temperature of 45 °C.

Keywords: tin, Syrymbet deposit, gravity concentration, leaching, sulfuric acid, cassiterite, stannin.

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Introduction

Tin has been one of the metals determining the development of mankind for a long time. So in an alloy of tin with copper, bronze was obtained, which made it possible to make a breakthrough in the development of civilization [1]. In the current time, tin has not lost its importance in the least. The electronic

industry, which is an indicator of the level of technological development, consumes up to 47% of all tin produced, which is used for the manufacture of various solders. In addition, tin is used for the production of tinplate, storage batteries and is used in the chemical industry [2]. Recently, in connection with the COVID-19 pandemic, electronic communication devices have become increasingly important, which are integral parts of the distance learning and work system.

Their production and, accordingly, the consumption of tin will only increase [3]. The price of tin in February 2021 was 23,435 \$/t [4]. Up to 300 kt/y of tin are produced currently [5]. Since the world mineral reserves of tin, which are economically profitable for mining, amount to 4.7 Mt [5], to eliminate economic risks, it is necessary to expand the material base of the tin industry. To do this, it is necessary to involve technogenic and secondary tin-containing waste in recycling. The development of environmentally and economically attractive comprehensive methods for processing tin-containing raw materials is a priority.

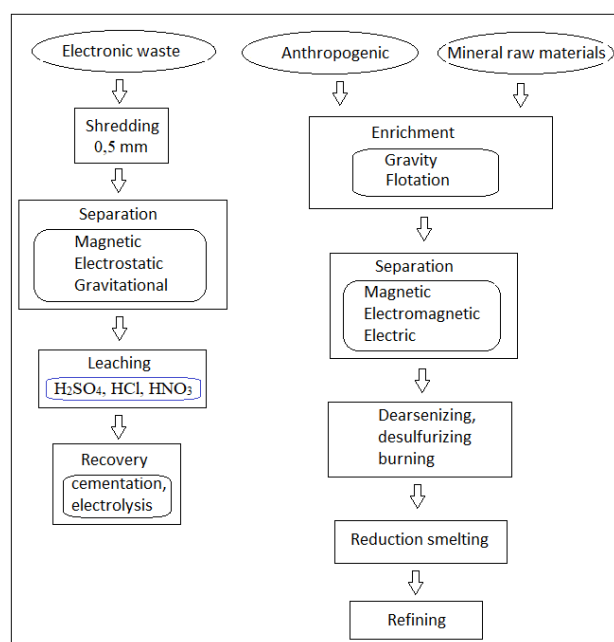


Figure 1 - Typical schemes for the processing of tin-containing raw materials

Typical schemes for processing tin-containing raw materials are shown in Figure 1. The method of processing any given tin-containing raw material depends on the form in which it is contained in the material. So in electronic waste, tin is in a metallic form, within the composition of an alloy (solder) with lead and other elements [6]. The melting point of the solder is from 180 °C. Therefore, often to remove the solder, electronic boards are heated to the melting temperature of the solder, or they are burned in furnaces with electric or fuel heating [6]. In this case, harmful substances are released as a result of the decomposition of the plastic. Also, the increased consumption of electricity is associated with additional CO₂ emissions into the atmosphere [7]. Therefore, the most efficient from the point of view of energy consumption and environmental protection are the hydrometallurgical methods of

processing electronic secondary raw materials using various reagents [8]. Anthropogenic waste materials, such as tailings of polymetallic ore concentration, contain tin in the form of minerals - cassiterite, stannine, etc. The schemes for their processing are close to the scheme for processing mineral raw materials.

In the direction of developing various approaches to the processing of technogenic and secondary tin-containing raw materials, constant work is underway, hydrometallurgical [9], pyrometallurgical and combined processing methods are being developed [10].

In addition to involving tin-containing waste in recycling, it is also necessary to increase the efficiency of processing mineral raw materials.

