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Thermodynamic justification of chloride sublimation of nonferrous metals from chalcopyrite-magnetite ore Irisu in the presence of calcium chloride

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Abstract. The presence of nonferrous metals, particularly copper, in the chalcopyrite-magnetite ore of the Irisu deposit precludes its use in metallurgical production. This requires preliminary metal extraction. This article presents the results of a study on the extraction of nonferrous metals from Irisu ore by chloride sublimation roasting. The study was conducted using computer thermodynamic modeling and the HSC-10 software package, which is based on the minimum Gibbs free energy principle. Calcium chloride was used as the chlorinating agent. The effects of temperature and pressure on the chloride sublimation of nonferrous metals and the behavior of iron and sulfur during this process were determined. It was established that the interaction of Irisu ore with calcium chloride is accompanied by the formation of gaseous chlorides: $\text{AgCl}_{(g)}$, $\text{CoCl}_{2(g)}$, $\text{Cu}_2\text{Cl}_{2(g)}$, $\text{Cu}_3\text{Cl}_{3(g)}$, $\text{Cu}_4\text{Cl}_{4(g)}$, $\text{CuCl}_{(g)}$, $\text{FeCl}_{2(g)}$, $\text{PbCl}_{(g)}$, $\text{PbCl}_{2(g)}$, $\text{ZnCl}_{2(g)}$. A decrease in pressure from 0.1 to 0.001 bar reduces the temperature of complete chloride sublimation of copper to 683°C, zinc – 597°C, lead – 593°C, silver and cobalt to 700°C. The degree of chloride sublimation of iron at 700°C is only 0.24%. In the cinder, it is present to a greater extent in the form of Fe_3O_4 and to a lesser extent in the form of Fe_2O_3 and FeO . Under these conditions, sulfur is almost completely (99.99%) converted into SO_2 . Chloride sublimates formed at 700°C and 0.001 bar contain 33.94% copper, 11.57% lead, 5.98% zinc, 2.88% cobalt, 0.2673% silver and 5.49% iron. In this polymetallic concentrate, compared to the ore, the content of copper, zinc and silver increased by 44.6 times, lead – by 44.5 times, cobalt – by 45.3 times.

Keywords: chalcopyrite-magnetite ore, calcium chloride, thermodynamic modeling, temperature, pressure, chloride sublimation, copper, lead, zinc, cobalt, silver, sulfur.

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1. Introduction

Iron-bearing ores, including those in Kazakhstan, where estimated iron ore reserves are 12.5-16.6 billion tons [1-3], often contain nonferrous metals [4-5]. Therefore, not all ores are suitable for direct metallurgical processing. The Irisu chalcopyrite-magnetite deposit, with reserves of 327.1 million tons, is located in Tyulkubas district of Turkestan region. The deposit's ore field consists of Middle Paleozoic carbonate rocks intruded by alkaline gabbroic intrusions.

The main minerals are magnetite, pyrite, chalcopyrite, pyrrhotite, cobaltite, sphalerite, and galena. The ore contains 30-60% iron, 0.32-0.93% copper, 0.24% lead, 0.09% zinc, and 0.04% cobalt [6-8]. The ore also contains selenium, tellurium, thallium, and 0.56-6.5 g/t silver. In addition to 150 million tons of iron, the ore also contains 2 million tons of copper, which is a valuable resource for ferrous and non-ferrous metallurgy. The ore from the Susingen deposit, with reserves of 25 million tons, also falls into this category [9].

Processing iron-bearing ores containing nonferrous metals involves a combination of physical and chemical technologies, such as magnetic separation, flotation, and leaching, including bioleaching. A common drawback of these methods is the multi-stage nature and insufficient recovery of nonferrous metals and often iron as well. Thus, during the processing of sulfide-magnetite ore (35.7% Fe, 0.64% Cu, 1.2 g/t Au), which successively uses X-ray radiometric separation, wet magnetic separation and flotation, 93.6% of copper is extracted into copper concentrate (23.7% Cu, 18.9 g/t Au and 60 g/t Ag), only 76.6% of iron is extracted into magnetite concentrate (66.5% Fe), and only 27% of gold is extracted into gold-bearing concentrate (50 g/t).

During the flotation of copper-magnetite ore (0.3-0.5% Cu) by flotation into copper concentrate (18.5% Cu) only 77.8% of copper was extracted [10]. From the wet magnetic separation tailings of ferrous ores containing 0.29% sulfide copper, no more than 80% of copper was extracted into concentrate (25.3% Cu) by flotation [11], and from similar ore of

another Cheremshansky tailings dump only 65.3% of copper was extracted into concentrate [11]. Preliminary (before magnetic separation) magnetic pulse treatment of ore containing 0.14% sulfide copper allowed to increase the copper extraction into sulfide product from 54 to 65% [12]. Using multi-stage wet magnetic separation and flotation of its tailings from iron ore containing copper into magnetic concentrate (65-66% Fe), 79-80% of Fe was extracted, and from tailings into copper concentrate (15.2% Cu) – only 54% of copper [13]. Magnetic separation of the Irisu deposit ore and flotation of its tailings yielded 87-90% iron recovery into magnetic concentrate (69-75% Fe), 75-84% copper recovery into copper concentrate (18.64% Cu), and 67.2-77.3% cobalt recovery into cobalt-pyrite concentrate.

