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ТҮЙІНДЕМЕ

Ұсақтау теориясы мен флотациялау теориясы әлі күнге дейін жалпылама түсінікке ие емес. Бұл мақалада авторлармен ықтималдылықтық-детерминатталған жоспарлы эксперимент негізінде шарлы диірмендерде ұсақтаудың ықтималдық теориясын пайдалану арқылы бірдей математикалық үлгі аясында флотациялау және ұсақтау үрдістерін кешенді зерттеу әдісі жасалған. Ұсақтау ұзақтығынан, ксантогенаттың шығымынан және флотация ұзақтығынан негізгі концентрат флотациясынан мысты алу, жеке және жалпылама құрамының тәуелділігі алынған. Фракциялық құрамның есептеулері нәтижесінде нақты фракция шығымының төмендеуіне әкеліп соқтыратын, шламды фракцияның шығымын ұлғайту есебінде ұсақтаудың ұзақтығынан мысты бөліп алу және құрамына қарай экстремальды сипаты ұсақтаудың ықтималдық үлгісі бойынша негізделген. Үрдістің көпфакторлы үлгісі алынған және оның негізінде матрица-номограммасы есептелінген, жәнеде ол ұсақтау және флотациялау үрдістерінің тиімді режимдерінің аймағын анықтау арқылы технологиялық карта ретінде пайдаланылуы мүмкін.

Түйінді сөздер: дайындау, ұсақтау, флотация, ықтималдылықтық-детерминатталған үлгі, көп факторлы үлгі.

ABSTRACT

Grinding and flotation theories still have not a generalized expression. In this article, the authors developed a method for integrated studying of the processes of grinding and flotation in the frame of single mathematical model with using probabilistic theory of grinding in ball mills based on probabilistic and deterministic planning of experiment. Partial and generalized dependences of copper content and recovery into the concentrate of the basic flotation from the grinding duration, from consumption of xanthate and from the duration of flotation were obtained. By using the calculations of fractional composition on the basis of the probabilistic model of grinding it was explained the extreme nature of the dependencies of copper content and extracting on the duration of grinding due to increasing of the output of slimy fractions, resulting in a decrease of the yield of the desired fraction. Multifactor model of the process has been obtained and based on it the matrix-nomogram was calculated, which can be used as a technological sheet with the accentuation of the zone of optimal modes of grinding and flotation processes.

Keywords: design, grinding, flotation, probabilistic and deterministic model, multifactor model

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Complex use of mineral resources. No. 1. 2017.

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On MERCURY SELENIDE DISSOCIATION in SELENIUM DISTILLATION CONDITIONS

Abstract: The analysis of published data of dissociation of mercury selenide on metal and chalcogen shows a lack of consensus on the forms of mercury presence in vapor phase over its selenide, although the majority of researchers consider decomposition process of chalcogenide and mercury transition to the vapor phase as a primary one. In this respect, the applied method of the designed partial pressure diagrams with the reference constants applied, allows to determine thermodynamically stable phases of mercury-selenium system for the distillation refining conditions of chalcogen at the temperature interval 400-672 °C, and the pressures 1.3·10⁻⁵–0.1 MPa, whereas, gas phase is represented by vaporous selenium. Due to the thermodynamic study of mercury selenide dissociation in conditions of distillation recovery and selenium refinement, the partial pressure diagram is designed in coordinates $T - \ln p_{Se(g)} - \ln p_{Hg(g)}$. On the basis of this diagram with lower partial pressures of mercury vapor, the elemental mercury is indicated as thermally stable phase over its selenide, and at considerable partial pressures of mercury vapor, mercury selenide occurs as the stable phase in vapor. An increasing partial pressure of mercury vapor reduces a region of thermal stability of mercury selenide. Equilibrium region between gaseous mercury and its crystalline selenide is degenerated at boiling point of selenium. At the partial mercury vapor pressure equaled to atmospheric, the field of the selenite existence is degenerated as well. In a process of the selenium distillation separation from mercury impurity in vacuum at its lower content in the initial one and respectively lower partial pressure of mercury vapor, the chalcogenide decomposition into vaporous metal and chalcogen takes place.

Key words: selenium, mercury, mercury selenide, pressure, partial pressure diagram, thermodynamics

Introduction. The interest in physicochemical properties of mercury-selenium system is due to the capabilities of mercury selenide in solving practical problems related to substances photosensitivity with high mobility of current carriers, resistance, semi-transparent contacts [1-3], as well as a complexity in separating selenium from mercury admixture by distillation method.

