



Reduction of Copper and Iron Oxide Mixture with Local Reducing Gases

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Abstract—The article analyzes the scientific problems of the copper industry. In particular, the main problem with the classical production of copper is the causes of large amounts of slag and the negative impact of these wastes on the environment. Accordingly, the main component that forms the slag is iron, and the higher its content in the original copper concentrate, the more slag is formed, and at the same time a large amount of copper metal is released into the waste. The departure is indicated by evidence. To prevent this problem, a technology has been proposed to reduce copper sulfide concentrates by first oxidizing them in a “Hot Layer” furnace at 850 °C and then using ammonia vapors. The recovery process was carried out in a Waelz furnace (or rotary tube furnace) using a stepwise recovery method in the temperature range of 550 - 1000 °C. The results of chemical and phase analysis of samples taken from laboratory and semi-industrial experiments in the process are presented in the form of tables and XRD. The results were discussed and the thermodynamic possibilities of the process were studied. During the reduction process, the equilibrium states of the reactions of the oxides with ammonia vapors were studied and it was concluded that the temperature inside the furnace should be kept around 677 °C for the process to flow optimally.

Keywords— copper, iron, concentrate, oxidizing roasting, recovery, Waelz furnace, optimal temperature, thermodynamic parameters, candle-end, magnetic fraction.

I INTRODUCTION AND LITERATURE REVIEW

is known that 85% of the world’s copper is obtained by pyrometallurgy and 10-15% by hydrometallurgy. The choice of technology for copper production depends primarily on the mineral form of the copper in the ore. For example, if the ore contains copper in the form of complete sulfides, then, of course, pyrometallurgical methods are used [1]. If in the form of oxides, then hydrometallurgical or combined methods are used. In addition, metallurgical production also

depends on the natural, economic and geological potential of the region, i.e. the availability of coke, natural gas and similar natural resources required for production is important [2, 3].

Most enterprises around the world, such as the Almalayk Mining and Metallurgical Combine (AMMC, Uzbekistan), use the classic pyrometallurgical scheme of blister copper production. Accordingly, copper sulphide ores are first enriched by flotation to obtain a concentrate containing 16-20% copper. The obtained copper concentrate is loaded into metallurgical furnaces for thermal processing at high temperatures [4]. Metallurgical plants have several types of smelting furnaces designed to process copper raw materials. Examples include smelting furnaces such as the Reverberatory, the Oxygen Torch, and the Vanyukov Furnaces. Although the principles of operation of these smelting furnaces are different, the products are similar, such as copper matte (30-50% Cu), slag and industrial gases. The intermediate product is copper, which is converted into matte, where blister copper (96-98% Cu) is obtained by oxidizing unnecessary elements in the matte in the presence of atmospheric oxygen. The blister copper is then poured into anode molds during electrolysis and sent for electrolysis, resulting in high-quality copper cathodes (99.99% Cu) [5, 6, 7, 8, 9, 10].

This classic technology has its advantages and disadvantages. For example, smelting furnaces and converters generate large amounts of waste slag and require a large area to dispose of it [11, 12]. Additional equipment, space and funds will be required to recycle this waste slag. If the slag is not sent for recycling, it will become more and more harmful to the environment. In addition, the Reverberatory, Vanyukov, and fire-cleaning furnaces use large amounts of fuels, such as natural gas and fuel oil, to maintain high temperatures. This increases the cost of extracted copper and reduces the net profit remaining from copper production [13]. It should be noted that the content of copper in the slag from some fur-

nances is much higher, for example, the content of copper in the oxygen-torch furnace slag is about 1%, and the content of copper in the converter furnace slag is about %. This is much higher than the allowable amount for waste. Now the processing of these slags is mandatory and cannot be used as a building material [14]. Because these wastes contain large amounts of precious metals such as copper, gold and silver. So the question is, can these metals be separated from slag? In response, we can say that when the slag cools slowly, it forms a very strong crystal lattice, which requires a great deal of strength and energy to break down the solid structure. In addition, large amounts of copper in the slag are oxidized and cannot be separated by flotation. As a result, the process of crushing solid slag is very difficult and requires a lot of effort, energy and money. As a result, the cost of the finished product in copper production increases and the technology is not economically viable [15, 16, 17, 18, 19].

In some countries, copper ores in the form of oxides or mixtures (i.e., oxides and sulfides) are found, so the technology of copper extraction is based on a combined method. For example, ore or concentrate is first burned by oxidation and then processed by hydrometallurgical methods. Alternatively, blister copper can be obtained by reducing the oxidized copper concentrate formed after firing in coke ovens in the presence of coke. This technology is preferred in that it is less phased than its predecessors. However, the main disadvantage of this technology is that it cannot be used in plants in countries with low coke reserves or no coke at all (including Uzbekistan). In addition, when oxidized copper concentrate is recovered in a mine furnace in the presence of coke, large amounts of iron are transferred to the blister copper, which degrades the quality of the blister copper. Separation of blister copper from iron requires an additional oxidation process, as well as additional fluxes. As a result, more slag is formed, and the problem of loss of copper with slag arises [20].

