# ХИМИЯЛЫҚ ТЕХНОЛОГИЯ ХИМИЧЕСКАЯ ТЕХНОЛОГИЯ CHEMICAL TECHNOLOGY

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# The extraction of cadmium from zinc-containing materials and ores by the Waelz process using oil sludge

Methods of extraction of cadmium from ores and zinc-containing materials are considered in the article. The Waelz process of Achisai ores (0.1–0.2 % of Cd) is carried out in the presence of 45–55 % of coke from the mass of ore charge in furnaces. Up to 92-95 % of cadmium is extracted into the sublimates. The yield of sublimates is 16–18 % of the mass of the ore charge. Sublimates of the Waelz process contain from 0.05 to 1.2 % of Cd. The efficiency of the processing cadmium-containing ores and semi-products by the Waelz process largely depends on the degree of replacement of coke breeze with less expensive materials. Research results are presented, which justify the possibility of using oil sludge while the Waelz processing cadmiumcontaining materials, by calculating  $\Delta G_T^0$ , determined thermodynamic probability of cadmium recovery from cadmium-containing compounds in the presence of carbon, oil sludge and its constituent hydrocarbons in different temperature zones of the Waelz furnace. Due to thermodynamic modeling with the use of the software complex «Astra» there were established the equilibrium recovery degree and transition of cadmium to the gas phase, the composition of the gas phase in the temperature range of 300-1500 K and pressures of 0.05-0.5 MPa. It is established that the initial reactivity of the reductant with respect to CdO varies in a series, and with respect to CdS this series has the form: H<sub>2</sub>>C<sub>n</sub>H<sub>m</sub>>>CdSO<sub>4</sub>>H<sub>2</sub>O>C. At high temperatures, the form of the reductant does not affect the distillation of Cd (it is > 99 % at T > 1300 K). The interaction in the system CdO-CdS-oil sludge is observed at temperature > 400 K by the reduction of Cd from CdO. Subsequently, Cd is reduced from CdS at T > 1100 K reaching maximum at T  $\geq$  1300 K.

*Keywords:* industrial products, zinc concentrates, dust processing, pyrometallurgy, hydrometallurgy, the Waelz process, cadmium-containing compounds, cadmium recovery, oil sludge.

#### Introduction

Cadmium, which does not have independent deposits, is usually a zinc companion and is found in polymetallic ores containing from 0.02 to 2.5 % of Cd. Cd content in zinc and zinc-lead ores varies from 0.02 to 2.53 % (on average, about 0.3 %) with respect to Zn [1]. In metallurgical redistribution the behavior of cadmium is in many ways like zinc. Therefore, the problems of the need to extract cadmium are interrelated with the problems of obtaining zinc. According to the company Netro-Capital (Moscow), world production of Zn in 2015 had increased by 2.6 % compared to 2014 and amounted to 13.2 million tons. Moreover, the rate of increase in its annual production remained in 2016. The annual world production of Cd in recent years is 24.2–25.2 thousand tons. The rise in its production, for example in 2016, was 2.7 % [2]. Kazakhstan occupies the fifth place in the world (after Austria, the USA, Canada and Mexico) for cadmium reserves, there is increased the production of refined cadmium from 1000 tons (2012) to 1450 tons (2016). An increasing trend in the release of cadmium is observed, for example, in Japan, Mexico, and Australia and is at a constant level in Belgium, China and Russia. Kazakhstan occupies the seventh place in the production of cadmium (after Japan, China, the USA, Belgium, Mexico, Canada), produces 5.6 % of its world release. In

accordance the current conjuncture, it creates good prerequisites for expanding cadmium production in Kazakhstan, in particular cadmium brand KD-0 at JSC Kazzinc.

Bearing in mind that the trend of Zn production in Kazakhstan is growing, due to both the increase in output on the basis of Kazzinc production and the launch of new production facilities in Balkhash and Shymkent cities, problems of cadmium (Zn companion) extraction will affect the efficiency of development of complex processing of zinc materials. So, in the works of KazNU named after Al-Farabi [3] necessity of development of new ways of obtaining both zinc and cadmium, meaning their perspective for obtaining electronic engineering materials is revealed. In the future, a rise in the output of cadmium can be expected with the development of battery industry, the technology of new materials, for example, nano-materials which have significant differences in properties from the usual crystalline solid. In particular, a nanoparticle from cadmium becomes in the state of super ferromagnetic [4].

In the flotation of zinc-lead ores, 75 % of cadmium passes into zinc concentrate, 15 % to lead and 10 % to Cd is lost with tails. In zinc concentrates Cd content ranges from 0.08 to 0.18 %. When enriching Zn-Pb ores, 40–85 % of Cd passes into zinc concentrate, 2–12 % in lead and 3–51 % of cadmium remains in tailings [5]. When copper ore is enriched, 60 % of Cd passes into copper concentrate, 10 % to zinc concentrate and 30 % to tails and pyrite concentrate. When enriching lead ore, the degree of cadmium distribution is in proportion to zinc distribution. While processing zinc ores, according to the classical scheme: enrichment  $\rightarrow$  burning  $\rightarrow$  leaching  $\rightarrow$  electrolysis  $\rightarrow$  remelting, cadmium is distributed as follows: 0.2–0.23 % of Cd is contained in cinder, 0.15–0.2 % in dusts, 0.15 % — in materials after leaching of cinder, 0.41–0.58 % — in velcoxides [6].

