

Thermodynamical Properties of the Process of Sintering of Iron Storage Copper Concentration Factories with Lime

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Abstract— the article discusses the thermodynamic aspects of the process of liming the wastes of copper concentrators containing iron. When chemically analyzed the composition of copper concentrator waste, the iron content was 52.7%. Quantitative analysis based on the chemical composition of iron and silicon in the study revealed that the raw iron in the form of iron and silicon iron (II) -metasilicate. Based on this material composition, a method for the extraction of iron oxide from iron silicate in the presence of calcium oxide was proposed, and the conditions under which the process took place were studied. The mechanism of chemical phenomena occurring in the regions of interaction of iron (II) metasilicate and lime has been developed. Based on the mechanism of chemical reactions developed, each chemical reaction that occurs in the process is analyzed from a thermodynamic point of view. Thermodynamic analysis revealed that the limiting stage between the chemical reactions that take place in the iron (II) -metasilicate and lime system is the phase of diffusion of iron silicate and lime molecules. Due to this, the temperature required for the complete interaction of iron silicate with lime was 1598 K (1325 °C). It is at this temperature that the equilibrium constants of all chemical reactions have high values, as evidenced by the study of the kinetics of the process.

Keywords— copper concentrator waste, iron (II) -metasilicate, lime, auxiliary, thermodynamics, mechanism, limiting stage, optimal temperature.

1. INTRODUCTION

Most ores of heavy non-ferrous metals are relatively poor polymetallic rocks. Only a small fraction of the mined ore is suitable for processing directly in metallurgical plants. Ores are enriched by artificially increasing the amount of metals in the raw materials supplied for metallurgical processing, and sometimes precious metals are pre-separated. Enrichment processes allow to increase the amount of metals in the ore by tens and hundreds of times [1].

Enrichment of the raw material increases the amount of metal in it by removing most of the waste rock. If all the valuable components present in the original ore at the same time remain in the enriched product, it is a method of collective enrichment [2,3].

If the ores are polymetallic and there are a sufficient number of metals in addition to the separation of loose rocks, then it is necessary to separate each metal into a separate product suitable for independent metallurgical processing, then this method of selective enrichment (selective flotation) [4,5,6].

Many methods of mechanical enrichment are based on the use of differences in the physical properties of minerals: density, size, shape, color and brightness, moisture, magnetic sensitivity, and others. Prior to beneficiation, the ore is conditioned so that the minerals in it are completely freed from each other as much as possible. This is achieved during the preparatory work: the ore is crushed by sorting the crushed material according to its size [7,8].

The main methods of mechanical enrichment of non-ferrous metal ores are flotation and gravity. Other enrichment methods used to process non-ferrous metal ores include magnetic separation, manual sorting, and electrostatic enrichment. In most cases, they are ancillary processes [9].

Heavy non-ferrous metal ores are often enriched by flotation, a method based on the selective adhesion of precipitated mineral particles to air bubbles. Particles of minerals that are poorly moistened with water stick to air bubbles and rise with them to the surface of the pulp, forming a mineralized foam on it. Particles of other minerals that are well moistened with water do not stick to the bubbles and remain in the bush. In this way, the separation of different minerals is achieved [10].

The main end products of enrichment are concentrates and wastes. Concentrate is a product of enrichment with a high content of valuable metals. Concentrates are usually named after the precious metal or mineral they contain - copper, zinc, molybdenum, pyrite or bornite. Concentrates that contain approximately the same amount of several metals are called collective concentrates. These include copper-zinc, copper-nickel, and others [11].

Enrichment wastes are mainly rocks that contain small amounts of valuable minerals that cannot be separated into concentrates. They are mainly processed by flotation technology of copper-molybdenum sulfide ores at the Almalyk Mining and Metallurgical Combine (AMMC) [12].

The sulfide copper concentrate obtained during the enrichment process is sent to a copper smelter for pyrometallurgical processing in order to separate copper, precious and rare metals. The molybdenum concentrate will be sent to the AMMC refractory and heat-resistant metals plant in Chirchik for further processing. The remains are stored in two landfills. Dump No. 1 has been operating since 1961, storing 20 percent of the total copper-molybdenum ore waste generated at the copper processing plant. The

total volume as of 01.01.2007 is 459.3 million tons, of which copper contains 0.115% or 530.6 thousand tons, gold - 0.209 g / t or 96.3 tons, silver - 1.06 g / t or 487.8 tons [13].

The existing landfill was established in 1971 and is divided into two areas by a transition device. From 1976 to 1998, wastes from lead-zinc production were stored at the lead concentrator landfill. The total accumulated volume as of 01.01.2007 was 502.4 million tons. copper - 0.108% or 544 thousand tons, gold - 0.2 g / t or 100.7 tons, silver - 1,053 g / t or 529.1 tons. Currently, landfills are of great interest in terms of their readiness and proximity to the developed infrastructure for mining and processing of minerals. The extraction of precious metals from the processing of these wastes is one of the most pressing problems of non-ferrous metallurgy today [14].

