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HYDROMETALLURGICAL METHOD OF PROCESSING OF CRUDE TELLURIUM DIOXIDE TO PRODUCE PURE TELLURIUM DIOXIDE IN ORDER TO PREPARE PURE TELLURIUM DIOXIDE FOR REFINING

Abstract. The paper presents the results of investigations on the subsequent processing of the tellurium dioxide to produce pure tellurium dioxide and the subsequent refining of pure tellurium dioxide to produce metallic high purity tellurium. On the basis of the studies carried out, the following can be concluded: the depth of purification of tellurium dioxide from lead and copper impurities is much higher in comparison with the available methods. In addition, replacing the energy-intensive and prolonged (usually several hours) operation of cooling the solution to 0 °C with a simpler solution processing operation performed by adding a small amount of cheap and affordable reagent, iron chloride (III) for several minutes, greatly simplifies and accelerates process, and also reduces the cost of its implementation.

Key words: tellurium, impurities, refining, vapor dissolution, ferric chloride (III).

The refining and hydrometallurgical manufactory of lead production in Southern Kazakhstan have significant reserves to increase the production of tellurium. The task of this work was to develop methods for high extraction of tellurium with minimal costs. The production of tellurium dioxide by a hydrometallurgical method usually does not require complicated equipment, high temperatures and pressures, but causes certain difficulties in removing heavy metal impurities, especially copper, silver, plumbum, antimony, tin, hydrargyrum, and nickel. These difficulties increase with the production of high purity tellurium dioxide, when deep purification from these impurities is required.

Due to the fact that from the dust of agglomeration, the tellurium is not extracted from tellurium, and all the dust and lees of the hydrometallurgical manufactory are set in the head of the process, then in the end all the tellurium coming in with the raw material is in the agglomerate and enters the mine reduction melting. Similarly, tellurium is distributed and selenium. In the raw materials that are deposited on the lead plant, 12-15 tons of tellurium and 3.5 tons of selenium are contained per year.

The production of tellurium dioxide by hydrometallurgical method usually does not require complicated equipment, high temperatures and pressures, but it also causes known difficulties in removing impurities of heavy metals, first of all, such as copper, silver, plumbum, antimony, tin, hydrargyrum, nickel. These difficulties increase with the production of high purity tellurium dioxide, when deep purification from these impurities is required.

Previously known works [1-5] on the purification of tellurium dioxide from copper and lead impurities include the interaction of the tellurium dioxide produced by processing telluric slurry from the neutralization of selenium solutions with sodium hydroxide solution, the treatment of the resulting sodium tellurite solution with sodium sulfide, the separation of the precipitated into a precipitate of copper sulfides and lead by filtration, and treatment of the remaining solution with sulfuric acid to precipitate tellurium dioxide. After separation of the precipitate by decantation, its dehydration on the nutch filter, drying, grinding and testing, a commercial tellurium dioxide is obtained. A typical analysis of the product, %:

77.0 tellurium, 0.03 selenium, 0.02 silicic acid, lead is absent. But the product obtained is of poor quality, and the technological processes for cleaning working solutions are very complex and do not give a positive quality to the raw materials.

A method for purification from impurities [6] has been developed to produce high purity tellurium dioxide, used in the production of tellurite glasses for fiber optics, for the growth of paratellurite single crystals. The initial tellurium dioxide is calcined in a vacuum at a temperature of at least 550 °C. in a crucible made of inert material to tellurium dioxide, the calcined tellurium dioxide is melted, the resulting melt is vacuum distilled at a temperature of not more than 780 °C. The purified product is deposited on a substrate whose temperature is 450-650 °C. The invention makes it possible to increase the purity of tellurium dioxide from metal impurities and residual moisture. The lack of technology lies in the high-temperature range of the process.