Research [14] presents the results of studies of Fe-Cu-containing ore (1.79% Cu) using a magnetic separation and copper leaching scheme from separation tailings. This method allows for the recovery of only 72% copper.

Gravity enrichment of ore containing 16.5% Fe, 0.13% Cu, and rare earth elements resulted in the conversion of 76.6% iron and 72.6% copper into the heavy fraction, and 77.9% rare earth elements into the light fraction. A combination of magnetic separation and bioleaching of magnetite concentrate yielded 80% of copper and 20% of zinc [15].

The above data demonstrates that existing multi-stage methods do not provide a high level of separation of iron from nonferrous metals in copper-magnetite ores. Currently, they do not meet modern requirements for the integrated use of raw materials. The problem of integrated processing of copper-magnetite ores can be successfully solved by developing a technology that allows for the complete separation of iron from nonferrous metals in a single process step, followed by the production of marketable products from magnetite concentrate. Chloride sublimation is an effective method for the selective extraction of nonferrous metals from iron-containing raw materials. The main advantage of this method is the ability to virtually completely suppress iron chlorination, leaving it in the cinder and extracting the nonferrous metals into chloride sublimes. Based on this, chloride-electrothermal technology may be an effective method for processing Irisu iron-bearing ore. This involves chloride-sublimation roasting in the first stage, with the extraction of copper and other nonferrous metals into a polymetallic concentrate – chloride sublimes and iron-containing magnetite concentrate – from which a ferroalloy is produced in the second stage by electric smelting. The authors of this article have previously conducted studies on the chloride-sublimation of nonferrous metals from various polymetallic natural and technogenic raw materials, with virtually complete iron retention in the cinder [16, 17]. This article presents the results of studies on the equilibrium chloride sublimation of nonferrous metals from chalcopyrite-magnetite ore at the Irisu deposit in the presence of calcium chloride.

2. Materials and methods

The study was conducted using thermodynamic modeling with the HSC-10 software package [18], based on the minimum Gibbs free energy principle, to determine the equilibrium distribution of nonferrous metals and iron (α , %) in the Irisu ore (IO) – CaCl₂ – O₂ system. The temperature range for the studies was 300-1700°C, and the pressure range was 0.1-0.001 bar. The ore used in the study was from the Irisu

deposit, containing (wt%): 69.4 Fe₃O₄, 10.0 SiO₂, 6 CaCO₃, 5.8 MgCO₃, 3.3 Al₂O₃, 2.2 CuFeS₂, 0.3 PbS, 0.2 ZnS, 0.1 CoS, 0.002 Ag. To improve the efficiency of the research and obtain maximum information from the processes under study, the method of second-order rotatable research design (Box-Hunter plans) was also used in the work, with the resulting regression equations [19] being used to construct volumetric and planar images of the optimization parameters [20, 21]. The temperature and pressure ensuring maximum chloride sublimation of nonferrous metals and minimum chloride sublimation of iron were determined from the image of the overlapping planar images.

3. Results and discussion

The primary material obtained using the HSC-10 complex allowed to establish that in the system under consideration, at a pressure of 0.1 bar, the reaction occurs with the formation of Ag_(g), AgCl, AgCl_(g), Al₂SiO₅, CaCl_{2(g)}, CaSiO₃, CaSO₄, Cl_(g), CO_(g), CO_{2(g)}, CoCl₂, CoCl_{2(g)}, Cu_(g), Cu₂Cl_{2(g)}, Cu₃Cl_{3(g)}, Cu₄Cl_{4(g)}, CuCl, CuCl_(g), CuCl_{2(g)}, Fe₂O₃, FeCl₂, FeCl_{2(g)}, FeCl_{3(g)}, FeO, FeS, FeSiO₃, MgO, MgSiO₃, O_{2(g)}, Pb_(g), PbCl_(g), PbCl₂, PbCl_{2(g)}, SO_{2(g)}, Zn_(g), ZnCl_(g), ZnCl₂, ZnCl_{2(g)}.

Figure 1 shows the effect of temperature on the degree of metal distribution in the RI – CaCl₂ – O₂ system at 0.1 bar. It is evident that the formation of the target gaseous chlorides: Cu₄Cl_{4(g)}, Cu₃Cl_{3(g)}, Cu₂Cl_{2(g)} and CuCl_(g) occurs, respectively, in the following temperature ranges: 400-1300°C, 400-1400°C, 900-1500°C, and >800°C.