Metallurgists have studied the main reason for the release of large amounts of copper into the waste and concluded that this is due to the formation of large amounts of slag mass during the process. Because if the process produces 1 ton of slag containing 2% copper, the loss of copper with slag is 20 kg, if 100 kg of slag containing 2% copper, this amount is 2 kg. In this process, the consumption of copper is reduced by about 10 times compared to previous technology. This means that the main cause of this problem is the formation of large amounts of slag mass [21].

The main slag-forming component in copper-iron ores from the Kalmakir deposit (Uzbekistan) is iron. Because copper contains more chalcopyrite (CuFeS_2) in the ore. In such ores, the distribution of copper to chalcopyrite (CuFeS_2) and covellin (CuS) minerals is 9:1, respectively.

This does not allow iron to be removed by selective flotation of minerals. As a result, iron, which is chemically bound to copper, also converts to concentrate, preventing the percentage of copper from increasing. Therefore, it can be concluded from the analysis that either iron or raw material should be disposed of before liquefaction in metallurgical furnaces, i.e. during flotation enrichment, or another method should be chosen instead of liquefaction [22]. So far, no measures have been taken to get rid of the iron that forms a chemical compound with copper in the process of preparing the raw material for processing (i.e., flotation enrichment). But instead of melting, you can find another, more efficient method. One such method is the ammonia reduction of oxidized copper concentrates. This can also be called the "aminothermic method". A similar study was performed in a laboratory, in which ammonia was passed through a tube containing heated copper (II) oxide [23]. However, only pure copper (II) oxide samples were used as raw materials in this study, and this method has not yet been used for copper-iron concentrates. The reduction reaction of pure copper (II) oxide takes place at a temperature of 500-550 °C, as a result of which ammonia vapors react with heated copper (II) oxide to form nitrogen, copper and water:



In some literatures, this reaction has also been referred to as Louis's theory of acid-base, the reaction between acid and base (i.e., neutralization). Here CuO is considered as an acid, NH_3 as a base. But it is well known that this is an oxidation-reduction reaction (Redox). The electronic balance of the process is as follows:

$3\text{Cu}^{+2} + 6\text{e}^- \rightarrow 3\text{Cu}^0$ (reduction process);
 $2\text{N}^{-3} - 6\text{e}^- \rightarrow \text{N}_2^0$ (oxidation process). Hence, copper (II) oxide (CuO) is an oxidant and ammonia (NH_3) is a reducing agent [24].

The purpose of this study is to obtain pure copper metal and metallized iron raw material from copper-iron concentrates based on the method and mechanism of the above research.

The novelty of the study of ammonia reduction of oxidized copper-iron concentrates is that in the Waelz furnace (rotary tube furnace) is also recovered high oxides of iron, which formed a chemical compound with copper, resulting in the formation of copper-iron metallized powder. The resulting product is then sent to a magnetic separator to separate the metallized copper and iron powder.

Ammonia reduction studies of oxidized copper-iron concentrates have several advantages, including:

- as a result of this research, the formation of slag in copper production will be sharply reduced;

- recovery of copper and other precious metals from waste;
- metallized raw materials for the production of iron as an additional product;
- as well as environmental protection due to the fact that the reaction does not emit toxic gases.

The following tasks were performed to conduct the study:

The following tasks were performed to conduct the study: The mineralogical composition of chalcopyrite copper concentrate was determined; The optimal conditions of the oxidative roasting process of chalcopyrite copper concentrate were studied and the chemical and mineralogical composition of the candle-end was determined; The thermodynamic possibilities of the process of reduction of copper by heating with ammonia vapors were studied and analyzed.

II THE EXPERIMENTAL PART OF THE STUDY

A Materials and method of research

The research material is chalcopyrite copper concentrates of Almalyk Mining and Metallurgical Combine (AMMC), the chemical composition of which is as follows: Cu - 20%, S - 36%, Fe - 33%, SiO₂ - 6%, CaO - 0.5%, etc.

Research Methodology was done in accordance with the experience of A.A. Yusupkhodjayev [25]. The results of the experiment presented in this article were recovered at the zinc plant AMMC (Uzbekistan) in the presence of ammonia vapors first roasted in a copper sulfide concentrate in a "Hot Layer" furnace and then heated in a rotary tube furnace (Waelz furnace). The copper metal was separated from the iron powder by the method of magnetic separation [26].

In determining the amount of elements with a concentration greater than 0.1% for chemical analysis of materials, we used OES JARRELL-Ach 70,000 optical emission spectrograph (USA) and for elements with a concentration less than 0.1%, JOEL JMS 0.1MB mass-spectrograph (Japan).

Microsoft Office Excel 2007 was used to calculate the thermodynamic parameters of the chemical reactions that take place in the process [27].

B Mineralogical and quantitative analysis of copper concentrates

To determine the mineralogical composition of copper concentrate, 100 kg of concentrate was taken, divided into equal parts and loaded into a diffractometer called COSMA. COSMA is an online diffractometer that reports the quantitative composition of the individual crystalline phases in the material that is constantly passing through the instrument.



Fig. 1: Mineralogical and phase analysis diffractometer - COSMA.