Intermediate products are formed in the production of conditional concentrates, which also contain cadmium. Electrothermal method [7], processing by weighted melting [8], the Waelz process and hydrometallurgical processing [9] are proposed for the processing of copper-lead-zinc industrial products. Thus, for hydrometallurgical processing of industrial products (Zn — 24.8 %, Pb — 6.86 %, Cu — 3.89 %, S — 28.2 %, Fe — 15.8 %) after burning, sulfatization, leaching with weak sulfuric acid, calcination at 650 °C and leaching with acidified (sulfuric acid) water, Zn recovery in the solution was 96.9 %, Cu — 95,9 %, Cd — 95.4 %.

Processing copper-zinc industrial product by autoclaving at Unipromed Institute it was possible to manage to extract 95–97 % of Cd and 92–96 % of Zn into the solution. The scheme provided for the production of Cu-Cd materials for the processing copper-zinc raw materials, the technology of sulfatization of a completely burnt Cu-Zn industrial product or concentrate with treated electrolyte in the fluidized bed has been developed. The technology is provided, in particular, from a concentrate containing 12.27 % of Cu, 6.1 % of Zn, 0.68 % of Pb, 0.03 % of Cd, there is obtained marketable cadmium with a degree of cadmium transfer to the target product of 85.5 %.

The paper reports the processing Cu-Zn concentrate containing Cd using the technology of its balanced burning, which makes it possible to separately process Cu-Zn sulfide raw materials by sulfating firing method in CC furnaces with full balance of sulfate sulfur. The scheme involves the production of Cu-Cd materials

While processing the collective Cu-Zn-Pb concentrate (Cu-25 %, Zn-9 %, Pb-2.6 %) by KIVCET, process, the oxidized zinc sublimates with a content of 0.1–0.2 % Cd, 73–75 % Zn and 4–5 % Pb were obtained. At the same time, the degree of extraction of Zn and Cd in the sublimate was at least 70–75 %. It is necessary to note the work on the chloride processing of Achisai zinc ore, clinkerwaelz process, ores by the chloride-by-gas method, which allows transferring 92–98 % of Cd to chloride sublimates [10].

According to Institute UNIPROMED, the main part of cadmium from copper-containing concentrates (from 60 to 90 %) goes into dust during their pyrometallurgical processing. In this case Cd content is maximal in the dusts of mine melting (0.01–0.5 %) and minimal in the dust of burning fires (0.01–0.2 %) [11]. Dusts of copper production (for extraction of Cd) are processed by hydrometallurgical and pyrometallurgical methods. In processing the dust of a reflector furnace containing masses %:10–13.5 Zn; 2.45–2.86 Pb; 0.08 Cd with the addition of matte to dust there was extracted 64.7–73.9 % of Cd; 63.5–76.5 % of Zn; 74–85 %. Thin dusts of pyrosection, containing Cd from 0.16 to 0.58 % [12] are proposed to be processed hydrometallurgically. In one-stage leaching from the dusts 98–99 % of Cd, 85–88 % of Cu, 95–97 % of In, 98–99 % of Zn are extracted. The concentrate containing Cd, In, Ge is burn at 350–400°C, dissolved in hydrochloric acid with distillation of GeCl<sub>4</sub>. Of the residues, Cd is isolated by distillation with zinc dust. Wherein, cross-cutting (from the dust) extraction of cadmium is 75 %.

Cadmium-containing oxide ores were subjected to be Waelz processed in Kazakhstan (Achishai village) and Poland. The Waelz process of the Achisai ores (0.1-0.2% of Cd) together with the mine smelting slag CHS is carried out in the presence of 45-55% of the coke from the ore charge mass in the furnaces  $41\times2.5$  m and  $50\times3.6$  m. In the sublimation 95 % of cadmium is extracted. Cd content in the sublimations is 0.12%. Sublimate yield is 16-18% of the ore charge mass. The Wafer Waelz process is from 0.05 to 1.2% Cd (UCCPC — 0.7 to 1.2%, CHETZ 0.8 to 1.1%, LC 0.35 to 1.2%, Electrozinc 0.35 — 0.55%, Ukrzink 0.25 — 0.3% and Achpolimetall 0.05 — 0.12%). Moreover, from 54 to 81.8% of cadmium in the sublimates is in the type of oxide and silicate forms, from 4.5 to 35.5% in sulphide and ferritic forms and from 11 to 16.2% in the form of cadmium sulfate.