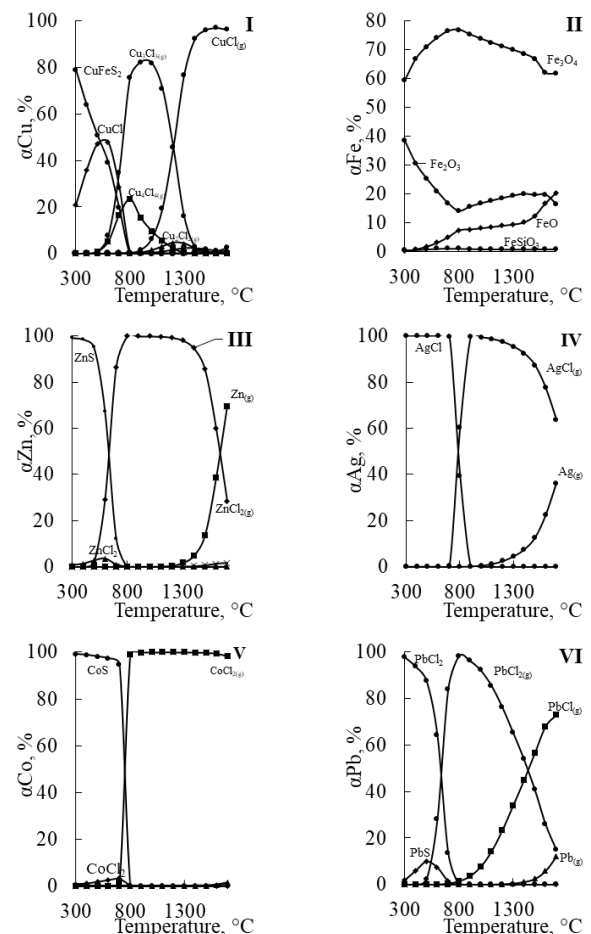


Figure 1. Effect of temperature on the degree of distribution Cu (I), Fe (II), Zn (III), Ag (IV), Co (V), Pb (VI)

Iron is practically not chlorinated in the system, accounting for only 0.23-0.33% at 800-1700°C. Predominantly (59.6-75.3%), iron remains in the form of Fe₃O₄ in the temperature range of 300-1700°C. To a lesser extent, iron is converted into Fe₂O₃ (38-15%), and only 0.32-8.2% into FeO.

The target zinc-containing product, gaseous ZnCl_{2(g)}, begins to appear in the system at 400°C. The maximum of this process (99.5-99.9%) occurs at 800-1200°C. Then, as the temperature increases to 1700°C, the decomposition of ZnCl_{2(g)} begins, forming gaseous ZnCl(g) and Zn(g).

Complete chlorination of silver to form AgCl occurs at 300°C. The maximum conversion of silver to gas (99.7%) in the form of AgCl occurs at 900°C. Then, as the temperature increases to 1700°C, the decomposition of AgCl(g) occurs, forming Ag(g) and chlorine (36.2% of gaseous silver is formed at 1700°C). The chlorination of CoS to form CoCl₂ begins at 400°C, and gaseous CoCl₂ begins at 800°C. In the temperature range of 900-1700°C, all cobalt is present as CoCl_{2(g)}.

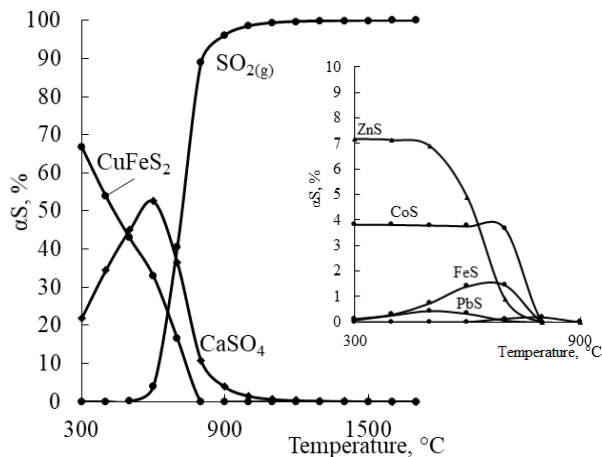
Chlorination of PbS is virtually complete at 300°C, forming PbCl₂, which persists up to 800°C. Formation of gaseous PbCl₂ occurs in the range of 400-1700°C, with a maximum (98.4%) at 800°C. At temperatures above 800°C, gaseous PbCl₂ forms: PbCl₂ = PbCl(g) + 0.5Cl₂. In the temperature range of 1300-1700°C, some elemental lead is in the gaseous state.

Table 1 shows the effect of temperature on the degree of conversion of metals (as the sum of chlorides and elements) into gas (hereinafter α_{Me(gas)}) at a pressure of 0.1 bar.