The phase diagram of Hg-Se is designed within the concentration range 50-100 at. % Se [4, 5], where HgSe compound is determined, and which forms the degenerate eutectic with selenium at temperature 220 °C. A monotectic reaction in the system is developed at temperature 686 °C, a stratification region in these conditions is exposed in mid ~71 and 85 at.% Se. The boundaries of monotectic dome are not defined.

The thermodynamic properties of mercury selenide have been specifically studied by the researchers' team. Initially, the vapor pressure of mercury selenide has been determined in the paper [6], wherein the authors defined the vapor pressure of selenium and alloys with a content of 2.67, 5.03 and 12.4 % within the temperature interval 425-650 °C, and calculated the vapor pressure of HgSe. However, the obtained data on pressure of selenium vapor occurred to be underestimated and are recognized [7] as unreliable.

The different research methods on specifying pressure and composition of the mercury selenide vapor have been developed at the nearly time. [7-10].

In the study [8], the authors using the flow method within the temperature interval 340-482 °C, and the Knudsen method of 323-243 °C, determined the saturated vapor pressure of mercury selenide, the values of which are described by equation: $\lg p \text{ [mm Hg]} = 9,032 - 5976 \cdot T^{-1}$. Whence $\Delta N_{\text{om}} = 114.2 \text{ kJ/mol}$.

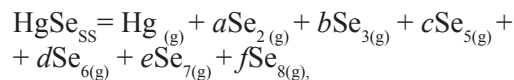
R.A. Isakova and her co-workers [9] defined the vapor pressure of mercury selenide at 350-450 °C by the transfer method in the argon jet, conforming to the dependency:

$\lg p \text{ [mmHg]} = 11,064 - 7521,92 \cdot T^{-1}$, and approximate enthalpy and sublimation entropy values, equal to 143.9 kJ/mol and respectively 156.65 J/(mol • K).

The researcher [11], using the unit with continuous pressure dependency of the vapor temperature, applying the radioactive isotope ^{75}Se and two effusion chambers with different ports diameter, specified the vapor pressure of mercury selenide at 486-596 K. The pressure of mercury selenide vapor, in this case, is defined as dependency: $\lg p \text{ [mmHg]} = 8,175 - 5750,1 \cdot T^{-1}$. The sublimation enthalpy has been equaled to 109.9 kJ/mol.

Mass spectrometric analysis of vapor phase during sublimation and distillation of selenium [11, 12] showed the presence of Se_n^+ types ions in the vapor, where n varies from 1 to 8. Thus, for sublimation (175 °C) the vapor composition is specified as %: $\text{Se}_5 \leq 29.0$, $\text{Se}_6 \geq 57.5$, $\text{Se}_7 \geq 11.4$ and $\text{Se}_8 \geq 2$. There-with, a lower quantity of Se_9^+ and Se_{10}^+ ions has been detected in the vapor. As the temperature increases, the proportion of Se_2 molecules is increasing and the content of Se_5, Se_6 decreasing. The dissociation energy of Se_2 is defined as $297.9 \pm 8 \text{ kJ/mol}$.

Mass spectrometric studies of the vapor phase over mercury selenide [11-14] indicated a significant dissociation of the compound at temperature increasing 142 °C in the reaction:



temperature dependency (257-297 °C) of equilibrium constant is shown by the equation [13]: $\lg K = 9,995 - 8771 \cdot T^{-1}$.

In the study [14], a method specifying vapor optical density over HgSe at 860 °C indicates an absence of gaseous molecules of mercury selenide and the consistency of vapor phase composition against previously published data. An enthalpy of mercury selenide formation indicated (at 300 K) equals to 45.2 kJ/mol, with the entropy of 20.9 J/(mol•K).

However, when studying the composition of the vapor phase [15] by A. D. Pogorelov's method, based on the values comparison of the substance carry-over in inert gas stream and hydrogen, it has been stated that mercury selenide is marginally dissociated (2.2 %) at temperature 480 °C.

A while later, when studying the thermal dissociation process of the mercury selenide vapor [16] by the dissociation suppression method, a total vapor pressure of mercury selenide is specified for the temperature interval 300-550 °C as per the equation: $\lg p \text{ [MmHg]} = 7.32 - 4681 \cdot T^{-1} \pm 0,15$, where the dissociation degree in the interval makes up 98.7-99.2 %.