Scientists [7] have developed a method for purifying tellurium dioxide from copper and lead impurities. The method is based on the interaction of the tellurium dioxide produced by processing the tellurium sludge from the neutralization of selenium solutions, with a solution of sodium hydroxide. In this case, the obtained sodium tellurite solution is treated with sodium sulfide, followed by separation of precipitated copper and lead sulphides by filtration. After that, the filtrate is deoxidized with sulfuric acid to precipitate the dioxide of tellurium. After separation of the precipitate by decantation, its dehydration on the nitch filter, drying, pulverization and testing, a commercial tellurium dioxide is obtained. A typical analysis of the product, %: 77.0 tellurium, 0.03 selenium, 0.02 silicic acid, lead is absent. This method was not viable, as it had the following drawbacks: low purity of the product obtained; the difficulty of cleaning the solution of tellurite natrium from the impurities of copper and lead by means of sodium sulfide in production conditions where it is difficult to ensure the accuracy of the dosage of the reagent; the difficulty of cleaning the solution of tellurite natrium from the impurities of copper and lead by means of sodium sulfide in production conditions where it is difficult to ensure the accuracy of the dosage of the reagent; the use of sodium sulfide as a reagent does not allow to purify the solution from the impurities of tin, antimony and arsenic.

Along with this method, the following scientists developed [8] a method for purification of tellurium dioxide from mixtures of heavy metals. Dioxide of tellurium, obtained by oxidation of technical tellurium with nitric acid, interacts with sodium hydroxide solution, and precipitates of heavy metal impurities are separated, followed by separation of tellurium dioxide from the resulting solution of tellurite sodium by treating the solution with hydrochloric acid to pH 3, 0-3.5. This method is simpler than the previous one, since it does not require the use of a special reagent, sodium sulfide, the interaction of which not only with the solution but also with the impurity sediment can cause the dissolution of some of them (possible contamination with sulfur) and make it difficult to purify the solution. The advantages of this method are as follows: after dissolution of tellurium dioxide in the deposit, gold and selenium completely leave, which can be used in hydrometallurgy of gold. When neutralizing the solution with hydrochloric acid, additional purification of tellurium takes place from copper, lead, silver, manganese, nickel and other impurities. But despite the perfect methods of solving the problem, there are the following disadvantages:

- the need to use as raw material only a material that is fairly pure in tellurium (technical tellurium with a purity of at least 98.5%);
- a low degree of purification of tellurium dioxide from iron (34.5%) and silicon (51.5%) in the alkaline solution stage;
- impossibility of deep purification of tellurium dioxide from lead and copper impurities in the stage of treatment (neutralization) of an alkaline solution with hydrochloric acid, because of their precipitation from the solution together with tellurium dioxide [9, 10].

The most perfect technical essence is the method of purifying tellurium dioxide from copper and lead impurities [11]. The method involves interaction of tellurium dioxide with a solution of sodium hydroxide and a two-stage treatment of the resulting solution of sodium tellurite with a mineral acid separating the precipitate of metal impurities after the first stage while cooling the solution to 0 °C and separating the precipitate of the dioxide of the tellur after the second stage of treatment. The first stage of treatment of the sodium telluride solution with a mineral acid (for example, sulfuric acid) is usually carried out to a pH of 9-10. At the same time, tellurides of copper, lead and other heavy metals fall into the precipitate, as well as a certain amount of tellurium dioxide itself (5-10% of the original quantity). The solution is cooled

to 0 °C to reduce it to the lowest possible concentration of copper and lead tellurites, since the solubility of the latter decreases with decreasing temperature. The second stage of treatment is, as a rule, up to pH = 3-4. In this case practically all the tellurium dioxide contained in the solution falls into the precipitate, as well as part of the impurities that are soluble in it. The method makes it possible to obtain tellurium dioxide with a lead content of $4 \cdot 10^{-3}$ % and copper $1 \cdot 10^{-3}$ % even at high concentrations (up to 5%) of these metals in primary tellurium dioxide. The following nuances are not taken into account:

- low depth of purification of tellurium dioxide from lead, copper and other heavy metals;
- the need to cool the sodium tellurium solution to 0 °C after the first stage of treatment with acid, which requires special refrigerating equipment, an increase in production areas, additional energy and labor costs.

On the basis of the foregoing, our task is to improve the purity of the final product.

A characteristic feature of modern metallurgical production is the integrated use of raw materials. Increasing the extraction of basic and associated metals is the main task of metallurgists in the modern world of growing innovative technologies.