Table 1. Effect of temperature on the degree of distribution of elements in gas

Element	Temperature, °C									
	300	400	500	600	700	800	900	1000	1500	1700
Ag	–	–	–	0.01	0.33	60.52	100	100	100	100
Co	–	–	–	0.05	2.06	99.60	100	100	100	100
Cu	–	0.07	1.81	13.22	51.68	99.46	100	100	100	100
Fe	–	–	–	–	0.03	0.23	0.24	0.24	0.25	0.33
Pb	–	0.05	2.41	28.29	84.77	99.94	100	100	100	100
Zn	–	0.05	2.07	29.21	86.70	99.99	100	100	100	100

Table 1 shows that at 0.1 bar and 900°C, Zn, Cu, Pb, Co, and Ag completely transform into gas. Almost all the iron remains in the cinder. Only 0.24% of the iron transforms into gaseous FeCl₃. Figure 2 shows the effect of temperature and pressure on the degree of metal conversion to the gas phase. It is evident that decreasing the pressure from 0.1 to 0.001 bar lowers the temperature for complete gasification of zinc and lead to 600°C, and for Cu, Co, and Ag to 700°C. At 700°C, the degree of iron chloride sublimation is only 0.25%.



When producing cinders, it is important that they contain a minimum amount of sulfur.

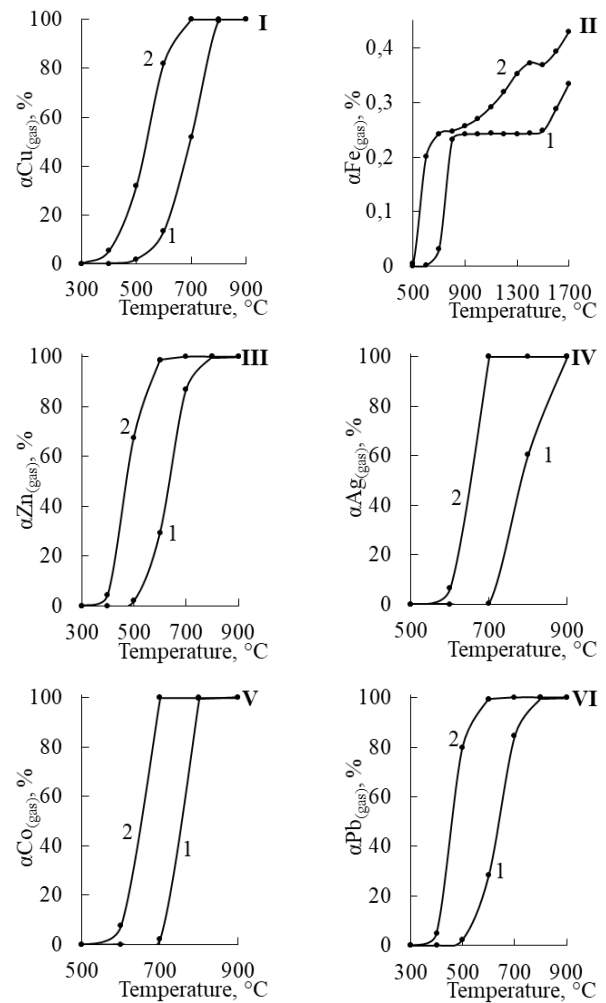


Figure 2. Effect of temperature and pressure on the degree of metal extraction into the gas phase (pressure: 1 – 0.1 bar; 2 – 0.001 bar)

Figure 3 shows that the main sulfur-containing substances in the system are CuFeS₂, CaSO₄, SO₂, ZnS, PbS and CoS. Reducing the pressure from 0.1 to 0.001 bar allows for a reduction in the temperature of virtually complete (99.29%) sulfur conversion to SO₂ from 1300 to 700°C. Only 0.7% sulfur remains in the cinder.

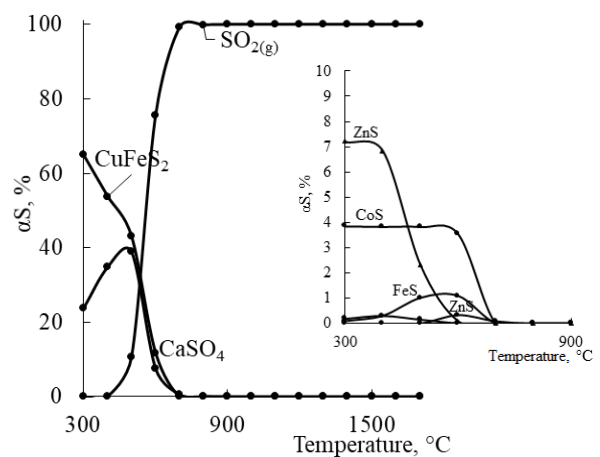


Figure 3. Effect of temperature and pressure on the degree of sulfur distribution (pressure: I – 0.1 bar; II – 0.001 bar)

To determine the temperature and pressure that will maximize the extraction of copper, zinc, lead, silver, and cobalt into gaseous chlorides, further research is being conducted using a second-order rotatable design [19]. Table 2 presents the experimental design matrix and the results of studying the effects of temperature and pressure on the conversion of the main metals from the ore into the gas phase.

