УДК 669.283
DOI: 10.36979/1694-500X-2022-22-12-72-79

ПОЛУЧЕНИЕ, ОЧИСТКА И РАСТВОРЕНИЕ ОКСИХЛОРИДНЫХ СОЕДИНЕНИЙ МОЛИБДЕНА В ВОДЕ

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Аннотация: Расширение областей применения молибдена и его соединений повышенной чистоты требует изучения различных способов их очистки. Рассмотрено низкотемпературное хлорирование технического диоксида молибдена, очистка газовой смеси от примеси в системе фильтров, конденсация и растворение в воде очищенных оксихлоридных соединений молибдена. На фильтрах из таблетированного хлорида натрия происходит очистка газообразного диоксидихлорида молибдена от алюминия, железа, хрома и никеля с образованием в малолетучих соединений. Захвата кремния этим фильтром не обнаружено. Очистки от вольфрама на фильтрах гранулированного оксида молибдена практически не происходит. Очищенные оксихлоридные соединения молибдена десублимируются в виде компактных и пухообразных продуктов, имеющих заниженное содержание хлора относительно стехиометрического состава диоксидихлорида молибдена. Компактные оксихлоридные соединения молибдена растворяется в дистилированой воде практически без осадка. При растворении пухообразных соединений молибдена образуется ощутимый осадок, в который переходит значительная часть примесей.

Ключевые слова: молибден; оксихлоридные соединения; сублимация; конденсация; растворение; полимолибденовые кислоты.

МОЛИБДЕН ОКСИХЛОРИД КОШУЛМАЛАРЫН АЛУУ, ТАЗАЛОО ЖАНА СУУДА ЭРИТҮҮ

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Аннотация: Молибденди жана анын жогорку тазалыктагы бирикмелерин колдонуу тармактарынын кеңейиши аларды тазалоонун ар кандай ыкмаларын изилдөөнү талап кылат. Молибдендин техникалык диоксидин төмөнкү температурада хлорлоо, фильтр системасындагы газ аралашмасын аралашмалардан тазалоо, конденсация жана молибдендин тазаланган оксихлорид кошундуларын сууда эритүү каралган. Натрий хлоридинин таблеткаларынын чыпкаларында молибден диоксид хлоридинин газын алюминийден, темирден, хромдон жана никелден тазалоо жүрүп, аз учуучу кошулмаларды пайда кылат. Бул чыпка аркылуу кремнийди кармоо аныкталган жок. Гранулдуу молибден кычкылынын чыпкаларындагы вольфрамды тазалоо дээрлик жок. Тазаланган молибден оксихлоридинин кошулмалары молибдендин диоксидинин стехиометриялык курамына салыштырмалуу хлордун бааланбаган курамына ээ болгон компакт жана үлпүлдөк азыктар түрүндө десублимацияланат. Молибдендин компакттуу оксихлориддик кошулмалары дээрлик чөкмөсүз тазаланган сууда эрийт. Молибдендин үлпүлдөк кошулмаларын эриткенде, сезилүүчү чөкмө пайда болот, ага аралашмалардын кыйла бөлүгү өтөт.

Түйүндүү сөздөр: молибден; оксихлориддик кошулмалар; сублимация; конденсация; эритүү; полимолибдик кислоталар.

PREPARATION, PURIFICATION AND DISSOLUTION OF MOLYBDENUM OXYCHLORIDE COMPOUNDS IN WATER

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Abstract. Expansion of the fields of application of molybdenum and its compounds of high purity requires the study of their various purification methods. The paper considers low-temperature chlorination of technical molybdenum dioxide, purification of the gas mixture from impurities in the filter system, condensation and dissolution of purified molybdenum oxychloride compounds in water. On filters made of tableted sodium chloride, gaseous molybdenum dioxide is purified from aluminum, iron, chromium and nickel with the formation of low-volatile compounds. The capture of silicon by this filter was not detected. Purification of tungsten on filters of granular molybdenum oxide practically does not occur. Purified molybdenum oxychloride compounds are desublimated in the form of compact and fluffy products with an underestimated chlorine content relative to the stoichiometric composition of molybdenum dioxide. Compact molybdenum oxychloride compounds dissolve in distilled water with little or no precipitation. When dissolving fluffy compounds of molybdenum, a tangible precipitate is formed, into which a significant part of the impurities passes.