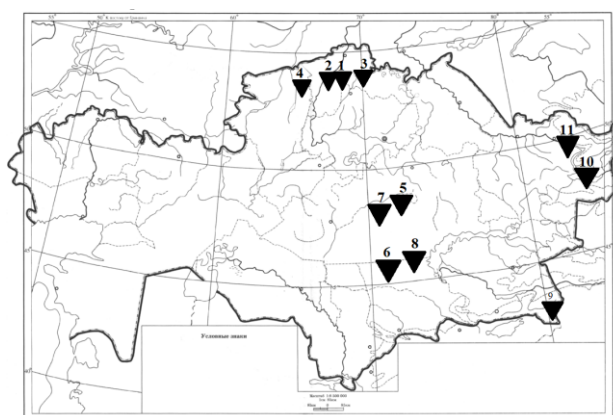


Figure 2 - The largest tin deposits in Kazakhstan Syrymbet -1, Sarybulak -2, Donetskoe - 3, Usken - 4, South Atasu - 5, Maykol - 6, Karaoba - 7, Bis - 8, Karagaily-Aktas-9, Karasu -10, Kalay tapkan – 11

The state balance sheet in Kazakhstan includes tin reserves at the following deposits: Akhmetkino, Bakennoye, Belogorskoye, Verkhnebaimurzhinskoye, Yubileinoye, Medvedka, Kalai-Tapkan, Zhalanash, Karaoba, Syrymbet and others. The largest of them are shown in Figure 2. The ores are characterized by a relatively high content of tin, but as shown by technical and economic calculations, they require pre-enrichment in the process of mining [11]. Northern Kazakhstan is represented by the Syrymbet and Sarybulak (Syrymbet ore field), Donetskoye and Usken deposits. Central Kazakhstan is represented by the Karaoba and Maikol deposits. South Kazakhstan is represented by the Karagayly - Aktas and Biye fields. East Kazakhstan is represented by the Karasu and Belogorskoye fields. The most promising project is the development of the Syrymbet deposit, which ranks first in importance among 15 undeveloped tin deposits in the world. According to the

International Tin Association (ITA), Kazakhstan has tin reserves in the amount of 351 kt [12]. The Syrymbet field development project provides for the extraction of 90.4 kt of tin in concentrate [13].

Placer and bedrock ores are the most important mineral sources for tin production. The main mineral of tin mining is cassiterite (SnO_2) [14]. Due to its high specific gravity, it is usually enriched by gravity methods [15]. However, only relatively large cassiterite particles can be separated by gravity methods. This is usually in the order of 50-60% of the tin content in the ore. Therefore, to increase the efficiency of extracting tin from mineral raw materials, gravity methods are combined with flotation methods [16]. The most profitable are the ores of alluvial deposits. Placer tin ores are enriched by gravity, bedrock - by magnetic separation and combined gravity-flotation methods. In addition to cassiterite, tin in ores can also be found in the form of stannine (Cu_2FeSn_4). In this case, the content of tin in the frame of the total amount can reach up to 70% [17]. At present, the ores of tin deposits have a low content of tin, a lot of impurities, which makes such ores difficult to concentrate by traditional methods. In the case of gravitational enrichment, part of the tin can go into the tailings [18]. Cassiterite goes into tailings because of its small size and stannine because of its lower density compared to cassiterite. To extract tin from tailings and poor ores, various methods are used, the essence of which is the distillation of tin in the form of chlorides, sulfides and oxides. The processes of stripping tin in the form of oxides and sulfides are used at many enterprises [19], but these processes take place at high temperatures, which requires significant fuel costs and complex hardware design. In the presence of acid-soluble forms of tin-containing raw materials, hydrometallurgical methods of tin extraction are the most effective from the point of view of reducing energy and material costs. Sulphuric acid is a typical reagent for hydrometallurgical methods [20]. It would be logical to assume that tin can be extracted from stannine by leaching since, unlike cassiterite, it is soluble in acids.