Thus, the main methods of mechanical enrichment of non-ferrous metal ores are flotation and gravity. Other methods of enrichment used in the processing of non-ferrous ores are magnetic separation, manual sorting of ores and electrostatic enrichment, but in most cases they are ancillary processes [15,16].

2. MATERIALS AND METHODS

2.1. Materials

Iron ore stored at the Almalyk Mining and Metallurgical Combine's copper concentrator was selected as research objects. The chemical composition of AMMC concentrator waste is presented in Table 1.

Table 1. Chemical composition of wastes of concentrator of JSC "AMMC" selected for the experiment, %

Fe	Si	Al	Mg	Ca	Cu	K	S
52.7	25.42	4.98	1.55	4.54	0.871	2.75	0.688
Na	Zn	Pb	Co	Mn	Ti	Mo	Zr
2.07	2.23	0.643	0.131	0.312	0.273	0.358	0.457

The values in Table 1 show that the chemical composition of the concentrator waste is significantly higher (i.e., 52.7%). In addition, the amount of silicon is significant (25.42%). This indicates that the material composition of this material is mainly composed of oxygenated compounds of iron and silicon.

In order to separate the silicate iron from the concentrator waste, it is first necessary to remove the iron from the silicate. In this study, an assimilation method was used to separate iron oxide from iron silicate. Lime (CaO) was selected as a reagent to displace iron oxide from the silicate composition.

2.2. Methods

In order to extract iron oxide from the concentrator plant waste, it is necessary to determine in the form of a compound of iron in the raw material. To do this, the quantitative analysis method was used in this study. The ratio of the percentage of iron and silicon in the original material, measured in 100 g, was determined in moles: $n_{Fe} = 52.7 / 56 = 0.941$ mol, $n_{Si} = 25.42 / 28 = 0.907$ mol. In this case, the $n_{Fe} : n_{Si}$ mole ratios are 1: 1. This indicates that the compound of iron and silicon that corresponds to this ratio is a mineral containing $FeO \cdot SiO_2$ or $FeSiO_3$. Thus, the lime-assisted process was carried out with $FeSiO_3$ - an iron (II) -metasilicate compound. ThermoBase-2.15 and Microsoft Excel programs were used to determine the thermodynamic values of chemical reactions in iron (II) -metasilicate and lime systems [17].

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:

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

Here: ΔH_{reac} - enthalpy of the corresponding chemical reaction, kJ / mol;

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

T is the absolute temperature of the system, K.

Depending on the Gibbs energy value of the system, the following conclusions can be drawn about whether the reactions proceed spontaneously under standard conditions and the direction of the reaction:

a) If the value of the change in Gibbs energy in a chemical reaction is $\Delta G_{298} > 0$, ie positive, these reactions cannot proceed spontaneously under standard conditions;

b) If $\Delta G_{298} < 0$, i.e. negative, these reactions occur spontaneously under standard conditions. These reactions are economically and technologically feasible;

d) If $\Delta G_{298} = 0$, then the system is in a state of chemical equilibrium. You need to change the system parameters (P, T, C, V) to shift the balance in the direction of the desired reaction.

The temperature dependence of the reaction equilibrium constant (K_E) is determined by the following formula:

$$\Delta G = - RT \ln K_E \quad (b)$$

Where: R is the universal gas constant, $R = 8.31696 \cdot 10^{-3}$ kJ / (grad · mol);

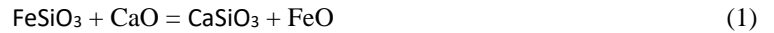
K_E is the equilibrium constant of the corresponding chemical reaction.

(b) The equilibrium constant from a mathematical expression is:

$$K_E = e^{-\frac{\Delta G}{RT}} \quad (c)$$

3. RESULTS AND DISCUSSION

The general chemical equation for the addition of iron (II)-metasilicate to lime is:



The thermodynamic values of all the substances involved in the reactions were calculated for standard conditions, and their initial values are given in Table 2 [18].

Table 2. Appropriate thermodynamic quantities of substances (at 298 K)

Substance	FeSiO ₃	CaO	CaSiO ₃	FeO
ΔH° (kJ/mol)	-1194.9	-635.1	-1635.1	-265
ΔG° (kJ/mol)	-1117.5	-603.5	-1549.8	-244
ΔS° (J/(mol·K))	93.93	38.1	81.92	60,8

Using the values given in Table 2, the results of the chemical reactions of the lime augmentation process for iron (II)-metasilicate under Hess's law were calculated under standard conditions and are presented in Table 3.

Table 3. Values of sintering reactions under standard conditions (298 K)

No	Thermodynamic quantities	FeSiO ₃ + CaO = CaSiO ₃ + FeO
1	ΔH_{reac} , kJ/mol	-70.1
2	ΔG_{reac} , kJ/mol	-72.8
3	ΔS_{reac} , J/(mol·K)	10,69

From the values of the thermodynamic calculations presented in Table 3 under standard conditions, it can be seen that the chemical reaction under study is an exothermic reaction whose standard Gibbs energy value is negative, i.e. at 298 K the reaction occurs spontaneously. An increase in entropy is observed in the particles formed in the auxiliary reaction system under study [19].