Along with the available methods, foreign scientists [12-15] have developed a method for obtaining tellurium of high purity. Purity (99.9995%) can be achieved by repeated distillation technique under a dynamic vacuum of $\sim 5 \cdot 10^{-3}$ Torr, using a research setup made of quartz tube. The analysis of the impurity of purified tellurium made inductively by double plasma optical emission spectrometry (ICP-OES) confirmed the reduction of the total impurity content from 87 to 4 ppm for three consecutive distillations in a single experimental process. The main impurities in tellurium, such as Al, Ag, Pb, Cu, Bi, Ni, Fe, Mn and Mg, are effectively removed after purification. Analytical results are discussed with regard to vapor pressures (pv) of impurities. The evaporation level (We) and the permeability line (λ) are calculated under experimental vacuum conditions, distillation temperature (T) and system measurements. But the economic value using high-tech devices is higher than the cost price of tellurium, and does not provide for the industrial introduction of technology.

In the process of mine melting, tellurium practically completely passes into the vertebale. 600 kg of tellurium is lost with the waste slag, the average tellurium content in the slag is 0.0003%, i.e. make up - 5% of the loaded with raw materials. The distribution of selenium is somewhat worse, losses with slags reach 2 tons, more than 55 percent of the total amount, the selenium content in BPC slags averages 0.001 percent. This situation is natural from a comparison of the properties of sulfur, selenium and tellurium. Sulfur, contained in the agglomerate by 70-80%, passes into the dump slag (the sulfur content in the slag is 2-2.3%), selenium, as an element more "metallic" than sulfur, goes about half to the slag, the rest to the vertices, and tellurium is the most "metallic" of the elements of Group 6 passes almost entirely into crude lead.

Rough lead is fed to continuous de-laying, part of the slurries that the reflecting furnace could not pass, enter the smelting furnace in a small smelting furnace. In the matte of the reflector furnace, the tellurium content is 0.023%; within a year, 1,200 kg of tellurium and 575 kg of selenium are sent with the product of the matte of the reflecting furnace (the content of the mud in matte is 0.011%), which is about 10% of tellurium, with raw materials and 15% selenium. With the commodity matte of a small smelting furnace, 0.9 t of tellurium (its content is 0.015%) is sent for the year, which is 7% of the raw material and 0.3 t of selenium - 8% of the raw material.

Therefore, under the normal conduct of the process of continuous de-identification, i.e. with an optimal amount of sulfur, arsenic dissolves in the matte in the form of Cu_3As , Fe_2As , in the absence of sulfur, spieses may appear, in this case arsenic practically completely disappears from the ground lead and significant losses of antimony begin.

When loading the sulphidizer - PbS , the matte is washed out and there is practically no loss of antimony with matte, the content of antimony in matte does not exceed 0.1%, while the arsenic content is 2-3%.

In Cu_2S , 14% of metallic lead dissolves at $T = 1100$ °C; in matte containing 20-22% lead, the sulphide content accounts for 6-8%, which dissolves PbSe and PbTe , the content of Te in matte depends on some degree of lead content in matte.

The arsenic content in the lead was at a level of 0.02-0.004%; 94-90% of arsenic was converted into matte and 6-10% into lead-depleted lead, and tellurium by 75-80% passed into de-ground lead.

In the process of fine-tuning matte in a small reflecting furnace, the content of tellurium, as well as silver, is somewhat lower [16].

Thus, 75-80% of tellurium passes into de-lead lead and a high extraction of tellurium through the plant is possible only with a high degree of obscuration of the ground lead.

In factory conditions, 3 tons of tellurium is dispatched for a year with sodium antimonate, 0.57 tons of tellurium is sent to the storage facility with calcium arsenate, and 0.8 tons is extracted into the gray foam. Thus, in lead after distellurization there are 4.37 tons of tellurium. During the same time, 102.8 tons of alkaline telluric melts with a content of 8.67% of the body are obtained, i.e. 8.9 t of tellurium were recovered. The degree of distellurization is an average of 67% per year.

Therefore, the goal of this project is the development of an integrated technology for producing tellurium of high purity of TV-4 brand from tellurium concentrate.

The conducted studies of obtaining tellurium dioxide from alkali melts of lead production were successfully crowned, as evidenced by the results obtained and samples of products of laboratory and experimental-industrial tests, which were presented in other works of the authors of this article.