The results are presented in real time in the form of moving curves in the control room of the device and can be added to the process control system for automatic correction [28].

The analyzed statistical set contained 160 values for each component, which allowed a reliable conclusion based on the results obtained in the experiment [29].

The results of the phase analysis showed that AMMC concentrates contained chalcopyrite (CuFeS₂), covellin (CuS), pyrite (FeS₂), hematite (Fe₂O₃), quartz (SiO₂) and salts of alkali and alkaline-earth metals (Figure 2). In this type of concentrate, the distribution of copper metal to chalcopyrite and covellin minerals was approximately 9:1. The distribution of the other elements and the quantitative analysis of the minerals can be clearly seen in Table 1.

C Analysis of the optimal conditions of the copper concentrate roasting process

The roasting of copper concentrates was carried out in the "Hot layer" furnace. At the same time, the volume of oxygen in the air sprayed in the furnace for the normal operation of the process was 35% and the degree of desulfurization was 96.47%. The temperature was adjusted to 850 oC for com-

Compounds	Quantity	Cu	Fe	S	O2	SiO ₂	CaO	Others
CuFeS ₂	51,9858	18	15,821	18,164				
CuS	3,0091	2,0		1,0091				
FeS ₂	31,4829		14,656	16,826				
Fe ₂ O ₃	3,6061		2,5222		1,0839			
SiO ₂	6,0					6,0		
CaO	0,5						0,5	
Others	3,4161							3,4161
Total	100	20	33	36	1,0839	6,0	0,5	3,4161

TABLE 1: MINERALOGICAL (RATIONAL) COMPOSITION OF DRY CONCENTRATE OF AMMC COPPER CONCENTRATE

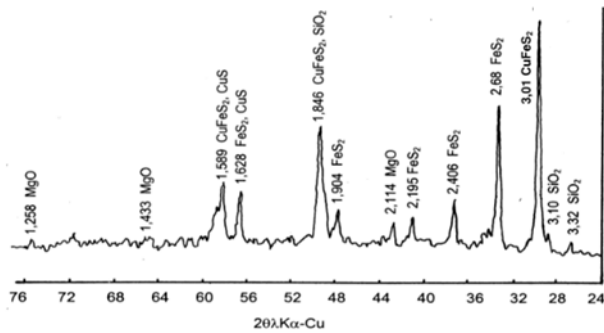
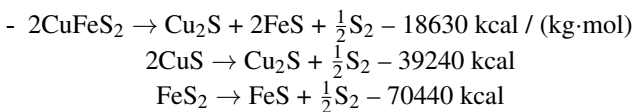
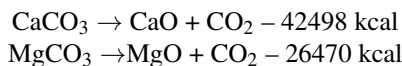


Fig. 2: One of the XRD of several chalcopyrite and pyrite concentrates.

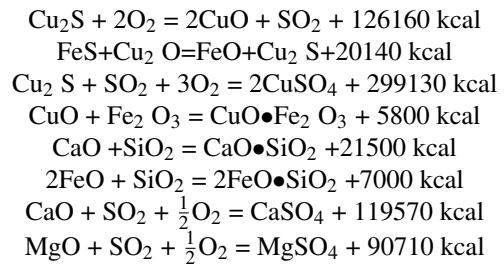
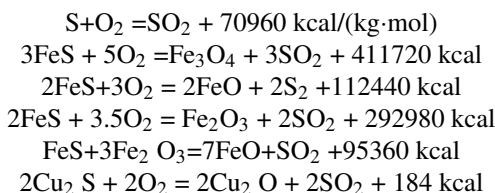
plete firing. The air pressure from the bottom of the furnace was 12 MPa. When the concentrate is loaded into the furnace, several physicochemical processes take place under the influence of temperature and oxygen. Initially, sulfide minerals decompose under the influence of temperature:



In addition, carbonates of some alkaline earth metals decompose:



The resulting low-sulfide minerals and sulfur vapor are then oxidized by oxygen. The thermochemical reactions of the process are as follows:



An increase in the concentration of oxygen in the sprayed air is one of the factors leading to the complete and perfect oxidation of sulfur.

D.M. Chizhikov and his staff determined the degree of oxidation (v) depending on the concentration of sulfidic metals and oxygen in the air (1073 K, 10 min.). It looks like this (Table 2):

O ₂ , %	1	5	20	25
v, %				
PbS	27.2	87.1	95.6	97.0
FeS	4.8	-	87.5	-
Cu ₂ S	24.3	59.0	97.2	-
CdS	46.0	90.5	99.4	-

TABLE 2: THE DEGREE OF OXIDATION OF SULFIDES DEPENDS ON THE VOLUME FRACTION OF OXYGEN

The essence of this process lies in the tendency of copper and its additives to oxygen. Because this tendency is of great importance for high-temperature compounds that melt. This depends on the Gibbs energy content or the degree of dissociation of the oxides in the solution, that is, the pressure of the gases formed as a result of the dissociation at that temperature, and this pressure changes with temperature.