In VNIITSVETMET, a method has been developed for the sulfatization of zinc materials by a boiling bed using sulfuric acid [13]. The technological chain of this method is as follows:

At the time of leaching the sulphate product, a zinc solution and Pb-Fe residue are produced.

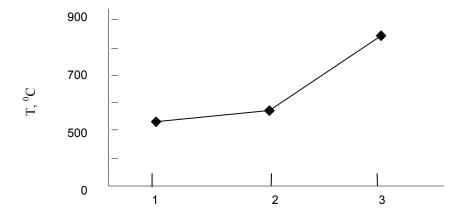
At the same time, cadmium recovery from the materials into the solution was 91.9 %, Zn — 92 %, Cu — 92 %. The content of Pb in the residue is 9–10 %, and Zn is 3.5–4 %. Pb-Fe materials are recommended to send to lead production for extraction of Pb. A drawback of this method lies in large consumption of fuel oil (256 kg/t) and the need for Pb-Fe melting of the residue.

In the Waelz process of zinc materials in the sublimation up to 95 % of cadmium is recovered. The rest of Cd goes to the clinker. In the sublimes there is Cd, the rational composition of which is CdO + silicates Cd (50.1-55.6 %), CdSO<sub>4</sub> + CdCl<sub>2</sub> (5.6-16.6 %), CdS (4.2-22.4 %), CdO·Fe<sub>2</sub>O<sub>3</sub> (5.5-9.0 %), the rest (11.1-22.2 %).

If in literature there is sufficient systematic information about Zn recovery from various compounds with various substances, then with respect to Cd this information is less systematized. Cadmium oxide is an oxide prone to dissociation, so it refers to easily recovery oxides. At temperature 950 °C the degree of dissociation is 69 %, and at temperature 1250 °C is 87 %. Noticeable volatilization of CdO is noted at temperature 900–1000 °C. The vapor pressure of CdO is 760 mm Hg is noted at 1559 °C. Moreover, cadmium oxide dissociates in the gas phase at the temperature > 1150 K:

$$2CdO = 2Cd + O_2$$

The temperature in the beginning of CdO recovery depends on the type of the carbonaceous reductant, in accordance with Figure 1, increasing from coal to graphite.



1 — coal from sugar; 2 — charcoal; 3 — graphite

Figure 1. Influence of the temperature in the beginning of Cd recovery from CdO on the type of carbonaceous reductant

### Method

In slags, ores, cadmium materials are contained in the form of CdO, CdS, CdSO<sub>4</sub>, CdO·SiO<sub>2</sub>, CdO·Fe<sub>2</sub>O<sub>3</sub>, and CdCO<sub>3</sub>. Some thermodynamic calculations of Cd recovery from its compounds have been published in the literature. However, a complete comparative analysis of Cd recovery is not carried out for all zones of the Waelz furnace using waste products from hydrocarbon raw materials, for example, oil sludges and elements Zn, Pb, Fe formed in the Waelz process. We used the thermodynamic analysis to recover cadmium from its various compounds by calculating the change in the free Gibbs energy ( $\Delta G_T^0$ ) [14]. The calculation of ( $\Delta G_T^0$ ) was carried out with the help a computer program developed by Auezov SKSU [15] based on the equation:

$$\Delta G_{T}^{0} = \Delta H_{298} + \int_{298}^{T_{1}} \Delta C_{p_{1}} dT \pm \Delta H_{1} + \int_{T_{1}}^{T_{2}} \Delta C_{p_{2}} dT \pm \Delta H_{2} + \dots + \int_{T_{n}}^{T} \Delta C_{p_{n}} dT -$$

$$-T \left( \Delta S_{298}^{0} + \int_{298}^{T_{1}} \Delta C_{p_{1}} dT / T \pm \Delta H_{1} / T_{1} + \int_{T_{1}}^{T_{2}} \Delta C_{p_{2}} dT / T \pm \Delta H_{2} + \dots + \int_{T_{n}}^{T} \Delta C_{p_{n}} dT / T \right),$$

where,  $\Delta H_{298}$  and  $\Delta S^0_{298}$  — is change in enthalpy and entropy of the system at 298 K, kJ/mol and J/(mol·deg);  $\Delta C_{p1}$ – $\Delta C_{pn}$  — is change in heat capacity of the system in the corresponding temperature range;  $T_1$ – $T_n$  — are temperatures of the first and last phase and modification transitions of the reaction participants, K; T — is final calculation temperature, K;  $\Delta H_1$ – $\Delta H_n$  — is thermal effects of the corresponding phase and modification transitions, kJ/mol;

The thermodynamic constants required for the calculation were taken from sources [16].