Keywords: molybdenum; oxychloride compounds; sublimation; condensation; dissolution; polymolybdic acids.

In modern technology, the role of molybdenum is quite significant. Traditionally, it has been used mainly in the creation of heat-resistant alloys [1, 2]. However recently, molybdenum has begun to be used in such important industries as: powder metallurgy, electro-vacuum technology, semiconductor electronics, nuclear power [3, 4]. With the discovery of new technologies for the production of high-purity molybdenum compounds, the areas of their research and use have significcantly expanded [5–8].

Usually molybdenum is extracted from concentrates at pyrometallurgical and hydrometallurgical processing plants. Hydrometallurgical conversion is multi-stage and requires cumbersome and complex hardware design of the process, since solutions must be cleaned in different ways from a large number of different impurities in it [9]. Considering the high elasticity of vapors of molybdenum and tungsten chlorides and oxychlorides, pyrometallurgical processes of chlorination of compounds of these metals are widely used in metallurgy for the production of the pure products [10, 11]. On the issues of chlorination of molybdenum raw materials and the production of molybdenum oxychlorides, a large number of works were carried out by Glukhov with employees [12, 13].

In order to obtain pure molybdenum compounds, a highly technological scheme is implemented in this work, including low-temperature chlorination of technical molybdenum dioxide, purification of the gas mixture from impurities in the filter system, condensation and dissolution of purified molybdenum oxychloride compound in water by the production of molybdenum acids.

Methodics of research. The mechanism for the production of molybdenum dioxychloride consists of a nickel chlorinator, a block of active filters and a condenser of purified molybdenum oxychlorides. Low-temperature chlorination is carried out at a temperature of 190–220°C and consisted in supplying chlorine gas to a chlorinator in which the initial molybdenum dioxide concentrate was already heated to the required temperature.

To purify the products of the chlorination reaction from impurities, a gas stream containing a mixture of chlorine derivatives of molybdenum, tungsten, aluminum, iron and other impurity chlorides was passed sequentially through heated to 200–250° With two filter nozzles. The first contained tableted sodium chlorides, the second - granular molybdenum trioxide. The purified gas stream from the filter system enters the condenser, in which it is desublimated. This chlorination method is highly selective with a deep degree of molybdenum extraction from technical raw materials [14]. The low temperature of the chlorination reaction makes it possible to manufacture equipment from relatively inexpensive structural materials, and especially- nickel.

Results and discussions. According to the used technology, the main part of the impurities is removed at the chlorination stage. The impurities contained in the initial molybdenum oxide, with the exception of iron, aluminum and tungsten, either do not react with chlorine at temperatures up to 220 ° C, or form non-volatile chlorides at this temperature. The resulting molybdenum dioxide is sublimated at a temperature of 157 °C and

flies away from the reaction zone. Iron and aluminum create chlorides with boiling and ignition temperatures of 315 and 183 °C, respectively, and tungsten forms a mixture of oxychlorides, of which only tungsten oxytetrachloride has a high vapor pressure (Temperature of boiling = 224 °C) [11].

During the purification of molybdenum vapor-gas dioxodichloride, the accompanying impurities in the form of aluminum, iron, nickel and chromium chlorides bind to alkali metal chlorides into low-volatile, low-melting compounds of the NAECLN type by reaction:

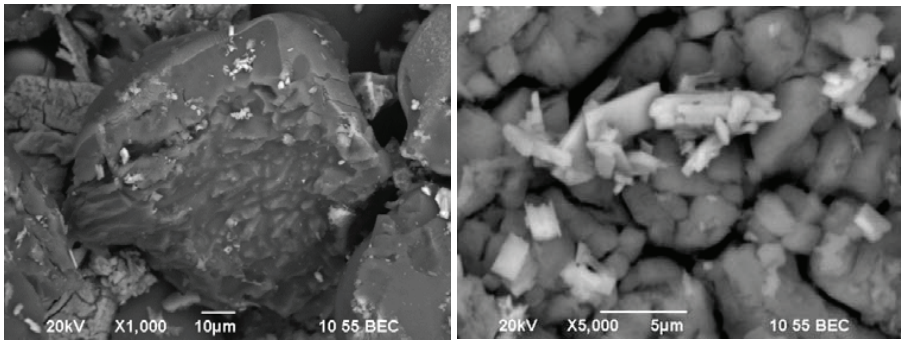
$$NaCl + MeCl_n = NaMeCl_{n+1.} \quad (1)$$