If we look at the change in Gibbs energy in the formation of oxides at a given temperature, we see the following. The degree of stability of Cu, Ni and Fe oxides at high temperatures during pyrometallurgy changes in the following sequence:

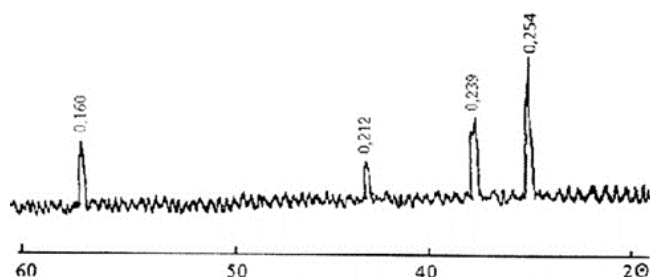
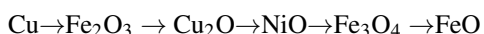


Fig. 3: Radiograph of oxidized copper-iron concentrate



Thus, the tendency of metals to oxygen is expressed by the change in Gibbs energy of the formation of chemical compounds from the elements as a result of the reaction.

It is known that the greater the negative decrease in Gibbs energy in the formation of oxides and sulfides, the greater the tendency of metals to oxygen and sulfur. Or, conversely, the higher the positive ΔG (Gibbs energy) (2, 4, 6, etc.), the weaker bond and the higher decomposition or oxidation.

The rational composition of copper concentrates obtained from the oxidative annealing process is given in Table 3.

From this table it can be seen that the main part of the copper in the roasted concentrate is chemically combined with iron. This is due to the fact that the valence oxides of copper (I) and (II) have basic properties and interact with amphoteric iron (III) oxides, resulting in the formation of more stable substances in the system - ferrites. These ferrites are insoluble in various dilute acids and alkalis under normal conditions during hydrometallurgical processing. Therefore, they require pyrometallurgical processing in the presence of reducing agents.

The chemical composition of the obtained oxidized copper concentrate is presented in Table 4.

Phase analysis of the roasted concentrate sample showed that the radiographic results (Figure 3) clearly showed that the most important compound in the system was copper (I) - ferrite ($\text{Cu}_2\text{Fe}_2\text{O}_4$ or $\text{Cu}_2\text{O} \bullet \text{Fe}_2\text{O}_3$). In addition, the results of the phase analysis showed that the sample contained small amounts of compounds such as CuO , Cu_2O , Fe_2O_3 , Fe_3O_4 , FeO , CuFeS_2 , SiO_2 , and CaO .

Figure 4 shows a view of the initial and post-incineration materials used in the study. A comparison of the results in Table 1 and Table 4 shows that the copper concentration increased by 5.15% after oxidative annealing. This is because oxygen replaces the sulfur in the compounds. This is because the equivalent of sulfur in sulfide compounds is 32 and the equivalent of oxygen in oxide compounds is 8. This shows that for every 32 g of sulfur replaced by 8 g of oxygen, the bulk of the concentrate decreases and the concentration of

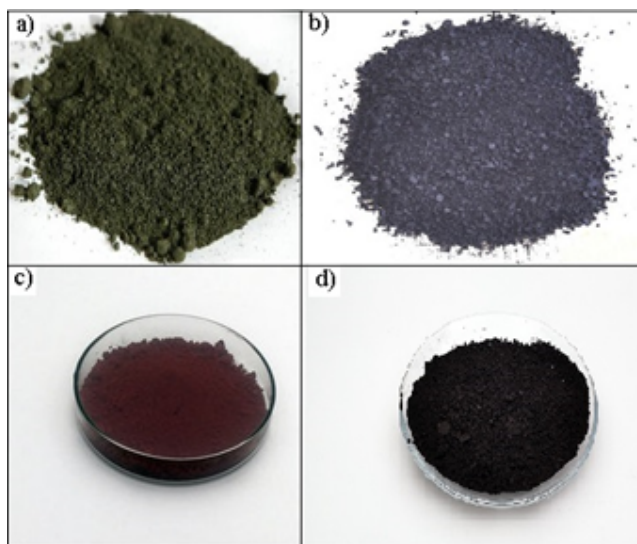


Fig. 4: The appearance of the various samples in the study: (a) - sulfide copper-iron concentrate, (b) - roasted copper-iron concentrate, (c) - refined copper powder, (d) - magnetic fraction.

copper and iron increases.

III THE RESULTS OBTAINED AND THEIR DISCUSSION

A Study of the reduction of oxidized copper concentrate by ammonia vapor

The process was carried out by stepwise reduction in a Waelz furnace in the temperature range of 550 - 1000 °C. The raw material was loaded from one side of the furnace and the product was taken from the opposite side. The only difference from conventional reducing process is that in this process, ammonia vapors are sprayed onto the surface of the heated oxide copper-iron concentrate through a special tube loaded by the furnace raw material in order to spray ammonia vapors under pressure into the furnace. The furnace had a diameter of 2.2 m, a length of 20 m, a slope angle of 3 °, a horizontal axis of rotation of 0.4 cycle per minute and a production capacity of 25 t / day, the furnace lining was made of chamotte bricks, natural gas was used as fuel. The size of the raw material loaded in the furnace was 0.3 – 0.5 millimeters, and the raw material moisture was 1 percent. A schematic view of an industrial Waelz furnace is shown in Figure 5.