The results of calculations of  $\Delta G_T^0$  reduction of cadmium (II) oxide by carbon, carbon monoxide (II), hydrogen, methane, iron, lead, zinc and cadmium sulfide by reactions:

and cadmium sulfide by reactions: 
$$CdO + C = Cd + CO$$
 (1) 
$$CdO + CO = Cd + CO_{2}$$
 (2) 
$$CdO + H_{2} = Cd + H_{2}O$$
 (3) 
$$3CdO + CH_{4} = 3Cd + 2H_{2}O + CO$$
 (4) 
$$4CdO + CH_{4} = 4Cd + CO_{2} + 2H_{2}O$$
 (5) 
$$CdO + Zn = Cd + ZnO$$
 (6) 
$$CdO + Pb = Cd + PbO$$
 (7) 
$$CdO + Fe = Cd + FeO$$
 (8) 
$$3CdO + 2Fe = 3Cd + Fe_{2}O_{3}$$
 (9) 
$$2CdO + C = 2Cd + CO_{2}$$
 (10) 
$$2CdO + CdS = 3Cd + SO_{2}$$
 (11) 
$$3CdO + FeS = 3Cd + FeO + SO_{2}$$
 (12) 
$$3CdO + ZnS = 3Cd + ZnO + SO_{2}$$
 (13) 
$$3CdO + PbS = 3Cd + PbO + SO_{2}$$
 (14) 
$$7CdO + 2FeS = 7Cd + Fe_{2}O_{3} + 2SO_{2}$$
 (15)

are given in [17] and Table.

Temperature effect on  $\Delta G_T^0$  reduction of Cd from CdO

Reactions No.	$\Delta G_{\rm T}^{\ 0}$ , kJ/g-at Cd							
	298 K	594 K	1038 K	1200 K	1300 K	1500 K		
1	2	3	4	5	6	7		
1	+89.06	+33.01	-55.42	-106.13	-137.43	-200.03		
2	-31.27	-34.73	-45.36	-64.75	-76.72	-100.66		
3	-11.13	-16.55	-41.85	-66.65	-81.96	-112.58		
4	+253.91	+247.63	+144.56	+86.78	+51.12	-18.88		
5	+100.55	+84.67	+52.61	+25.31	+8.46	-25.24		
6	-89.91	-89.62	-91.34	-103.62	-103.07	-101.97		
7	+37.25	+36.37	+36.58	-24.55	-32.13	-42.88		
8	-16.38	-24.84	-28.91	-59.11	-77.76	-115.06		

Table

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1	2	3	4	5	6	7
9	-20.44	-22.72	-30.89	-39.32	-44.52	-54.92
10	+112.46	+82.35	+32.45	+0.17	-22.21	-66.97
11	+98.03	+76.11	+39.31	+9.74	-8.51	-45.01
12	+77.22	+52.92	+14.21	-15.92	-34.52	-71.72
13	+85.48	+63.27	+25.56	-3.94	-22.16	-58.16
14	+93.86	+43.58	+21.32	+8.34	-7.45	-29.84
15	+61.64	+42.62	+10.34	-17.69	-33.35	-64.67

#### Results and Discussion

Dividing the temperature interval into three regions: low-temperature (298–600 K), medium temperature (600–1000 K) and high-temperature (1000–1500 K), we analyzed the efficiency of each reductant [18]. From table 1 it follows that in the first temperature region CO has the greatest reducing ability, then  $H_2$ . In this temperature range, carbon and methane, CdO, are not recovered. In the second temperature region, from the thermodynamic point of view, at temperature of more than 760 K, carbon begins to recover CdO. Moreover, at temperature 1000 K carbon has the greatest reducing ability, then carbon monoxide (II) and hydrogen. In the third temperature region at T = 1500 K, an increase in reducing ability of substances is observed in the series:  $C > H_2 > CO$ .

In waelz furnace, ZnO, PbO, and iron oxides are reduced to the form of Zn, Pb, and Fe [19]. As follows from Table, the greatest reducing ability with respect to CdO in the third temperature zone is iron, then zinc and lead, i.e. these metals are not inert with respect to CdO. Moreover, zinc and iron are able to reduce CdO already at 298 K. An important circumstance is that metal cadmium can form in the absence of C, CO, CH<sub>4</sub>, Zn, Fe, Pb. Thus, according to the reaction  $2CdO + CdS = 3Cd + SO_2$  metallic cadmium can be obtained at temperature of more than 1250 K in the presence of CdS.

In raw materials, in addition to oxide compounds, such sulfides (FeS, ZnS, PbS) can be present which upon interaction with CdO (especially FeS) can form Cd already at 1150 K. PbS has a lower reactivity with respect to CdO with the release of Cd. ZnS occupies an intermediate position between FeS and PbS. Thus, based on the thermodynamic analysis, it follows that at temperature of 1500 K, the CdO reductant form a series as the reactivity decreases:  $C(CO^*) > Fe(FeO^*) > Zn > H_2 > CO > FeS > (FeO^*) > C(CO_2^*) > FeS(Fe_2O_3^*) > ZnS > CdS > Pb > PbS > CH_4(CO_2) > CH_4(CO)$  (\* — one of the products is indicated in brackets).