Silicon, which is in a vapor-gas mixture, usually in the form of chlorosilane, forms a non-volatile compound of Na2SiCl6 when interacting with sodium chloride:

$$SiCl_4 + 2NaCl = Na_2SiCl_6. \quad (2)$$

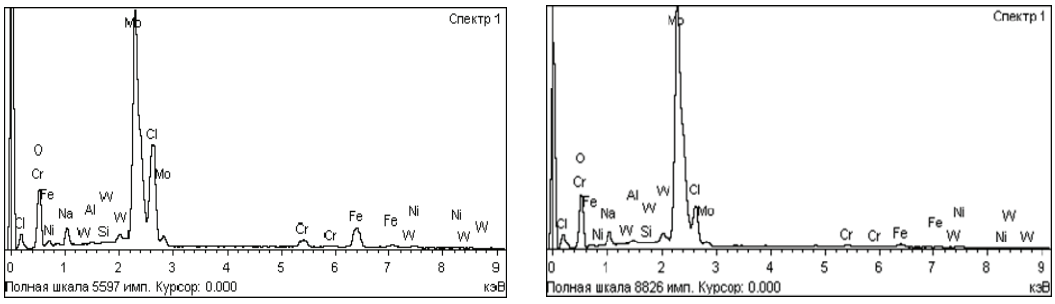
The complex chlorides formed by reaction (1), (2) at a temperature of 220 ° C have low vapor pressure and high thermal resistance, therefore it is assumed that the degree of purification of the gas stream from iron and aluminum will be high. Figures 1 and 2 show the type of particles of spent filters made of tableted sodium chloride and molybdenum trioxide, as well as their characteristic spectrograms obtained on a scanning electron microscope (SEM) at different magnifications.

The compositions of the filter particles from tableted sodium chloride obtained on SEM are shown in Table 1.



a b

Figure 1 – View of the filter particles from tableted sodium chloride (a) and molybdenum trioxide (b) obtained on SEM at different magnification



a b

Figure 2 – Characteristic spectrograms of filter particles from tableted sodium chloride (a) and molybdenum trioxide (b) obtained on SEM

Table 1 – Composition of filter particles from tableted sodium chloride, % of the mass

Chemical element	Spectrum 1	Spectrum 2	Spectrum 3
O	16,77	17,73	22,86
Al	0,15	0,19	0,22
Si	0	0,1	0
Cl	43,25	40,87	41,12
Cr	0,95	1,04	0,37
Fe	1,25	1,1	0,45
Ni	0,33	0,26	0,34
Na	32,31	35,12	29,63
Mo	5,13	3,62	4,66
W	0,17	0,13	0,31

The obtained data shows that the filter of sodium chloride tablets is cleaned of iron, nickel and chromium. The capture of aluminum and tungsten is very insignificant, and silicon chloride compounds are practically not captured by this filter at all.

Tungsten is the most undesirable and difficult-to-remove impurity in a molybdenum product. For purification from volatile tungsten compounds in the vapor-gas phase, a filter containing granular molybdenum trioxide was used, which also served to purify the vapor-gas stream from other molybdenum compounds. The process of purification from tungsten is described by the equation:

$$WOCl_4 + 2MoO_3 \rightarrow WO_3 + 2MoO_2Cl_2. \quad (3)$$

As can be seen, as a result of the reaction (3), tungsten trioxide should be formed, which has an insignificant vapor pressure at a temperature of 220 ° C and gaseous molybdenum dioxide, which is the main product of chlorination. The element composition of the spent filter particles from molybdenum trioxide obtained after the chlorination and purification process is shown in Table 2.