Table 2. Effect of temperature and pressure on the degree of conversion of copper, lead, and zinc into the gas phase

No.	Variables				$\alpha\text{Cu}_{(gas)}$, %	$\alpha\text{Pb}_{(gas)}$, %	$\alpha\text{Zn}_{(gas)}$, %
	Coded		Natural				
	X ₁	X ₂	lgP	T, °C			
1	+	+	-2.7	654	94.3	99.0	99.8
2	-	+	-1.3	654	46.4	75.1	75.3
3	+	-	-2.7	526	37.3	77.3	73.0
4	-	-	-1.3	526	9.0	15.6	16.0
5	1.414	0	-3	590	80.5	96.2	97.2
6	-1.414	0	-1	590	12.7	25.0	27.4
7	0	1.414	-2	680	87.0	98.2	100.0
8	0	-1.414	-2	500	13.4	22.4	18.5
9	0	0	-2	590	40.2	84.7	77.8
10	0	0	-2	590	40.8	85.0	77.6
11	0	0	-2	590	41.0	85.1	77
12	0	0	-2	590	41.6	85.7	76.6
13	0	0	-2	590	41.6	86.0	76.1

Using the data from the table in [20], the following regression equations were obtained:

$$\alpha\text{Cu}_{(gas)} = 136.09 - 0.56 \cdot T + 63.1 \cdot \lg P + 0.00058 \cdot T^2 + 8.5 \cdot (\lg P)^2 - 0.109 \cdot T \cdot \lg P \quad (1)$$

$$\alpha\text{Pb}_{(gas)} = -1450 + 3.89 \cdot T - 247.4 \cdot \lg P - 0.0026 \cdot T^2 - 22.33 \cdot (\lg P)^2 + 0.211 \cdot T \cdot \lg P \quad (2)$$

$$\alpha\text{Zn}_{(gas)} = 983.26 + 2.43 \cdot T - 203.95 \cdot \lg P - 0.0015 \cdot T^2 - 15.25 \cdot (\lg P)^2 + 0.18 \cdot T \cdot \lg P \quad (3)$$

Then, according to [21], 3D and planar images of the dependencies $\alpha\text{Cu}_{(gas)}$, $\alpha\text{Pb}_{(gas)}$, $\alpha\text{Zn}_{(gas)} = f(\lg P, T)$ were constructed. Table 3 presents the pressure and temperature values at the boundaries of the regions shown in Figure 4, where $\alpha\text{Me}_{(gas)}$ ranges from 90 to 100%.

Table 3. Pressure and temperature values at the boundaries of the regions where $\alpha\text{Me}_{(gas)}$ ranges from 90 to 100%

Metal	Points of the region	lgP	P, bar	T, °C	$\alpha\text{Me}_{(gas)}$, %
Copper	a	-2.3	0.005	680	90
	b	-2.5	0.003	680	100
	c	-3.0	0.001	623	100
	d	-3.0	0.001	601	90
Lead	t	-1.57	0.027	680	90
	f	-1.95	0.011	680	100
	h	-3.0	0.001	593	100
Zinc	u	-3.0	0.001	554	90
	o	-1.67	0.021	680	90
	p	-2.11	0.008	680	100
	l	-3.0	0.001	597	100
	e	-3.0	0.001	551	90

From Table 3 it follows that lead sublimes into chlorides by 90-100% in the temperature range of 554-680°C at 0.011-0.001 bar, zinc – at 551-680°C and 0.021-0.001 bar, and copper – at 601-680°C and 0.005-0.001 bar.

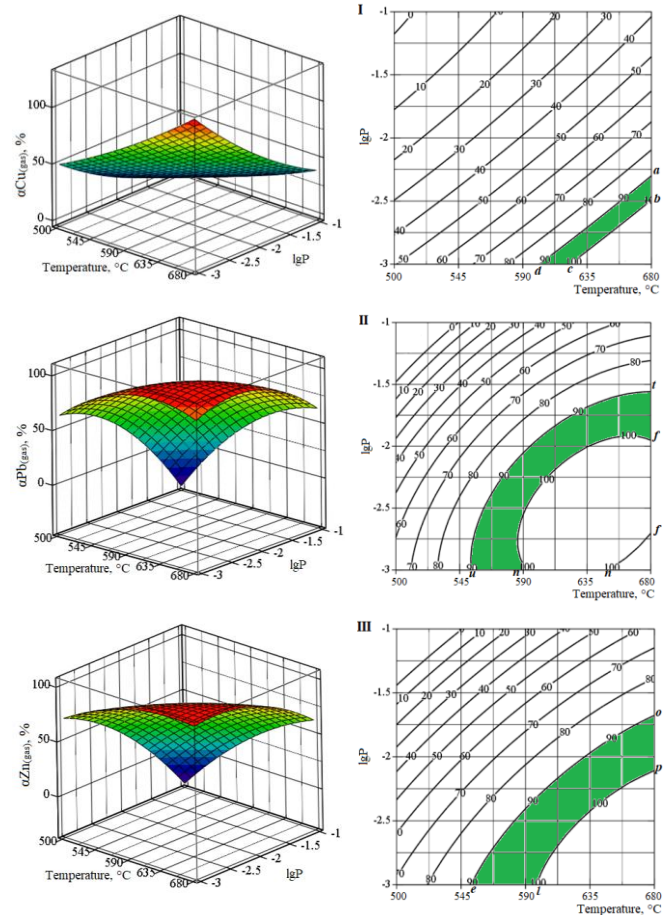


Figure 4. 3D and planar images of the effect of temperature and pressure on the degree of conversion n of metals into gas (metals: I – copper; II – lead; III – zinc)

Figure 5 and Table 3 show that copper undergoes chloride sublimation with greater difficulty than zinc and lead. Therefore, the conditions for copper chloride sublimation determine the optimal parameters for the chloride sublimation of copper, zinc, and lead. These conditions must also be consistent with the conversion of silver and cobalt into gas.