In the work [17], studying a crystalline structure of mercuric selenide sublimates to detect polytypic modifications and find out vapor composition with saturated-vapor pressure parameters by the membrane pressure gauge, indicated a dissociative type of evaporator HgSe. The vapor pressure of mercury selenide combined with published characteristics is presented by the equation: $\lg p \text{ [MmHg]} = (9.61 \pm 0.05) - (6445 \pm 24) \cdot T^{-1}$. The value of standard heat formation of HgSe, estimated in consistency with the second law of thermodynam-

ics, makes up 52.7 ± 6.3 kJ/mol with the entropy of 100.4 ± 4 J/(mol•K).

The researches [18] including the method of HgSe in hydrogen current at temperature interval 360-540 °C, indicates as well the dissociative character of evaporation in consistency with the reaction $2\text{HgSe}_{\text{solid}} = 2\text{Hg} + \Sigma x_n \text{Se}_n$. The dependency of the vapor pressure of mercury selenide for the given temperature interval: $\lg p [\text{atm}] = -7.0264 - 6579 \cdot T^{-1} \pm 0.012$.

Later, the thermodynamic studies were critically reviewed and generalized in the monograph [19], where characteristics of the paper [17] are recommended for the equation of temperature dependency of saturated vapor pressure of mercury selenide. Other thermodynamic constants of mercury selenide are given in the work [20].

The studies review shows that the authors still have no a common opinion on forms of presence of mercury in vapor phase over its selenide. Though, the majority of them consider the dissociative character of HgSe chalcogenide evaporation as a prioritized one.

Part of Calculation and Results Discussion. In this respect, using the method of designing of partial pressure diagrams [21] with the reference constants [22], we tried to define thermodynamically stable phases of the mercury-selenium system for refining distillation conditions of chalcogen, where the gas phase is represented by vaporous selenium.

The distillation recovery of selenium from industrial products and its refining developed at 400-500 °C (673-773 K), in the vacuum up to 13 Pa, and at boiling point 672 °C (945 K) has been indicated by us at atmospheric pressure [23, 24]. Therefore, the temperature range for the studies is picked as 673-945 K (400-672 °C), and the pressure as $1.3 \cdot 10^{-5}$ - 0.1 MPa.

Due to the fact that the boiling point of mercury at atmospheric pressure 357 °C [4], and HgSe vapor pressure is approximately equal to vapor pressure of liquid selenium, the decomposition reactions of crystalline and gaseous mercury selenide with formation of gaseous mercury and selenium are included (Table). The thermodynamic functions of gaseous selenium in the equilibrium constant estimation are taken from the paper [25].

Table – Reactions and equilibrium constants of reactions of mercuric selenide decomposition

No	Reactions	Values $\ln K_e$ Temperature, K	
		673	945
1.	$2\text{HgSe}_{(\text{cr})} = 2\text{Hg}_{(\text{g})} + \text{Se}_{2(\text{g})}$	-19,331	+0,246
2.	$2\text{HgSe}_{(\text{g})} = 2\text{Hg}_{(\text{r})} + \text{Se}_{2(\text{g})}$	+37,919	+38,692

Equilibrium constants:

$$\text{reaction 1 - } K_e = P_{\text{Se}_{2(\text{g})}} \cdot P_{\text{Hg}_{(\text{g})}}^2,$$

$$\text{reaction 2 - } K_e = P_{\text{Se}_{2(\text{g})}} \cdot P_{\text{Hg}_{(\text{g})}}^2 \cdot P_{\text{HgSe}_{(\text{g})}}^{-2}.$$

When designing the diagram, the vapor pressure of gaseous mercury selenide is included into the equilibrium constant. To simplify the analysis of the partial pressure diagram (Figure 1), its isobaric sections are shown (Figure 2) at the partial pressure of selenium vapor of 0.13, 1.33 and 6.67 kPa, assuming its equality to the operational pressure in the distillation process. The region and field set in the temperature and pressure ranges are highlighted in the figures; the equilibrium plane of reaction 1 is shaded in Figure 1.