By analyzing the composition of the particles from the molybdenum trioxide filter, it can be noted that the purification of the vapor-gas mixture from aluminum, iron and nickel continues on it, but it is significantly less than on the previous sodium chloride filter. It is also possible to note a slight purification from silicon. Chromium capture by this filter is not detected within the error of the analytical equipment. It is worth noting that the purification from tungsten on the molybdenum trioxide filter is insignificant, probably the reaction (3) with these parameters goes at a very low speed.

The purified gas stream from the filter system enters the condenser, in which it is desublimated. In the process of condensation, two types of molybdenum product were obtained: the first, formed on the walls of the condenser and representing a relatively compact yellow-green product, the second in the form of a loose powder consisting of fluff-like particles. The type of samples of desublimated molybdenum dioxychloride obtained on SEM at different magnification is shown in Figure 3, and the composition of their various fragments in Table 3.

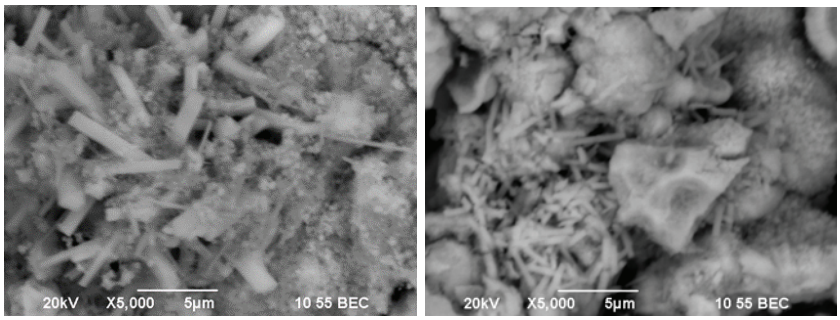
In all the samples studied, it is possible to note an insignificant content of iron and tungsten. Moreover, unlike compact ones, the content of iron and tungsten in fluff-like samples is less, which can be explained by higher desublimation temperatures of iron trichloride and tungsten oxytetrachloride, which are easily deposited on the hotter walls of the condenser.

The presence of iron and tungsten in almost all fragments of the samples suggests that the reaction (1) of the formation of non-volatile iron compounds on tableted sodium chloride and the reaction (3) of the formation of non-volatile tungsten trioxide compounds on granular molybdenum trioxide, with these parameters, has limited application and does not provide high selectivity of the process. It is possible to note only a slight capture of tungsten on filters made of both tableted sodium chloride and filters made of granular molybdenum trioxide.

Aluminum, nickel, chromium and other elements in both samples were not detected within the detection error, which gives reason to believe that with these parameters, reaction (1) can be used to purify molybdenum

Table 2 – Composition of molybdenum trioxide filter particles obtained by SEM, % of the mass

Chemical element	Spectrum 1	Spectrum 2	Spectrum 3
O	30,04	32,65	31,17
Al	0,05	0,10	0,12
Si	0,09	0,08	0,12
Cl	0,37	0,59	0,80
Cr	0,0	0,0	0,0
Fe	0,10	0,34	0,25
Ni	0,09	0,26	0,00
Mo	69,15	65,76	67,16
W	0,18	0,10	0,51



a b

Figure 3 – Electronic photos of compact (a) and spider-like (b) particles of molybdenum dioxide, obtained on SEM, at different magnification

Table 3 – Composition of compact and fluff-like particles of molybdenum dioxychloride obtained by SEM

Chemical element	Content, %					
	Compact particles			Fluff-like particles		
	Spectrum 1	Spectrum 2	Spectrum 3	Spectrum 1	Spectrum 2	Spectrum 3
O	33,53	18,11	22,32	31,60	28,51	26,83
Cl	0,65	26,69	23,21	0,00	11,02	10,05
Al	0	0,1	0	0	0	0
Cr	0	0	0	0	0	0,05
Si	0,1	0	0	0,1	0	0
Fe	0,10	0,21	0,12	0,00	0,10	0,00
Ni	0,05	0,00	0,1	0,00	0,00	0,00
Mo	64,49	50,51	53,21	68,40	59, 62	61,17
W	1,13	0,40	0,95	0,40	0,30	0,25

chloroxide compounds from these elements. The absence of silicon in desublimated samples of molybdenum oxychloride compounds suggests that the reaction (2) can be quite workable.