As can be seen from the state-of-the-art review, hydrometallurgical methods have not been well developed or applied for tin extraction. This outlines a gap in the current knowledge and practice. The purpose of this work is to study the chemical and phase composition of mineral raw materials - ore from the Syrymbet deposit, to study

the possibility of enriching raw materials and complex extraction of valuable components from it using hydrometallurgical methods.

Experimental part

Ore samples were selected for completing necessary analyses. One of the goals was to study the chemical and phase composition of the ore of the Syrymbet deposit, and the other was to study the possibility of enriching raw materials and extracting valuable components from them. To average the composition, the mineral raw materials were mixed, and the raw material was taken by the quartering method. All experiments were carried out in the laboratory at the premises of D. Serikbayev East Kazakhstan Technical University. Samples with a total weight of 1 kg were dried in a drying oven for 48 h, at a temperature of 80 °C. An ICP-MS 7500cx inductively coupled plasma mass spectrometer from Agilent Technologies (USA) was used to study the chemical composition of raw materials by the spectral method. An X'Pert PRO X-ray diffractometer manufactured by PANalytical (Netherlands) was used for the identification of the phase composition. The raw materials were divided into size classes to study the distribution of tin by size classes. Each fraction was weighed on a balance and prepared for further analysis. Also, samples of raw materials were prepared for analysis on a JSM-6390LV scanning microscope manufactured by JEOL Ltd. (Japan). To study the morphology of raw materials (Fig. 3), a BX-51 microscope (Olympus, Japan) was used.

A concentration table (SKO-2) and a gravity separator (ITOMAK 2K) were used to evaluate the possibility of enriching raw materials and extracting valuable components from them. When enriching raw materials through a concentration table - (CKO-2), the following parameters were used: vibration frequency - 310 /min, stroke length - 12 mm, S/L = 2/8. When enrichment through a centrifugal separator (Itomak – 2K), the following parameters were used: water pressure - 0.1 atm., rotation speed - 240 rpm. To determine the chemical composition of raw materials by the spectral method after gravitational enrichment, we used an ICP-MS 7500cx inductively coupled plasma mass spectrometer (Agilent Technologies, USA). To study the phase composition, an X'Pert PRO X-ray diffractometer was used.

To carry out the leaching, the tailings of the gravity concentration of the ITOMAK centrifugal

separator were used. An aqueous solution of sulfuric acid (H₂SO₄) was used as a reagent. The density of H₂SO₄ is 1.84 g/mL. To study the effect of concentration on the extraction of tin from the test material, aqueous solutions of sulfuric acid with a concentration of 20 g/L, 40 g/L, 60 g/L, 80 g/L, 100 g/L, 120 g/L, 140 g/L were used. S/L ratio = 1/3 (50 g / 150 g). Process temperature - 45 °C. Leaching was carried out in a heat-resistant laboratory glassware with stirring on a magnetic stirrer. To determine the chemical composition of raw materials by the spectral method after leaching, an ICP-MS 7500 cx inductively coupled plasma mass spectrometer (Agilent Technologies, USA) was used.

The discussion of the results

Figure 3 shows the topography and microstructure of the ore surface from the Syrymbet deposit.

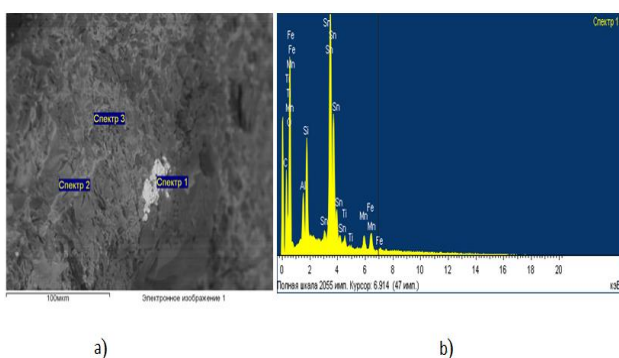


Figure 3 - Topography, the microstructure of the surface of an ore sample from the Syrymbet deposit - a, and profiles of the distribution of elements – b

The profiles of the distribution of elements in the selected area, made using a scanning microscope JSM-6390LV manufactured by JEOL Ltd. (Japan), can be seen there. Figure 4 shows an image of the surface morphology of the sample taken using a BX-51 microscope (Olympus, Japan).