After the reduction process, the powder from the furnace was sent to a magnetic drum separator. The metallized iron and its oxides were separated from the copper powder. The resulting copper powder fraction was sent to the fire-refining process, and the fraction of metallized iron and its oxides was sent to the Electric arc furnace (or induction furnace).

Compounds	Components							
	Cu	Fe	S	O	SiO ₂	CaO	Others	Total
CuFeS ₂	1	0.879	1.01	-	-	-	-	2.889
Fe ₃ O ₄	-	14.656	-	5.583	-	-	-	20.239
CuO	2	-	-	0.5	-	-	-	2.5
Cu ₂ OFe ₂ O ₃	17	14.942	-	8.433	-	-	-	40.375
Fe ₂ O ₃	-	2.522	-	1.0839	-	-	-	3.606
SiO ₂	-	-	-	-	6.0	-	-	6.0
CaO	-	-	-	-	-	0.5	-	0.5
Others	-	-	-	-	-	-	3.4161	79.5251

TABLE 3: QUANTITATIVE COMPOSITION OF OXIDIZED COPPER CONCENTRATES ACCORDING TO THE STUDY, KG

Cu	Fe	S	O	SiO ₂	CaO	Others
25.15	41.49	1.27	19.62	7.55	0.63	4.29

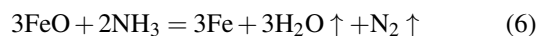
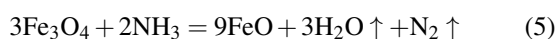
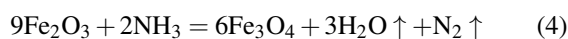
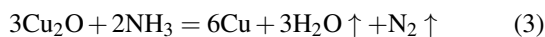
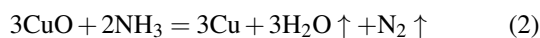
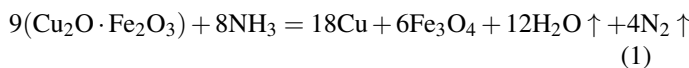
TABLE 4: CHEMICAL COMPOSITION OF OXIDIZED COPPER CONCENTRATES ACCORDING TO THE STUDY, %



Fig. 5: Rotary tube furnace (Waelz furnace).

B Analysis of chemical reactions that occur during the reduction process

When oxidized copper-iron concentrate was heat-treated in the presence of ammonia vapors, almost all of the copper minerals were reduced until metallic copper was formed. The chemical reactions of the process are as follows:



Cu	Fe	O	S	SiO ₂	CaO	Others
30.56	50.43	3.36	0.50	9.17	0.76	5.22

TABLE 5: CHEMICAL COMPOSITION OF THE PRODUCT OBTAINED AFTER THE REDUCTION PROCESS, %

From the above chemical reactions, it can be seen that when the main component copper (I) -ferrite is reduced by ammonia vapor, metallic copper and magnetite are formed in the reaction system. This process is the first stage of the reaction mechanism. In the later stages, the reduction of magnetite and wustite minerals takes place. The higher and lower oxides of copper in the system are also reduced by ammonia vapors, resulting in the formation of metallic copper as a product. The products of the reduction process are presented in Table 5.

According to the results of chemical analysis, all the copper was converted into metallic form. Most of the iron is in the form of metal, but a certain amount of iron is not reduced.

C Thermodynamic possibilities of reduction of oxidized copper-iron concentrates by ammonia vapors

The evaluation of the possible direction of chemical reactions between oxidized copper-iron concentrate and ammonia vapors was performed by changing the thermodynamic values of the system. Thermodynamic analyzes were performed taking into account the temperature dependence of the isobaric-isothermal potentials (Gibbs free energy). The change in Gibbs free energy (ΔG) is generally calculated using the following formula:

$$\Delta G_{\text{reac}} = \Delta H_{\text{reac}} - \Delta S_{\text{reac}} T \quad (7)$$

Where: ΔH_{reac} – enthalpy of appropriate chemical reaction, kJ / mol;

ΔS_{reac} – entropy of the corresponding chemical reaction, J / (mol • K);

T – the absolute temperature of the system, K.

Substances	ΔH_{298} , kJ/mol	ΔG_{298} , kJ/mol	ΔS_{298} , J/(mol·K)
CuO	-162.0	-134.3	42.63
Cu ₂ O	-173.2	-150.6	92.9
Fe ₂ O ₃	-822	-740	87
FeO	-265	-244	60.8
Fe ₃ O ₄	-1117.13	-1014.17	146.19
Cu ₂ O·Fe ₂ O ₃	-1025.33	-920.77	178.29
NH ₃ (vapor)	-46.2	-16.71	192.6
H ₂ O (vapor)	-241.82	-228.61	188.72
Cu	0	0	33.1
Fe	0	0	27.15
N ₂	0	0	191.5

TABLE 6: THERMODYNAMIC VALUES OF SUBSTANCES

Depending on the Gibbs energy value of the system, it can be concluded whether the reactions proceed spontaneously under standard conditions and the direction of the reaction:

- If the value of the change in Gibbs energy in a chemical reaction is $\Delta G_{298} > 0$, i.e. positive, these reactions cannot proceed spontaneously under standard conditions;
- If $\Delta G_{298} < 0$, i.e. negative, these reactions occur spontaneously under standard conditions. These reactions are economically and technologically feasible;
- If $\Delta G_{298} = 0$, then the system is in a state of chemical equilibrium and it need to change the system parameters (P, T, C, V) to shift the balance in the direction of the desired reaction.