Methane is capable of reducing CdO with formation of  $CO_2$  at temperature of more than 1352 K and with the formation of CO > 1468 K. By  $\Delta G^0_{1500}$  value it was determined that when Cd is reduced by carbon and hydrogen, the reactivity of cadmium-containing materials changes as follows:  $CdSO_4 > CdO > CdO \cdot Fe_2O_3 > CdO \cdot SiO_2 > CdS$  and when methane is reduced by  $CdSO_4 > CdO \cdot Fe_2O_3 > CdO > CdO \cdot SiO_2 > CdS$ .

Analysis of the equilibrium in the magnitude and sign of  $\Delta G^0_T$  does not allow taking into account all combinations of interaction of components among themselves. For taking into account these interactions, we performed a thermodynamic simulation of Cd reduction from CdO and CdS using the «Astra-4» software complex based on the principle of maximum entropy. The influence of the type and amount of reductant, temperature and pressure on the degree of distribution of components between materials and reaction products and on the composition of the Cd gas phase from CdO and CdS were determined [20].

Figure 2 shows temperature effect (T) and pressure on transition degree ( $\alpha$ ) of cadmium to the gas phase in CdO-C system, from which it follows that by decreasing the pressure (P) from 0.5 to 0.005 MPa Cd can be reduced at a maximum T from 1150 to 800 K. Gas phase composition of CdO-C system also depends on T and P (Fig. 3). The main components of the gas phase are Cd, CO and CO<sub>2</sub>.

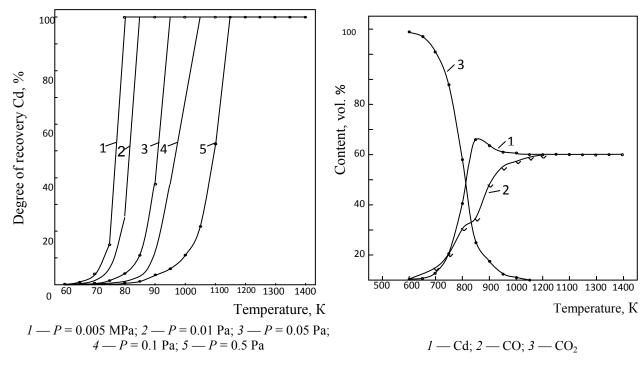


Figure 2. Effect of temperature and pressure on the degree of cadmium recovery and transition (into the gas phase (α) in CdO-C system)

Figure 3.Temperature effect on the gas phase composition of CdO-C system

#### Conclusions

In the cost of the Waelz process the proportion of coke is from 21.7 to 37.5 %. Therefore, it is quite natural to see interest in replacing coke with other less scarce materials. Thus, small anthracite and coal fines with a ratio of 0.46, coal silt, semi-coke and coke from brown coal, as well as brown coals of Karaganda, Lenger and Angren deposits are used in the Waelz process.

On an industrial scale it is shown that a 20 % degree of replacement of coke with Karaganda coal is possible. The reactivity of coals in the Waelz process of zinc-containing materials is greater than coke breeze. In our opinion, the question of partial replacement of the coke can be solved by using waste products from hydrocarbon raw materials processing, for example oil sludges, the calorific value of which is up to 37–39 MJ/kg. It was concluded that there is some restriction of the replacement of coke with coal, because the high content of volatiles can lead to the destruction of bag filters. At the end of the 1980s, work was started at the SKSSU to replace coke during the Waelz process of oxidized zinc ores to hydrolytic lignin. With partial replacement of coke with hydrolytic lignin, the degree of sublimation of Zn is increased by 2.6 %. Weltz-oxide contained 0.16–0.19 % of Cd (with a degree of sublimation of 95.8 %). When coke breeze was replaced with Taksomyrsai coal (coke/coal ratio = 8.4), the degree of distillation of Cd was 9.6 %, Zn — 90.2 %. The carbon content in the clinker decreased from 24 to 22.5 %, and in the cooler weltz-oxide from 12.9 to 12.1 %. Technical and economic calculations show that a 10–11 % replacement of coke with coal from the Taskomyrsai deposit will reduce cost price by 900–950 tenge.

#### References

- 1 Бабаджан А.А. Пирометаллургическая селекция: учеб. пособие / А.А. Бабаджан. М.: Металлургия, 1968. 298 с.
- 2 Алшанов Р.А. Казахстан на мировом минерально-сырьевом рынке: проблемы и их решение: Аналитический обзор / Р.А. Алшанов. Алматы: Ин-т мирового рынка, 2004. 220 с.
- 3 Могильный В.В. О некоторых закономерностях использования новых поверхностно-активных веществ в целях совершенствования технологии электроосаждения цинка, кадмия и таллия: автореф. дис. ... д-ра техн. наук: 05.16.02 «Металлургия черных, цветных и редких металлов» / В.В. Могильный. Алматы, 2003. 54 с.
  - 4 Новые материалы / под ред. Ю.С. Карабасова. М.: МИСиС, 2002. 736 с.