Figure 4 - Surface morphology of an ore sample from the Syrymbet deposit

After the classification of raw materials, the distribution of tin was determined according to eight standard-size classes. The results are presented in Table 1. According to the results of the analysis of the distribution of tin in eight standard size classes, it can be concluded that tin is mainly found in the fraction (-3 + 2) = 36%, and in the classes (-1.5 + 1), (-1+ 0.63), (-0.63 + 0.5), (0.5 + 0.31), (-0.31 + 0.05), tin is distributed almost evenly.

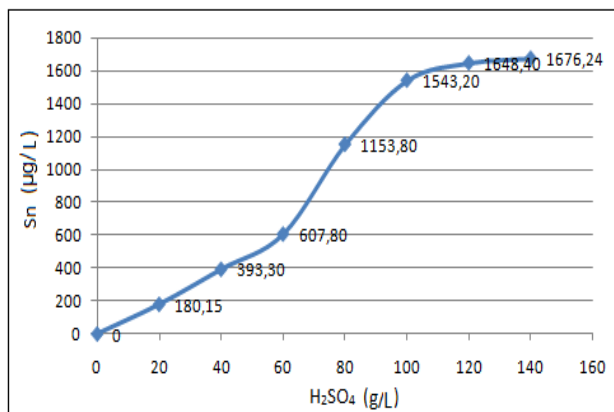
Table 1 - Distribution of tin by eight standard size grades and in the initial mineral raw materials

Size, mm	Output (g)	Content Sn (ppm.)	Distribution, Sn %
-3+2	317	2,757	36
-2+1.5	85.3	1,040	3
-1.5 +1	99.7	3,392	11.3
-1 +0.63	114.4	2,857	11.2
-0.63 +0.5	69.6	3,962	9.7
-0.5 +0.31	207.6	4,912	12
-0.31 +0.05	93	3,940	13
-0.05	3.2	3,535	3.9
Raw material		2,861	

The results of gravity concentration are shown in Table 2. The lowest tin content was found in the classes (-2 + 1.5) and (-0.05). The Itomak 2K gravity separator proved to be the most efficient in terms of the extraction of tin by the gravity method. The result of studying the phase composition of the concentrate showed that all the tin in the concentrate is in the form of cassiterite. It is likely that acid-soluble tin minerals (stannine) are found in the tailings. However, due to the fact that the sensitivity of the X-ray diffractometer makes it possible to analyze the substance at a content of >1%, it was not possible to establish the presence of acid-soluble tin-containing minerals in the tails. As a result of the leaching of the tailings of mineral processing at the ITOMAK unit, it was found that tin is extracted into the productive solution. Therefore, acid-soluble forms of tin are present in the tailings. In this case, the concentration of sulfuric acid has a significant effect on the extraction of tin (Fig. 5). The most effective extraction of tin (1,543 µg/L) was shown by an aqueous solution of sulfuric acid

Table 2 - Results of the performed gravity separation

Equipment	Output, (%)			Content Sn, %			Extraction Sn, %
	Concentrate	Tailings	Intermediate	Concentrate	Tailings	Intermediate	
SKO-2	0.012	93.7	6.288	4.75	0.135	0.16	19.9
ITOMAK 2K	0.008	99.92	-	12	0.016		34.2

**Figure 5** - Dependence of tin extraction depending on concentration

with a concentration of 100 g/L at a temperature of 45 °C. A further increase in the acid concentration showed only a slight increase. At an acid concentration of 120 g / L, the extraction of tin into the productive solution was 1648.4 µg / L, and at 140 g / L - 1676.24 µg / L. Thus, this method can be used for the comprehensive extraction of tin.