The standard thermodynamic values of the substances involved in the reactions under consideration were determined from the handbook, and these values are presented in Table 6 [26].

The temperature dependence of the equilibrium constant (K_{eq}) of a reaction is determined by the following formula:

$$\Delta G = -RT \ln K_{eq} \quad (8)$$

Where: R – universal gas constant, $R = 8,31696 \cdot 10^{-3}$ kJ/(grad·mol);

K_{eq} – equilibrium constant of the corresponding chemical reaction.

To find the equilibrium constant from mathematical expression 2, divide both sides of the equation by RT, then logarithm, and the result is:

$$K_{eq} = e^{-\frac{\Delta G}{RT}} \quad (9)$$

$$\Delta G_{\text{reac}} = -7.05 - 1.35817T \quad (10)$$

No	ΔG	ΔH°	ΔS°	T, K	$\ln K_{eq}$	K_{eq}
1	-550.318	-7.05	1.35817	400	165.5590	8E+71
2	-618.227	-7.05	1.35817	450	165.3233	6.3E+71
3	-686.135	-7.05	1.35817	500	165.1348	5.2E+71
4	-754.044	-7.05	1.35817	550	164.9805	4.5E+71
5	-821.952	-7.05	1.35817	600	164.8520	3.9E+71
6	-889.861	-7.05	1.35817	650	164.7432	3.5E+71
7	-957.769	-7.05	1.35817	700	164.6500	3.2E+71
8	-1025.678	-7.05	1.35817	750	164.5692	3E+71
9	-1093.586	-7.05	1.35817	800	164.4985	2.8E+71
10	-1161.495	-7.05	1.35817	850	164.4361	2.6E+71
11	-1229.403	-7.05	1.35817	900	164.3807	2.5E+71
12	-1297.312	-7.05	1.35817	950	164.3311	2.3E+71
13	-1365.220	-7.05	1.35817	1000	164.2864	2.2E+71
14	-1433.129	-7.05	1.35817	1050	164.2460	2.1E+71
15	-1501.037	-7.05	1.35817	1100	164.2093	2.1E+71
16	-1568.946	-7.05	1.35817	1150	164.1757	2E+71
17	-1636.854	-7.05	1.35817	1200	164.1450	1.9E+71
18	-1704.763	-7.05	1.35817	1250	164.1167	1.9E+71
19	-1772.671	-7.05	1.35817	1300	164.0906	1.8E+71

TABLE 7: VALUES OF GIBBS ENERGY AND EQUILIBRIUM CONSTANT AT SEVERAL TEMPERATURES OF THE PROCESS OF REDUCTION OF COPPER FERRITE WITH AMMONIA VAPOR

For each of the reduction reactions with ammonia vapor, the change in Gibbs energy at the initially given temperature was expressed by a general formula.

The general formula for the change in Gibbs energy for chemical reaction 1 (reduction of copper ferrite) is:

The changes in the free energy and equilibrium constants of the reduction reaction of copper ferrite at several temperatures are presented in Table 7. The values of Gibbs energy and equilibrium constant of the reaction were calculated when the temperature in the system changed every 50 units.

The results of the thermodynamic analysis presented in Table 7 show that since the reduction reaction of copper ferrite in the presence of ammonia vapors is an exothermic reaction, an increase in temperature in the system slows down the rate of the chemical reaction going in the right direction.

The value of the Gibbs energy in a system is a thermodynamic parameter that determines the probability of a reaction occurring or not at a given temperature. The graph in Figure 6 illustrates the temperature dependence of the Gibbs energy for reaction 1, and it can be seen from this graph that for this case the free energy (G) of the system decreases linearly as the temperature changes every 50 units, i.e. becomes negative. This means that as the temperature rises, the probability of copper ferrite reacting with ammonia vapors increases. Even at low temperatures, the value of Gibbs energy in the system has a negative number. This is because the values of

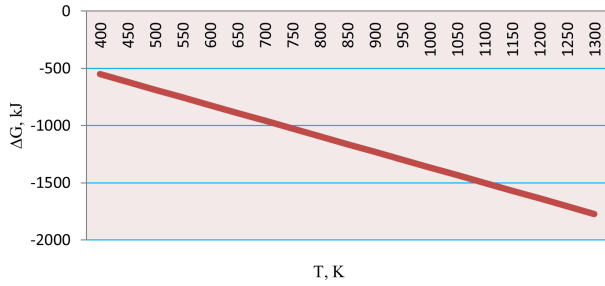


Fig. 6: Temperature dependence diagram of Gibbs energy for reaction 1

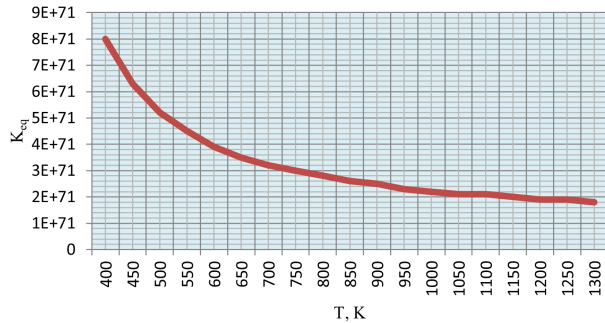


Fig. 7: Temperature dependence diagram of the equilibrium constant for reaction 1.

enthalpy and entropy in the Gibbs energy equation for reaction 1 have a negative value.