Analyzing the stoichiometric composition of compact and downy samples of molybdenum dioxide, it can be noted that they do not correspond to the stoichiometric formula MoO_2Cl_2, but are much closer to the formulas $MoO_{(2.25-2.4)}Cl_{(1-0.8)}$ for compact and $MoO_{(2.6-2.8)}Cl_{(0.2-0.1)}$ for downy samples. This behavior is explained by the fact that atmospheric oxygen easily displaces chlorine from molybdenum dioxide, and since the bulk density of freshly prepared fluff-like samples of molybdenum dioxide is usually about 50 kg / m^3, and they have a very large free surface, even in freshly prepared samples there is a noticeable shortage of chlorine.

Many works have been devoted to the problem of studying the dissolution of molybdenum-containing products [15, 16]. In our case, the dissolution of the molybdenum product was carried out in distilled water by reaction:

$$MoO_2Cl_2 + 2H_2O = H_2MoO_4 + 2HCl \quad (4)$$

According to equation (4), during hydrolysis, molybdenum and hydrochloric acids are formed. The reaction is exothermic, the dissolution takes place with the release of heat (the temperature of the solution increases by 20 ° C). At the same time, depending on the parameters of the experiment, the place of removal of the desublimate and the method of dissolution, solutions of different colors and with different amounts of sediment are formed.

The dissolution of compact samples of molybdenum oxychloride compounds in water at any temperature occurs almost completely with the formation of an insignificant, less than 0.5 %, precipitate. The resulting productive solution has a blue color due to the presence in the solution of paramolybdate ions Mo4O13-2, formed during the hydrolysis of various oxychloride compounds of molybdenum [17].

When the fluff-like samples of molybdenum compounds are dissolved in water, a pulp is formed, probably due to the formation of metamamolybdate ions Mo7O24-2 in solution, which have low solubility. The filtration rate of such pulp is good, the filtrate is transparent, about 30% of molybdenum acids pass into the precipitate. The element composition of molybdenum products: pulp, filtrate and cake is shown in Table 4.

For almost all impurity elements, a significant decrease in their content occurs during the transition from pulp to filtrate. For 3d metals such as iron, chromium, manganese, cobalt, copper, the reduction is one and a half to two times. For alkaline and alkaline earth elements, such as calcium, magnesium, potassium, it is three to five times, and for many elements, such as aluminum, silicon, zinc, silver and others, it is a decrease of more than ten times, that is, almost an order of magnitude. The mechanism of formation and formation of this sediment can be represented as follows.

Molybdenum acid is able to attach a different number of MoO_3 molecules to form polyacids, the derivatives of which are polymolybdates. Unlike normal molybdates, polymolybdates have a molar ratio of Me_2O: MoO_3 (where Me- Na^+, K^+, NH_4^+) less than one and varies widely. For the most part, they are isolated from solutions in the form of crystallohydrates with a different number of water molecules [17, 18].

Polymolybdates are obtained by neutralizing acidic solutions of polymolybdenic acids with alkali metal or ammonium ions in a certain range of pH values. At the same time, MoO-ions transform into polymer anions by attaching protons to polyions to form water molecules according to a simplified scheme [19]:

$$n \bullet MoO_4^{2-} + 2(n-1) \bullet H^+ \leftrightarrow Mo_nO^{2x-}_{3n+x} + (n-x) \bullet H_2O.$$