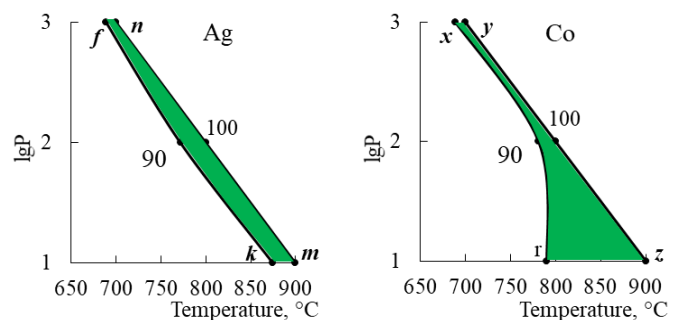


Figure 5. Effect of temperature and pressure on $\alpha\text{Me}_{(gas)}$ of silver and cobalt (the numbers near the line indicate the degree of conversion of metal into gas, %)

Figure 5 shows the $\alpha\text{Me}_{(gas)}$ regions for silver and cobalt from 90 to 100%, and Table 4 shows the pressure and temperature values for these regions. At a pressure of 0.001-0.01 bar, $\alpha\text{Ag}_{(gas)} = 90-100\%$ in the temperature range of 698-900°C, while cobalt does so at 689-900°C.

Comparing Tables 3 and 4, it follows that $\alpha\text{Ag}_{(gas)}$ and $\alpha\text{Cu}_{(gas)}$ decomposition occurs at higher temperatures.

Table 4. lgP and temperature values at the boundaries of the regions where $\alpha Me_{(gas)}$ for Ag and Co ranges from 90 to 100%

Metal	Points of the region	lgP	P, bar	T, °C	$\alpha Me_{(gas)}$, %
Silver	f	-3	0.001	698	90
	n	-3	0.001	700	100
	m	-1	0.1	900	100
	k	-1	0.1	875	90
Cobalt	x	-3	0.001	689	90
	y	-3	0.001	700	100
	z	-1	0.1	900	100
	r	-1	0.1	790	90

Thus, at 0.001 bar, $\alpha Cu_{(gas)} = 100\%$ occurs at 623°C, while for cobalt and silver, it occurs only at 700°C. Therefore, the optimal temperature should be determined by the chloride sublimation of silver (698-900°C and 0.01-0.1 bar).

Figure 6 shows the effect of temperature and pressure on the metal concentration in condensed sublimates.

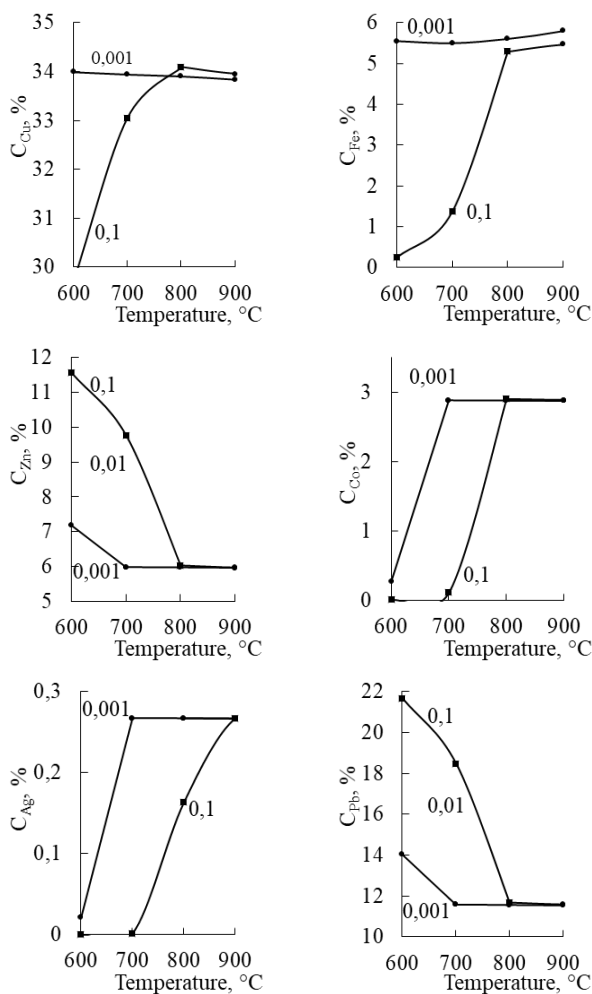


Figure 6. Effect of pressure and temperature on the concentration of metals in condensed sublimates (the numbers near the line indicate pressure in bar)