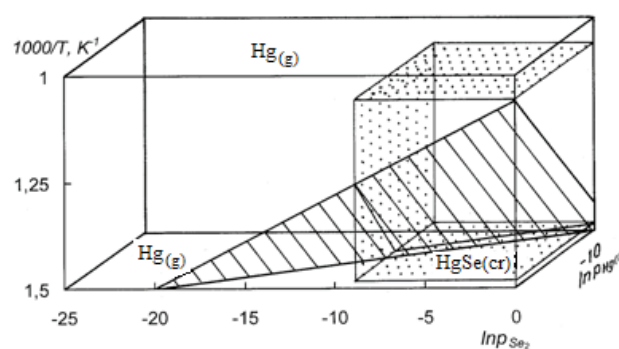


Figure 1 – Diagram of partial pressure of $\text{Hg}_{(\text{g})} - \text{Se}_{2(\text{g})}$

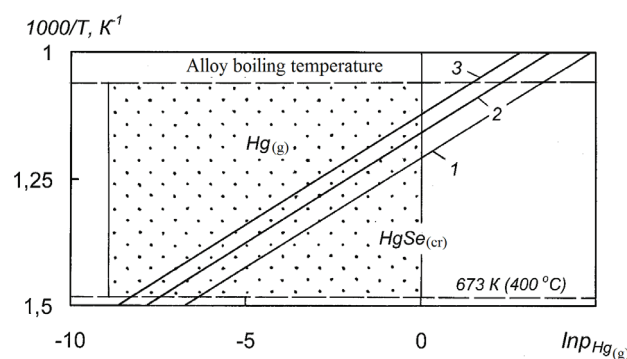


Figure 2 - Isobaric sections of the partial pressure diagram $\text{Hg}_{(\text{g})} - \text{Se}_{2(\text{g})}$ at the vapor pressure of selenium, kPa: 1 - 0.13; 2 - 1.33; 3 - 6.67

On the basis of the partial pressure diagram, it can be concluded that at the boiling point of selenium 945 K (672 °C) at atmospheric and moderately low partial mercury pressures, the mercury selenide is indicated as the thermodynamically stable phase. The thermal dissociation of mercuric selenide is possible only at the pressure of gaseous selenium 13 Pa and mercury vapor pressure less than 0.68 kPa (at 673 K). The equilibrium region between gaseous mercury and

its crystalline selenide degenerates (in the specified conditions), practically, at the boiling point of selenium - the equilibrium reaction plane 1 crosses over the selenium boiling point plane (945 K) at atmospheric pressure.

Analyzing the position of equilibrium lines of the dissociation reactions of mercury selenide on isobaric sections of the partial pressure diagram (Figure 2), it is evident that as the partial pressure of selenium vapor increases, the area of existence of elemental mercury vapor located above the lines decreases. The crystalline mercury selenide will be stable in the triangular field (Figure 2), limited by the partial pressure of mercury (0.13 ÷ 6.67) - 101.3 kPa and temperatures interval: 673 - (823 ÷ 890) K [400 - (550 ÷ 617) °C].

That is, in the distillation extraction conditions and refining of selenium in vacuum and partial pressure of mercury vapor over 6.67 kPa (50 mm Hg) (at relative temperatures), the latter will present as $\text{HgSe}_{(\text{cr})}$ compounding, which confirms the results of the authors' studies [15] and contradicts the results of studying upon composition of vapor phase in most of other works with applying the mass spectrometry [11-14, 18] (at methodically lower pressure) and stating that selenide dissociates completely.

At lower partial pressure of mercury vapor, the stable phase will be vaporous mercury. Thus, at steam pressure of selenium 13 Pa and the same mercury vapor pressure (at 673 K), the system falls into the region of thermodynamic stability of vapor mercury in the partial pressure diagram. The foregoing removes the contradiction in various studies' results.

Conclusions. Due to the thermodynamic study of the dissociation of mercury selenide under the distillation recovery conditions and selenium refinement, the partial pressure diagram, designed in the coordinates $T^{-1} - \ln p_{\text{Se}(g)} - \ln p_{\text{Hg}(g)}$, demonstrates elemental mercury as thermally stable phase over its selenide at lower partial pressures of mercury vapor, and at significant partial pressures of the mercury vapor, mercury selenide is determined as the stable vapor phase. Increasing the partial pressure for the mercury vapor reduces the region of thermal stability of mercury selenide.

The equilibrium region between gaseous mercury and its crystalline selenide degenerates at boiling point of selenium. At partial mercury vapor pressure, that equals to an atmospheric, the field of existence of selenide degenerates as well.

Thus, when refining selenium at low partial pressure of mercury (less than 6.67 kPa), due to its small content in purified chalcogen, the gaseous mercury is confirmed as the stable vapor phase.