In our case, when an oxychloride product with a significant deficiency of chlorine ions is dissolved, a large number of MoO3 molecules are formed.For example, when dissolving compact samples of molybdenum oxychloride compounds with a formula close to к $MoO_{(2,25-2,4)}Cl_{(1-0,8)}$, the formation of the paramolybdate ion $Mo_4O_{13}^{-2}$ occurs, and for fluff-like ones with the formula $MoO_{(2,6-2,8)}Cl_{(0,2-0,1)}$ less soluble metamamolybdate-ion $Mo_7O_{24}^{2-}$. Their formation can be represented by the following reactions:

$$4MoO_4^{2-} + 6H^+ \leftrightarrow Mo_4O_{13}^{2-} + 3H_2O,$$

$$7MoO_4^{2-} + 8H^+ \leftrightarrow Mo_7O_{24}^{2-} + 4H_2O.$$

Table 4 – Element composition of the dissolution products of fluff-like samples of molybdenum oxychloride compounds

Product	Content, ppm							
	Li	Na	Mg	Al	Si	P	S	K
pulp	0,237	40,02	10,43	44,60	150,53	0,02	0,01	13,42
filtrate	0,11	31,00	3,93	4,07	18,46	0,01	0,01	3,99
cake	0,41	108,52	22,73	141,88	194,23	0,03	0,03	33,05
Product	Content, ppm							
	Ca	Sc	Ti	V	Cr	Mn	Fe	Co
pulp	85,73	0,11	5,60	6,38	38,81	4,16	180,66	0,72
filtrate	14,97	0,17	0,58	0,54	26,36	2,25	107,43	0,54
cake	247,87	0,23	17,68	21,05	43,64	6,39	256,35	0,86
Product	Content, ppm							
	Ni	Cu	Zn	Ga	Ge	As	Se	Rb
pulp	27,88	3,92	5,71	0,13	0,08	2,35	1,85	0,22
filtrate	19,30	0,84	0,49	0,01	0,04	0,02	0,01	0,03
cake	30,03	10,93	18,55	0,34	0,09	8,23	6,15	0,18
Product	Content, ppm							
	Sr	Zr	Nb	Ag	Cd	Sn	Sb	Te
pulp	3,02	3,84	0,06	22,17	2,41	0,38	1,26	0,07
filtrate	0,15	0,02	0,02	0,35	1,28	0,08	0,63	0,04
cake	10,10	13,24	0,18	76,84	2,69	1,20	2,06	0,22
Product	Content, ppm							
	Cs	Ba	La	Ce	Pr	Nd	Sm	Pb
pulp	0,07	11,25	0,03	0,30	0,09	0,24	0,41	1,49
filtrate	0,01	1,71	0,01	0,19	0,05	0,20	0,14	0,27
cake	0,09	33,55	0,16	0,45	0,88	0,62	0,45	4,23

In equilibrium with these polyanions in solution, there may also be anions of the type $HMo_4O_{13}^-$, $HMo_7O_{24}^-$ or others formed as a result of the addition of protons to polyions [20]. The area of existence of various polymer forms in equilibrium with the MoO_4^{2-} nones at which polyions are formed varies widely and depends on the pH value and the concentration of molybdenum in solution, which complicates the predictive power of the results obtained.

Thus, low-temperature chlorination of technical molybdenum dioxide, purification of the gas mixture from impurities in the filter system, condensation and dissolution of purified molybdenum oxychloride compounds in water are considered.

It has been shown that low-temperature chlorination of molybdenum oxide compounds is a selective process. It was revealed that the filter of granular sodium chloride purifies the gas stream of molybdenum dioxide from the accompanying impurities of aluminum, iron, chromium and nickel, which bind to it in low-volatile fusible compounds. Silicon and tungsten are almost not captured by this filter and the filter of granular molybdenum oxide.

It is noted that the condensation of molybdenum dioxide dichloride occurs with the formation of compact and downy products, the chlorine content of which is close to the formulas $MoO_{(2,25-2,4)}Cl_{(1-0,8)}$ for compact and $MoO_{(2,6-2,8)}Cl_{(0,2-0,1)}$ for downy samples.

It was found that the newly obtained molybdenum desublimate is well soluble in water with the formation of molybdenum and various polymolybdenic acids. The dissolution of the compact product occurs with the formation of paramolybdates with almost no sediment, and when the downy purge is dissolved, metamolybdates are formed with the formation of a precipitate, into which a significant part of the impurities passes.

Поступила: 13.10.22; рецензирована: 27.10.22; принята: 31.10.22.

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