It is evident that in the region of 800-900°C the change in pressure has virtually no effect on the concentration of copper, lead, zinc, cobalt and silver, amounting to 33.7-34.0%; 11.7-11.6%; 5.97-5.95%, 2.9-2.97%, respectively. The concentration of iron at 600-900°C increases from (5.29 at 800°C) to (5.79 at 900°C). At 700°C and 0.001 bar, when the nonferrous metals had completely converted into gaseous chlorides, the concentration of copper in the condensed sub-

limes was 33.94%, lead – 11.57%, zinc – 5.98%, cobalt – 2.88%, silver – 0.27%, iron – 5.49%. Chloride sublimates are a polymetallic concentrate in which, in comparison with the ore, the concentration of copper, zinc and silver has increased by 44.6 times, lead – by 44.5 times, cobalt – by 45.3 times. The cinder after roasting the ore at 800°C and 0.001 bar contains by weight %: Fe_3O_4 – 59.81, Fe_2O_3 – 12.03, $CaSiO_3$ – 9.33, $MgSiO_3$ – 6.11, FeO – 5.12, Al_2O_3 – 3.52, SiO_2 – 1.91, $FeSiO_3$ – 1.33, MgO – 0.62, Al_2SiO_5 – 0.21, $CaSO_4$ – 0.01. It can be used in blast furnaces, steelmaking or for the production of ferroalloys.

4. Conclusions

Based on the conducted studies of the equilibrium interaction of Irisu copper-magnetite ore with calcium chloride in the presence of oxygen, the following conclusions can be drawn:

- the chlorination products are chlorides of copper (Cu_4Cl_4 , Cu_3Cl_3 , Cu_2Cl_2 and $CuCl$), lead ($PbCl_2$, $PbCl$), zinc ($ZnCl_2$, $ZnCl$), iron ($FeCl_3$, $FeCl_2$), silver ($AgCl$), and cobalt ($CoCl_2$);
 - according to the temperature of the beginning of formation of gaseous chlorides, metals form a series: Cu, Zn, Pb, Co, Ag and Fe; this temperature, like the temperature of complete extraction of chlorides into gas, shifts to the region of lower temperatures with decreasing pressure;
 - complete chloride sublimation of copper at a pressure of 0.001 bar occurs at 683°C, zinc – 597°C and lead – 593°C, silver and cobalt at 700°C (iron is chlorinated only by 0.24%);
 - chloride sublimates formed at 700°C and 0.001 bar contain 33.94% copper, 11.57% lead, 5.98% zinc, 2.88% cobalt, 0.2673% silver and 5.49% iron; chloride sublimates are a polymetallic concentrate in which, compared to the ore, the concentration of copper has increased by 44.6 times, lead – by 44.5 times, zinc and silver – by 44.6 times, cobalt – by 45.3 times;
 - sulfur present in the ore at a pressure of 0.001 bar and 700°C is almost completely (99.29%) converted to SO_2 .
- The cinder after roasting the ore at 800°C and a pressure of 0.001 bar contains the following by weight, %: Fe_3O_4 – 59.381, Fe_2O_3 – 12.03, $CaSiO_3$ – 9.33, $MgSiO_3$ – 6.11, FeO – 5.12, Al_2O_3 – 3.52, SiO_2 – 1.91, $FeSiO_3$ – 1.33, MgO – 0.62, Al_2SiO_5 – 0.21, $CaSO_4$ – 0.01, can be used in the production of cast iron, steel, and ferroalloys.

Author contributions

Conceptualization: V.M.S., M.A.T.; Data curation: V.M.S., M.A.T.; Formal analysis: D.K.A., Yu.P.U.; Funding acquisition: V.M.S., M.A.T.; Investigation: M.A.T., Yu.P.U.; Methodology: V.M.S., D.K.A.; Project administration: V.M.S., D.K.A.; Resources: V.M.S., M.A.T.; Software: M.A.T., Yu.P.U.; Supervision: V.M.S., M.A.T.; Validation: V.M.S., D.K.A.; Visualization: M.A.T., Yu.P.U.; Writing – original draft: V.M.S., M.A.T.; Writing – review & editing: V.M.S., M.A.T. All authors have read and agreed to the published version of the manuscript.

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Conflicts of interests

The authors declare no conflict of interest.

Data availability statement

The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

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Ирису кен орнындағы халькопирит-магнетит кенінен кальций хлориді қатысуында түсті металдарды хлоридті айдау процесінің термодинамикалық негіздемесі

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²Қазақстан Республикасының минералдық шикізатты кешенді өңдеу жөніндегі ұлттық орталығы, Алматы, Қазақстан

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Аңдатпа. Ирису кен орнындағы халькопирит-магнетит кенінің құрамында түсті металдардың, әсіресе мыстың болуы бұл кенді металлургиялық өндірісте тікелей пайдалануға мүмкіндік бермейді. Сондықтан кенді қолданар алдында одан металдарды алдын ала бөліп алу қажет. Мақалада Ирису кенінен түсті металдарды хлоридті айдау арқылы күйдіру әдісімен бөліп алу бойынша жүргізілген зерттеулердің нәтижелері келтірілген. Зерттеулер компьютерлік термодинамикалық модельдеу әдісімен, Гиббс энергиясының минимум принципіне негізделген HSC-10