- 5 Лакерник М.М. Металлургия цинка и кадмия: учеб. пособие / М.М. Лакерник, Г.Н. Пахомова. М.: Металлургия, 1969. 488 с.
  - 6 Чижиков Д.М. Кадмий: учеб. пособие / Д.М. Чижиков. М: AH СССР, 1962. 227 с.
- 7 Лакерник М.М. Электротермия в металлургии меди, свинца, цинка: учеб. пособие / М.М. Лакерник. М.: Металлургия, 1971. 296 с.
- 8 Снурников А.П. Лабораторные исследования гидрометаллургической переработки медно-свинцово-цинкового промпродукта / А.П. Снурников, В.М. Юренко // Цветные металлы. 1965. № 11. С. 77–80.
- 9 Рыскин М.Я. Пути повышения качества концентратов при обогащении медно-цинковых руд / М.Я. Рыскин, В.И. Горячкин, Е.Н. Синельщикова, С.И. Митрофанов // Цветметинформация. 1965. № 11. С. 16, 17.
- 10 Тлеукулов О.М. Комплексная безотходная хлоридная переработка полиметаллического окисленного сырья: автореф. дис. . . . д-ра техн. наук: 05.16.02 «Металлургия черных, цветных и редких металлов» / О.М. Тлеукулов. Л.: Горный ин-т, 1985. 42 с.
- 11 Снурников А.П. Комплексное использование сырья в цветной металлургии: учеб. пособие / А.П. Снурников. М.: Металлургия, 1977. 272 с.
- 12 Бабаджан А.А. Пути совершенствования технологии и требования к агрегату для процесса пироселекции / А.А. Бабаджан // Цветные металлы. 1959. № 4. С. 30–34.
- 13 Снурников А.П. Полупромышленные испытания сульфатизации цинковых кеков в кипящем слое / А.П. Снурников, А.Г. Пусько, В.М. Юренко // Цветная металлургия. 1965. № 9. С. 29–34.
- 14 Шевко В.М. Термодинамический анализ восстановления оксида кадмия (II) / В.М. Шевко, З.К. Абдикулова, С.Т. Тлеуова // Экология и образование: сб. науч. тр. Кентау: МКТУ им. Х.А. Ясави, 1999. С. 45–48.
- 15 Шевко В.М. Построение диаграмм парциальных давлений систем Bi-O-Cl и Cd-O-Cl с учетом образования оксохлоридов висмута и кадмия с использованием ЭВМ / В.М. Шевко, Д.К. Айткулов // Деп. в КазНИИНТИ. 25.06.1985. № 1010 Ка-85. С. 8, 9.
- 16 Карапетьянц М.Х. Основные термодинамические константы неорганических и органических веществ / М.Х. Карапетьянц, М.Л. Карапетьянц. М.: Химия, 1968. С. 400–469.
- 17 Казенас Е.К. Масс-спектрометрическое исследование процессов испарения и диссоциации оксидов меди, серебра, цинка, кадмия / Е.К. Казенас, М.А. Больших // Деп. в ВНИИНТИ. 30.05.1989. № 3583-В89. С. 25.
- 18 Glag I.E., Schoonrdad G.P. / I.E. Glag, G.P. Schoonrdad // Journal- South African Institute of Mining and Metallurgy. 1976. No. 1. P. 11–14.
  - 19 Pajank W. Rudy oimetalle neizelazne. 1976. No. 1. P. 627–633.
- 20 Синявер Б.В. Комплексная переработка свинцово-медно-цинкового концентрата за рубежом / Б.В. Синявер, С.Н. Абрамишвили, Ю.С. Галушко // Цветметинформация. 1974. № 18. С. 37–39.

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# Құрамында мырышы бар материалдар және кендерден вельц-процесс арқылы мұнай шламын пайдалана отырып кадмийді бөліп алу