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ТҮЙІНДЕМЕ

Сынап селенидінің метал мен халькогенге диссоциациялануы жайлы жарияланған мәліметтерді талдау кезінде сынап селенидінің булы фазасында сынаптың болу пішіндері жайлы бірыңғай пікірдің жоқтығы анықталған, бірақ зерттеушілердің көпшілігі халькогенидтердің ыдырауы мен сынапты булы фазаға ауысуың басты үрдіс деп санайды. Осыған байланысты парциалды қысымдар диаграммасын құрастыру әдісің пайдаланумен және анықтамалық константаларды қолдану арқылы, газды фазаны булы селен деп ұсынған жағдайда қысымы - $1,3 \cdot 10^{-5}$ – 0,1 МПа, температуралық интервалы 400 – 672 °С арналған халькогендерді дистилляциялық тазалау жағдайында сынап-селен жүйелерінің термодинамикалық тұрақты фазалары анықталды. Селенді дистилляциялық жағдайдағы тазалау мен шығаруға сынап селенидінің диссоциациялық әсерінің термодинамикалық зерттеулерінің нәтижесінде $T^{-1} - \ln p_{\text{Se}(g)} - \ln p_{\text{Hg}(g)}$, координаттарындағы парциалды қысымдардың диаграммасы құрастырылды, осының негізінде, кіші парциалды қысымда сынап буының термиялық тұрақты фазасының селенидтердің үстіндегі элементті сынап болып табылады, ал будағы үлкен сынап буының парциалды қысымдағы орнықты фаза сынап селениді болады. Сынап буының парциалды қысымының көтерілуі сынап селенидінің термиялық тұрақты аумағын кішірейтеді. Газтүрлес сынап пен оның кристалды селенидінің арасындағы тепе-теңдік аумағы селеннің қайнау температурасында құлдырай бастайды. Сынаптың парциалды бу қысымы атмосфералық қысымға тең болғанда селенидтердің қатар өмір сүру аумақтары құлдырайды. Кедей бастапқы құрамды сынап қоспалары мен селенді дистилляция үрдіспен бөліп алуда, тиісінше, сынап буының кішкене парциалды қысымында халькогенидтер бүтүрлес метал мен халькогендерге ыдырауы жүре бастайды,

Түйін сөздер: селен, сынап, сынап селениді, қысым, парциалды қысымдар диаграммасы, термодинамика.

РЕЗЮМЕ

При анализе опубликованных данных о диссоциации селенида ртути на металл и халькоген установлено отсутствие единого мнения о формах присутствия ртути в паровой фазе над ее селенидом, однако преобладающее большинство исследователей основным считают процесс разложения халькогенида и перевод ртути в паровую фазу. В этой связи, с применением метода построения диаграмм парциальных давлений и использованием справочных констант выполнено определение термодинамически стабильных фаз системы ртуть-селен применительно к условиям дистилляционного рафинирования халькогена для интервала температур 400 – 672 °С, давлений - $1,3 \cdot 10^{-5}$ – 0,1 МПа, при допущении, что газовая фаза представлена парообразным селеном. В результате термодинамического исследования реакции диссоциации селенида ртути в условиях дистилляционного извлечения и рафинирования селена построена диаграмма парциальных давлений в координатах $T^{-1} - \ln p_{\text{Se}(g)} - \ln p_{\text{Hg}(g)}$, на основании которой установлено, что при малых парциальных давлениях пара ртути термически стабильной фазой над ее селенидом является элементарная ртуть, при значительных парциальных давлениях пара ртути устойчивой фазой в паре будет селенид ртути. Повышение парциального давления пара ртути уменьшает область термической стабильности селенида ртути. Область равновесия между газообразной ртутью и ее кристаллическим селенидом вырождается при температуре кипения селена. При парциальном давлении пара ртути, равном атмосферному, поле существования селенида также вырождается. В процессе дистилляционного разделения селена от примеси ртути в вакууме при малом содержании в исходном и, соответственно, малом парциальном давлении пара ртути, будет происходить разложение халькогенида на парообразный металл и халькоген.

Ключевые слова: селен, ртуть, селенид ртути, давление, диаграмма парциальных давлений, термодинамика

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О ВОЗМОЖНОСТИ ФТОРО-СУЛЬФАТОАММОНИЙНОГО ВСКРЫТИЯ БАРИТОВОГО СЫРЬЯ

Резюме: Рассмотрена теоретическая возможность применения усовершенствованной фторидной технологии для переработки баритосодержащих отходов, полученных при флотационном обогащении сложной по минералогическому составу баритополиметаллической руды и имеющих в своем составе, %: до 37 барита; более 1 в сумме меди, свинца и цинка; до 0,3 редких металлов. Технология предусматривает совместное использование бифторида и сульфата аммония для удаления оксида кремния