Therefore, in this paper we present the results of studies on the subsequent processing of crude tellurium dioxide to produce pure tellurium dioxide and the subsequent refining of pure tellurium dioxide to produce metallic high purity tellurium.

Purification of tellurium dioxide from impurities of lead, copper and other heavy metals, including the reaction of the initial tellurium dioxide with a solution of sodium hydroxide and two-stage treatment of the resulting solution of sodium tellurite with mineral acid, separating the precipitate of the impurity metals after the first stage of treatment and precipitating the tellurium dioxide after the second stage, solution sodium tellurite before separating the precipitate of impurity metals, according to theoretical assumptions, is treated with iron (III) chloride. This makes it possible to obtain tellurium dioxide with lead content $(1-2) \cdot 10^{-3}$ and copper $1 \cdot 10^{-5}$ %. At the same time, the content of impurities of other heavy metals, for example, such as silver, gold, bismuth, selenium, mercury, nickel is not more than $1 \cdot 10^{-5}$ %.

The depth of purification of tellurium dioxide from the admixtures of lead and copper is much higher in comparison with the available methods. In addition, replacing the energy-intensive and prolonged (usually several hours) operation of cooling the solution to 0 °C with a simpler solution processing operation performed by adding a small amount of cheap and affordable iron (III) ferment for a few minutes greatly simplifies and accelerates process as well.

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ТЕЛЛУРДЫҢ ТАЗА ҚОСТОТЫҒЫН РАФИНАЦИЯЛАУҒА ДАЙЫНДАУ МАҚСАТЫНДА ТЕЛЛУРДЫҢ ҚОСПАЛЫ ҚОСТОТЫҒЫН ГИДРОМЕТАЛЛУРГИЯЛЫҚ ӘДІСПЕН ҚАЙТА ӨНДЕУ

Аннотация. Мақалада жоғарғы тазалықтағы металды теллурды алуды негізі болатын теллурдың таза қостотығын рафинациялауға дайындау мақсатында теллурдың қоспалы қостотығын гидрометаллургиялық әдіспен қайта өңдеу жолдары қарастырылған. Зерттеулер нәтижесінде келесіде тұжырымдар жасауға болады: қазіргі кезде қолданылып жатқан әдістермен салыстырғанда тазалығы әлдеқайда жоғары құрамында қорғасынның және мыстың қоспасынан тазартылған теллур қостотығын алу болады. Сондай-ақ, энергияны көп жұмсайтын және ұзақ уақытқа (әдетте бірнеше сағат) ерітіндіні салқындату операциясына қарағанда бірнеше минутта орындалатын арзан әрі қол жетімді темір (III)хлоридінің аз мөлшерін қосу арқылы қарапайым өңдеу операциясына алмастыру айтарлықтай жеңілдетеді және жеделдетеді, операцияның жүзеге асырудың құнын төмендетеді.

Түйін сөздер: теллур, қоспа, рафинациялау, чандық шаймалау, темір (III) хлориді.

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ГИДРОМЕТАЛЛУРГИЧЕСКИЙ СПОСОБ ПЕРЕРАБОТКИ ЧЕРНОВОЙ ДВУОКИСИ ТЕЛЛУРА ДЛЯ ПОЛУЧЕНИЯ ЧИСТОЙ ДВУОКИСИ ТЕЛЛУРА С ЦЕЛЬЮ ПОДГОТОВКИ ЧИСТОЙ ДВУОКИСИ ТЕЛЛУРА РАФИНИРОВАНИЮ

Аннотация. В статье представлены результаты исследований по последующей обработке черновой двуокиси теллура с получением чистой двуокиси теллура и последующая рафинация чистой двуокиси теллура для получения теллура металлического высокой чистоты. На основе проведенных исследований можно заключить следующее: глубина очистки двуокиси теллура от примесей свинца и меди значительно выше по сравнению с имеющимися способами. Кроме того, замена энергоемкой и длительной (как правило, несколько часов) операции охлаждения раствора до 0 °С более простой операцией обработки раствора, выполняемой путем добавления в течение нескольких минут небольшого количества дешевого и доступного реагента – хлорида железа (III) значительно упрощает и ускоряет процесс, а также снижает затраты на его осуществление.

Ключевые слова: теллур, примеси, рафинирование, чановое растворение, хлорид железа (III).