Conclusion

As a result of the work carried out, it was found that the extraction of the tin using a concentration table (SKO-2) was 19.9%. The most effective extraction by gravity methods is possible with the use of the gravity separator ITOMAK – 2K. The extraction of tin was 34.2%. In both cases, a significant portion of the tin remained in the tailings. Obviously, it is necessary to continue the work with the aim of greater extraction of tin into

concentrate, as well as extraction of tin from the tailings. The leaching carried out with an aqueous solution of sulfuric acid showed that, in addition to cassiterite, the ore contains acid-soluble forms of tin-containing mineral raw materials, which are effectively leached. At the same time, an increase in the concentration of sulfuric acid significantly increased the extraction of tin into the productive solution. This direction of work is promising, and further study of the effect of temperature and concentration of sulfuric acid will allow choosing the most economical regimes for leaching acid-soluble forms of tin-containing mineral raw materials. Summarizing the possibilities of expanding the base of tin-containing raw materials, it can be stated that Kazakhstan has all the prerequisites for development in this direction. The most promising in this regard are e-waste and anthropogenic raw materials. However, mineral raw materials are by far the main resource for the tin industry.

Conflict of interest. On behalf of all authors, the corresponding author declares that there is no conflict of interest.

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Қазақстанда құрамында қалайы бар шикізатты өңдеудің жай-күйі мен болашағы

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	<p>ТҮЙІНДЕМЕ</p> <p>Мақалада Қазақстан Республикасындағы қалайы өнеркәсібінің қазіргі жағдайы мен болашағы қарастырылған. Бағалау өсіп келе жатқан әлемдік сұранысты және отандық жоғары технологиялық саланың дамуын ескере отырып, қалайының отандық өндірісін дамыту тұрғысынан жүргізілген. Зерттеуде минералдық шикізат, техногендік және қайталама қалдықтар кіретін қалайы шикізат базасының негізгі отандық көздері қарастырылады. Қазіргі қалайы өнеркәсібі үшін минералдық шикізат маңызды болып табылатындықтан, Сырымбет кен орнының кенін кешенді өңдеу мүмкіндігі зерттелді. Жүргізілген зерттеулердің нәтижелері бойынша Сырымбет кен орнының қалайы бар минералды шикізатының құрамында касситериттен басқа, қышқылда еритін қалайы бар минералдар (станнин және т.б.) бар екені анықталды. Гравитациялық байыту кезеңінде концентратқа қалайының ең тиімді бөлінуі гравитациялық сепараторда болатынын көрсетті - 34,2%. Ерітінділеу кезеңінде қалайының ең тиімді бөлінуі 45 ° C температурада 100 грамм / литр концентрациясы бар күкірт қышқылының сулы ерітіндісінде болады (1543 мкг / л).</p> <p>Түйін сөздер: қалайы, Сырымбет кен орны, гравитациялық байыту, ерітінділеу, күкірт қышқылы, касситерит, станнин.</p>
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Состояние и перспективы переработки оловосодержащего сырья в Казахстане

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АННОТАЦИЯ

В статье рассматривается современное состояние и перспективы оловянной отрасли Республики Казахстан. Оценка проводится с точки зрения развития отечественного производства олова с учетом растущего мирового спроса и развития отечественной высокотехнологичной отрасли. В исследование включены основные отечественные источники сырьевой базы олова, в которую

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входят минеральное сырье, техногенные и вторичные отходы. Поскольку важнейшим для современной оловянной промышленности является минеральное сырье, изучалась возможность комплексной переработки руды месторождения Сырымбет. По результатам проведенных исследований установлено, что минеральное оловосодержащее сырье месторождения Сырымбет помимо касситерита содержит также кислоторастворимые оловосодержащие минералы (станнин и др.). На стадии гравитационного обогащения наиболее эффективное извлечение олова в концентрат показал гравитационный сепаратор - 34,2%. На стадии выщелачивания наиболее эффективное извлечение олова (1543 мкг / л) показал водный раствор серной кислоты с концентрацией 100 г / л при температуре 45 ° С.

Ключевые слова: олово, месторождение Сырымбет, гравитационное обогащение, выщелачивание, серная кислота, касситерит, станнин.

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