Мақалада құрамында мырышы бар кендерден кадмийді бөліп алу әдістері қарастырылған. Ащысай рудаларына (0,1-0,2 % Сd) 40-50 % кокс ұнтағы қосылып вельц-процесс арқылы пеште күйдірілді. Вельц-процесс кезінде кадмийдің айдалу дәрежесі 92-95 % құрайды. Вельц-процесс өнімдерінің құрамында 0,05-1,2 % Cd бар. Құрамында кадмийі бар кендерді және жартылай өнімдерді өңдеу тиімділігі кокс ұнтағын арзан материалмен алмастыруға байланысты. Мақалада құрамында кадмийі бар материалдарды өңдеу кезінде мұнай шламын қолдану мүмкіндігін негіздейтін зерттеу нәтижелері келтірілген, Гиббс энергиясының өзгеруін ( $\Delta G^0_{\mathrm{T}}$ ) есептеу арқылы, пештің әртүрлі температуралық аймағында көміртегін, мұнай шламын қолдана отырып, кадмийдің тотықсыздануының термодинамикалық ықтималдылығы анықталды. «Астра» бағдарламалық кешенді пайдалана отырып, термодинамикалық модельдеу арқылы кадмийдің тотықсыздануының тепе-теңдік дәрежесі және газды фазаға ауысуы, 300-1500 К температура және 0,05-0,5 МПа қысым аралығында газды фазаның құрамы анықталды. CdO-не қатысты тотықсыздандырғыштардың бастапқы реакцияласу қабілеті келесі қатар бойынша өзгереді:  $H_2$ > $CH_4$ > $C_2H_6$ > $C_2H_2$ >CO>C> $H_2$ S>Zn; ал CdS-не қатысты бұл қатар келесі түрге ие:  $H_2>C_nH_m>CdSO_4>H_2O>C$ . Жоғары температурада тотықсыздандырғыштың түрі кадмийді айдауға әсерін тигізбейді (ол T > 1300 K болғанда  $\alpha > 99 \%$  құрайды). CdO - CdS - мұнайшлам жүйесінде әрекеттесу, Т > 400 К кезінде СdО-нен Сd-дің тотықсыздануы байқалады. Әрі қарай T > 1100К кезінде CdS-нен Cd-дің тотықсыздануы жүзеге асып, ол  $T \ge 1300$  К кезінде максимумға жетеді.

Кілт сөздер: жартылай өнім, мырыш концентраты, шаңды өңдеу, пирометаллургия, гидрометаллургия, вельц-процесс, құрамында кадмийі бар қосылыстар, кадмийдің тотықсыздануы, мұнай шламы.

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# Извлечение кадмия из цинксодержащих материалов и руд вельцеванием с использованием нефтяного шлама

В статье рассмотрены способы извлечения кадмия из руд и кеков. Вельцевание ачисайских руд (0,1-0,2 % Cd) проводилось в печи в присутствии 45-55 % кокса от массы рудной шихты. В возгоны извлекается до 92-95 % кадмия. Выход возгонов составляет 16-18 % от массы рудной шихты. Возгоны вельцевания содержат от 0,05 до 1,2 % Сd. Эффективность переработки кадмийсодержащих руд и полупролуктов вельцеванием во многом зависит от степени замены коксовой мелочи на менее дорогостоящие материалы. Приведены результаты исследований, обосновывающие возможность использования нефтяного шлама при вельцевании кадмийсодержащих материалов, расчетом энергии Гиббса  $\Delta G_T^{\ 0}$  определена термодинамическая вероятность восстановления кадмия из кадмийсодержащих соединений в присутствии углерода, нефтяного шлама и составляющих его углеводородов в различных температурных зонах вельц-печи. Термодинамическим моделированием с использованием программного комплекса «Астра» установлена равновесная степень восстановления и перехода кадмия в газовую фазу, состав газовой фазы в температурном интервале 300-1500 К и давлениях 0,05-0,5 МПа. Установлено, что начальная реакционная способность восстановителей по отношению к CdO изменяется в ряду:  $H_2$ > $CH_4$ > $C_2H_6$ > $C_4H_{10}$ > $C_2H_2$ >CO>C> $H_2S$ >Zn, а по отношению к CdS этот ряд имеет вид:  $H_2 > C_n H_m > CdSO_4 > H_2O > C$ . При высоких температурах вид восстановителя не оказывает влияния на отгонку Cd (она составляет α >99 % при T > 1300 K). Взаимодействие в системе CdO − CdS − нефтяной шлам отмечается при температуре T >400 K восстановлением Cd из CdO. В последующем при T > 1100 K происходит восстановление Cd из CdS, достигая максимума при  $T \ge 1300 \text{ K}$ .

*Ключевые слова*: промпродукты, цинковые концентраты, переработка пылей, пирометаллургия, гидрометаллургия, вельцевание, кадмийсодержащие соединения, восстановление кадмия, нефтяные шламы.