Figure 7 shows the temperature dependence of the equilibrium constant of reaction 1. This graph shows a sharp decrease in the chemical equilibrium between 400 and 1000 K, and a stabilization of the curve at temperatures above 1000 K. Note that at each given temperature, the value of the chemical equilibrium constant contains very large values, i.e., the rate of the chemical reaction remains high. This means that the limiting stage, which determines the rate of reaction of copper ferrite with ammonia vapors, is not the kinetic mode, but the diffusion mode. In this case, the acceleration of the reaction depends on the number of collisions between the molecules of the reactants. This is determined by the rate of diffusion of substances and the size of the reaction surface.

In a similar manner, general formulas for finding the Gibbs energy for all reduction reactions were developed:

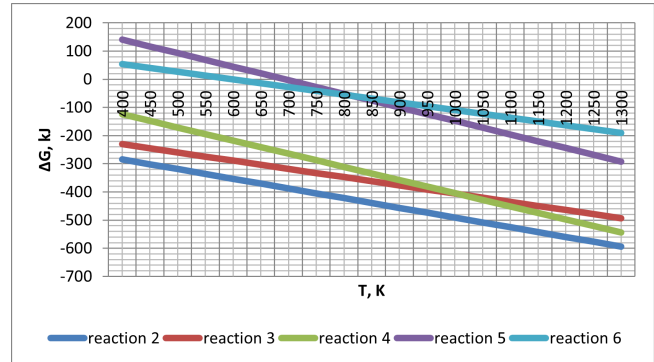


Fig. 8: Temperature dependence of Gibbs energies of reactions 2 – 6.

$$\text{For reaction 2 : } \Delta G_{\text{reac}} = -146.860.34387T \quad (11)$$

$$\text{For reaction 3 : } \Delta G_{\text{reac}} = -113.46 - 0.29236T \quad (12)$$

$$\text{For reaction 4 : } \Delta G_{\text{reac}} = 62.16 - 0.4666T \quad (13)$$

$$\text{For reaction 5 : } \Delta G_{\text{reac}} = 333.33 - 0.48109T \quad (14)$$

$$\text{For reaction 6 : } \Delta G_{\text{reac}} = 161.94 - 0.27151T \quad (15)$$

$$(16)$$

The changes in the Gibbs energy and equilibrium constants of the reduction reaction of metal oxides in reactions 2 – 6 in the presence of ammonia vapors are presented in Tables 8 and 9, respectively.

Reactions 2 and 3, that is, the reduction reaction of tenorite and cuprite with ammonia vapor, have the same characteristics as reaction 1, and this reaction also flows in a diffusion mode. In reaction 4 (reduction of hematite), iron is more prone to reducing agents than other iron oxides due to its high oxidation state, and the Gibbs energy value is negative even at low temperatures.

From the results in Table 8 and the graph in Figure 8, it can be seen that the slowest chemical reaction of all the reactions in the system is reaction 5 (i.e., the reduction of magnetite to wustite). This reaction starts at a temperature of 700 K, and the reaction slowly shifts from the equilibrium state to the right, that is, to the side where the products are formed.

In the graph shown in Figure 9 and Table 9, the equilibrium constant of reaction 5 (reduction of magnetite) begins to increase from 1 in the temperature range 700 – 750 K, for example, the equilibrium constant of the reaction at 700 K is $K_{eq} = 1.80429$, and at 750 is $K = 82.2982$. The equilibrium constant of reaction 6 (reduction of wustite) begins to shift to the right at 600 K, and at 650 K the equilibrium constant $K_{eq} = 14.763$. This means that these two reactions are the slowest-limiting chemical reactions in the overall system, and the process is considered to be kinetic. Taking into