бағдарламалық кешенін қолдану арқылы жүргізілді. Хлорлаушы реагент ретінде кальций хлориді пайдаланылды. Температура мен қысымның түсті металдардың хлоридті айдалуына, сондай-ақ темір мен күкірттің мінез-құлқына әсері анықталды. Ирису кені кальций хлоридімен әрекеттескенде келесі газ тәрізді хлоридтердің түзілетіні анықталды: $\text{AgCl}_{(г)}$, $\text{CoCl}_{2(г)}$, $\text{Cu}_2\text{Cl}_{2(г)}$, $\text{Cu}_3\text{Cl}_{3(г)}$, $\text{Cu}_4\text{Cl}_{4(г)}$, $\text{CuCl}_{(г)}$, $\text{FeCl}_{2(г)}$, $\text{PbCl}_{(г)}$, $\text{PbCl}_{2(г)}$, $\text{ZnCl}_{2(г)}$. Қысымды 0.1-ден 0.001 барға дейін төмендету мыстың толық хлоридті айдалу температурасын 683°C -қа, мырыштікіні 597°C -қа, қорғасындікіні 593°C -қа, ал күміс пен кобальттікіні 700°C -қа дейін төмендететіні анықталды. 700°C температурада темірдің хлоридті айдалу дәрежесі небәрі 0.24% құрайды. Күйдіріндіде темір негізінен Fe_3O_4 және аз мөлшерде Fe_2O_3 мен FeO түрінде кездеседі. Бұл жағдайларда күкірттің басым бөлігі іс жүзінде толық (99.99%) SO_2 түрінде газ фазасына өтеді. 700°C температура және 0.001 бар қысымда түзілген хлоридті айдамалар құрамында 33.94% мыс, 11.57% қорғасын, 5.98% мырыш, 2.88% кобальт, 0.2673% күміс және 5.49% темір бар. Бұл полиметалл концентратында кенмен салыстырғанда мыс, мырыш және күміс мөлшері 44.6 есе, қорғасын 44.5 есе, кобальт 45.3 есе артқаны анықталды.

Негізгі сөздер: халькопирит-магнетит кені, кальций хлориді, термодинамикалық модельдеу, температура, қысым, хлоридті айдау, мыс, қорғасын, мырыш, кобальт, күміс, күкірт.

Термодинамическое обоснование хлоридовозгонки цветных металлов из халькопирит-магнетитовой руды Ирису в присутствии хлорида кальция

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Аннотация. Присутствие цветных металлов и особенно меди в халькопирит-магнетитовой руде месторождения Ирису не позволяет использовать эту руду в металлургическом производстве. Для этого необходимо предварительно извлечь металлы из руды. В статье приводятся результаты исследования по извлечению цветных металлов из Ирисуской руды хлоридовозгоночным обжигом. Исследования проводились методом компьютерного термодинамического моделирования и использованием программного комплекса HSC-10 основанного на принципе минимума энергии Гиббса. В качестве хлорирующего агента использовали хлорид кальция. Определялось влияние температуры и давления на хлоридовозгонку цветных металлов и поведение при этом железа и серы. Установлено, что взаимодействие руды Ирису с хлоридом кальция сопровождается образованием газообразных хлоридов: $\text{AgCl}_{(г)}$, $\text{CoCl}_{2(г)}$, $\text{Cu}_2\text{Cl}_{2(г)}$, $\text{Cu}_3\text{Cl}_{3(г)}$, $\text{Cu}_4\text{Cl}_{4(г)}$, $\text{CuCl}_{(г)}$, $\text{FeCl}_{2(г)}$, $\text{PbCl}_{(г)}$, $\text{PbCl}_{2(г)}$, $\text{ZnCl}_{2(г)}$. Уменьшение давления от 0.1 до 0.001 бар снижает температуру, полной хлоридовозгонки меди до 683°C , цинка - 597°C , свинца - 593°C , серебра и кобальта до 700°C . Степень хлоридовозгонки железа при 700°C составляет только 0.24%. В огарке оно в большей мере присутствует в виде Fe_3O_4 и в меньшей мере - в виде Fe_2O_3 и FeO . Сера в этих условиях практически полностью (99.99%) переходит в SO_2 . Хлоридные возгоны, образующиеся при 700°C и 0.001 бар содержат 33.94% меди, 11.57% свинца, 5.98% цинка, 2.88% кобальта, 0.2673% серебра и 5.49% железа; В этом полиметаллическом концентрате в сравнении с рудой, содержание меди, цинка и серебра увеличилось в 44.6 раза, свинца – в 44.5 раза, кобальта – в 45.3 раза.

Ключевые слова: халькопирит-магнетитовая руда, хлорид кальция, термодинамическое моделирование, температура, давление, хлоридовозгонка, медь, свинец, цинк, кобальт, серебро, сера.

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