### References

- 1 Babadzhan, A.A. (1968). Pirometallurhicheskaia selektsiia [Pyrometallurgical selection]. Moscow: Metallurhiia [in Russian].
- 2 Alshanov, R.A. (Eds.). (2004). Kazakhstan na mirovom mineralno-syrevom rynke: problemy i ikh resheniia [Kazakhstan in the world mineral and raw materials market: problems and their solutions]. Almaty: Institut mirovoho rynka [in Russian].
- 3 Mogilny, V.V. (2003). O nekotorykh zakonomernostiakh ispolzovaniia poverkhnostno-aktivnykh veshchestv v tseliakh sovershenstvovaniia tekhnolohii elektroosazhdeniia tsinka, kadmiia i talliia [On some regularities of the use of new surfactants in order to improve the technology of electrodeposition of zinc, cadmium and thallium]. *Extended abstract of Doctor's thesis*. Almaty [in Russian].
  - 4 Karabasov, Yu.S. (Eds.). (2002). Novyie materialy [New materials]. Moscow: MISiS [in Russian].
- 5 Lakernik, M.M., & Pakhomova, G.N. (1969). *Metallurhiia tsinka i kadmiia [Metallurgy of zinc and cadmium]*. Moscow: Metallurhiia [in Russian].
  - 6 Chizhikov, D.M. (1962). Kadmii [Cadmium]. Moscow: AN SSSR [in Russian].
- 7 Lakernik, M.M. (1971). Elektrotermiia v metallurhii medi, svintsa, tsinka [Electrothermy in metallurgy of copper, lead, zinc]. Moscow: Metallurhiia [in Russian].
- 8 Snurnikov, A.P., & Yurenko, V.M. (1965). Laboratornye issledovaniia hidrometallurhicheskoi pererabotki medno-svintsovotsinkovoho promprodukta [Laboratory research of hydrometallurgical processing of copper-lead-zinc industrial products]. *Tsvetnye metally Non-ferrous metals*, 11, 77–80 [in Russian].
- 9 Ryskin, M.Ya., Goryachkin, V.I., Sinelshchikova, E.N., & Mitrofanov, S.I. (1965). Puti povysheniia kachestva kontsentratov pri obohashchenii medno-svintsovykh rud [Ways to improve the quality of concentrates during the enrichment of copper-zinc ores]. *Tsvetmetinformatsiia Non-ferrous metals information*, 11, 16–17 [in Russian].
- 10 Tleukulov, O.M. (1985). Kompleksnaia bezotkhodnaia khloridnaia pererabotka polimetallicheskoho okislennoho syria [Integrated non-waste chloride processing of polymetallic oxidized raw materials]. *Extended abstract of Doctor's thesis*. Leningrad [in Russian].
- 11 Snurnikov, A.P. (1977). Kompleksnoe ispolzovanie syria v tsvetnoi metallurhii [Complex use of raw materials in non-ferrous metallurgy]. Moscow: Metallurhiia [in Russian].
- 12 Babadzhan, A.A. (1959). Puti sovershenstvovaniia tekhnolohii i trebovaniia k ahrehatu dlia protsessa piroselektsii [Ways of improving technology and requirements to the aggregate for the process of pyro-selection]. *Tsvetnye metally Non-ferrous metals*, 4, 30–34 [in Russian].
- 13 Snurnikov, A.P., Pusko, A.G., & Yurenko, V.M. (1965). Polupromyshlennye ispytaniia sulfatizatsii tsinkovykh kekov v kipiashchem sloe [Semi-industrial tests of sulfatization of zinc materials in the fluidized bed]. *Tsvetnaia metallurhiia Russian Journal of Non-ferrous Metals*, 9, 29–34 [in Russian].
- 14 Shevko, V.M., Abdikulova, Z.K., & Tleuova, S.T. (1999). Termodinamicheskii analiz vosstanovleniia oksida kadmiia (II) [Thermodynamic analysis of cadmium oxide recovery (II)]. *Ekolohiia i obrazovanie Ecology and Education*. Kentau: Kh.A. Yassawi IKTU [in Russian].

- 15 Shevko, V.M., & Aitkulov, D.K. (1985). Postroenie diahramm partsialnykh davlenii system Bi-O-Cl i Cd-O-Cl s uchetom obrazovaniia oksokhloridov vismuta i kadmiia s ispolzovaniem EVM [Construction of partial pressure diagrams of Bi-O-Cl and Cd-O-Cl systems taking into account the formation of bismuth and cadmium oxochlorides using a computer]. *Dep. in KazNIINTI*, 1010 Ka-85, 8–9 [in Russian].
- 16 Karapetyants, M.Kh., & Karapetyants, M.L. (1968). Osnovnye termodinamicheskie konstanty neorhanicheskikh i orhanicheskikh veshchestv [Basic thermodynamic constants of inorganic and organic substances]. Moscow: Khimiia [in Russian].
- 17 Kazenas, E.K., & Bolshikh, M.A. (1989). Mass-spektrometricheskoe issledovanie protsessov ispareniia i dissotsiatsii oksidov medi, serebra, tsinka, kadmiia [Mass spectrometric study of the processes of evaporation and dissociation of oxides of copper, silver, zinc, cadmium]. *Dep. in VNIINTI*, 3583B89, 23–25 [in Russian].
  - 18 Glag, I.E., & Schoonrdad, G.P. (1976). J.S. Afric. Inst. Mining and Metallurgy, 1, 11-14.
  - 19 Pajank, W. (1977). Rudy oimetalle neizelazne, 1, 627-633.
- 20 Sinyaver, B.V. Abramishvili, S.N, & Galushko, Yu.S. (1974). Kompleksnaia pererabotka svintsovo-medno-tsinkovoho kontsentrata za rubezhom [Complex processing of lead-copper-zinc concentrate abroad]. *Tsvetmetinformatsiia Non-ferrous metals information*, 18, 37–39 [in Russian].