No	T, K	reaction 2	reaction 3	reaction 4	reaction 5	reaction 6
1	400	-284.408	-230.404	-124.480	140.894	53.336
2	450	-301.602	-245.022	-147.810	116.840	39.761
3	500	-318.795	-259.640	-171.140	92.785	26.185
4	550	-335.989	-274.258	-194.470	68.730	12.610
5	600	-353.182	-288.876	-217.800	44.676	-0.966
6	650	-370.376	-303.494	-241.130	20.622	-14.542
7	700	-387.569	-318.112	-264.460	-3.433	-28.117
8	750	-404.763	-332.730	-287.790	-27.488	-41.693
9	800	-421.956	-347.348	-311.120	-51.542	-55.268
10	850	-439.150	-361.966	-334.450	-75.597	-68.844
11	900	-456.343	-376.584	-357.780	-99.651	-82.419
12	950	-473.537	-391.202	-381.110	-123.706	-95.995
13	1000	-490.730	-405.820	-404.440	-147.760	-109.570
14	1050	-507.924	-420.438	-427.770	-171.815	-123.146
15	1100	-525.117	-435.056	-451.100	-195.869	-136.721
16	1150	-542.311	-449.674	-474.430	-219.924	-150.297
17	1200	-559.504	-464.292	-497.760	-243.978	-163.872
18	1250	-576.698	-478.910	-521.090	-268.033	-177.448
19	1300	-593.891	-493.528	-544.420	-292.087	-191.023

TABLE 8: THE VALUES OF GIBBS ENERGY (G) AT SEVERAL TEMPERATURES OF 2 – 6 REACTIONS

No	T, K	reaction 2	reaction 3	reaction 4	reaction 5	reaction 6
1	400	85.5620	69.3153	37.4489	-42.3869	-16.0457
2	450	80.6529	65.5227	39.5267	-31.2447	-10.6326
3	500	76.7256	62.4886	41.1889	-22.3309	-6.020
4	550	73.5124	60.0061	42.5490	-15.0379	-2.7589
5	600	70.8347	57.9374	43.6823	-8.9603	0.1937
6	650	68.5690	56.1870	44.6413	-3.8177	2.6921
7	700	66.6270	54.6866	45.4633	0.902	4.8336
8	750	64.9438	53.3863	46.1757	4.103	6.6895
9	800	63.4711	52.2485	46.7990	7.530	8.3135
10	850	62.1717	51.2446	47.3490	10.7024	9.7464
11	900	61.0166	50.3522	47.8379	13.3241	11.0201
12	950	59.9831	49.5537	48.2754	15.6698	12.1597
13	1000	59.0529	48.8351	48.6691	17.7810	13.1853
14	1050	58.2114	48.1850	49.0253	19.6911	14.1133
15	1100	57.4463	47.5939	49.3491	21.4275	14.9569
16	1150	56.7478	47.0543	49.6447	23.0130	15.7271
17	1200	56.1075	46.5596	49.9158	24.4663	16.4332
18	1250	55.5184	46.1045	50.1651	25.8034	17.0828
19	1300	54.9746	45.6843	50.3953	27.0376	17.6824

TABLE 9: VALUES OF THE EQUILIBRIUM CONSTANT OF REACTIONS 2 – 6 AT SEVERAL TEMPERATURES IN NATURAL LOGARITHMS ($\text{LN}K_{eq}$)

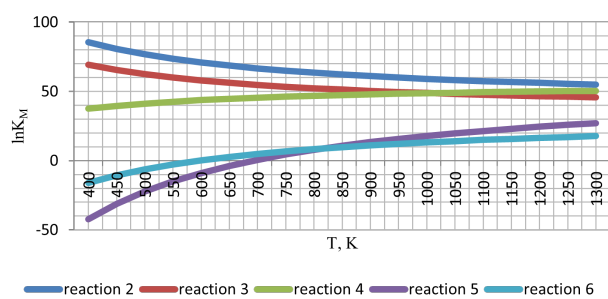


Fig. 9: Temperature dependence diagram of equilibrium constants of reactions 2 – 6.

account all the research done, we can choose 950 K as the optimal temperature for the reduction process. This is because at this temperature, the thermodynamic parameters of all reactions in the system shift the chemical equilibrium towards the formation of products according to Le Chatelier's principle. The reason that a temperature above 1000 K cannot be an optimal condition is that at a temperature of 1083 °C, the copper powder melts and adversely affects the process. The angle of inclination of the furnace is set at 3° so that the nitrogen gas, water vapor and similar gases formed as a result of the reaction leave the reaction system. As the hot gas flow rises, it is discharged through the furnace pipes. This same geometric approach to the process helps to increase the correct reaction rate according to the Le Chatelier principle.

IV CONCLUSION

Based on the analysis of waste-free and innovative methods of reduction of oxidized copper-iron concentrates, the main possibilities of extraction of metals from rich copper concentrates were identified. The most convenient way to implement this technology is a Waelz furnace (or rotary kiln), which uses ammonia vapor as a reducing agent. The basic parameters of the furnace required to ensure the flow of the process are indicated. This method made it possible to extract both copper metal and metallized iron raw materials from oxidized copper concentrates in one go. In addition, the loss of precious metals in copper concentrate with waste - slag was prevented.

The chemical composition and mineralogical composition of the semi-finished product obtained by oxidative roasting of copper sulfide concentrate were determined. According to this, the main component is copper (I) –ferrite in the system.

The reduction of oxidized copper concentrate with ammonia vapors increased the separation of metals from the finished product. The main reason for this is that the system does not produce slag that is difficult to process.

The specific chemical reactions that take place during the

recovery process, their mechanism and thermodynamic capabilities are described.

Factors that negatively affect the speed of the process and ways to overcome them were discussed and an optimal temperature of 950 K (677°C) was selected to improve the flow of the reduction process.

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