Based on the results of the values in Table 3, an appropriate mathematical expression for the relationship between the increase in temperature and the reaction of iron (II) metasilicate with lime was developed, which looks like this:



Based on the calculated mathematical expression, the probability that each sulfidation chemical process will occur when the temperature in the reaction system rises by every 100 units was determined. The results obtained are presented in Table 4.

Table 4. Values of Gibbs energies at different temperatures of lime support of iron (II) -metasilicate

No	T, K	T, °C	ΔG^T , kJ/mol
1	398	125	-184,86
2	498	225	-185,96
3	598	325	-187,06
4	698	425	-188,16
5	798	525	-189,26
6	898	625	-190,36
7	998	725	-191,46
8	1098	825	-192,56
9	1198	925	-193,66
10	1298	1025	-194,76
11	1398	1125	-195,86
12	1498	1225	-196,96
13	1598	1325	-198,06

Table 4 presents the corresponding Gibbs energies of the chemical reaction of iron (II) -metasilicate with lime in the temperature range 398 - 1598 K (i.e., 125 - 1325 °C), and the flow of the reaction as the temperature increases. the probability increases. This can be clearly seen in Figure 1.

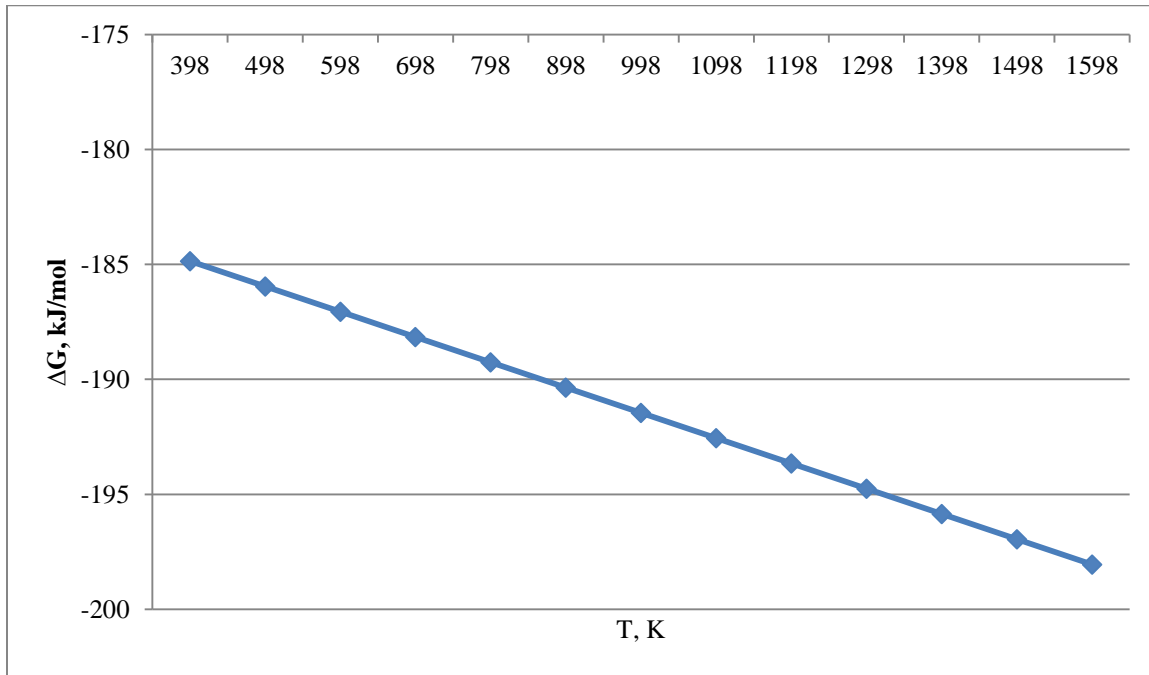


Fig.1. Ellingham diagram of the reaction of iron (II) -metasilicate with lime

In the graph shown in Figure 1, the equilibrium constants of chemical reactions at given temperatures for sulfidation reactions were determined based on the mathematical expression (c) of the chemical reaction of lime (II) -metasilicate with lime and the values of free energies in Table 4, and these values are presented in Table 5.

Table 5. Values of equilibrium constants of iron (II) -metasilicate with lime at different temperatures

№	T, K	T, °C	K_E
1	398	125	1,0575
2	498	225	1,0460
3	598	325	1,0384
4	698	425	1,0330
5	798	525	1,0290
6	898	625	1,0258
7	998	725	1,0234
8	1098	825	1,0213
9	1198	925	1,0196
10	1298	1025	1,0182
11	1398	1125	1,0170
12	1498	1225	1,0159
13	1598	1325	1,0150

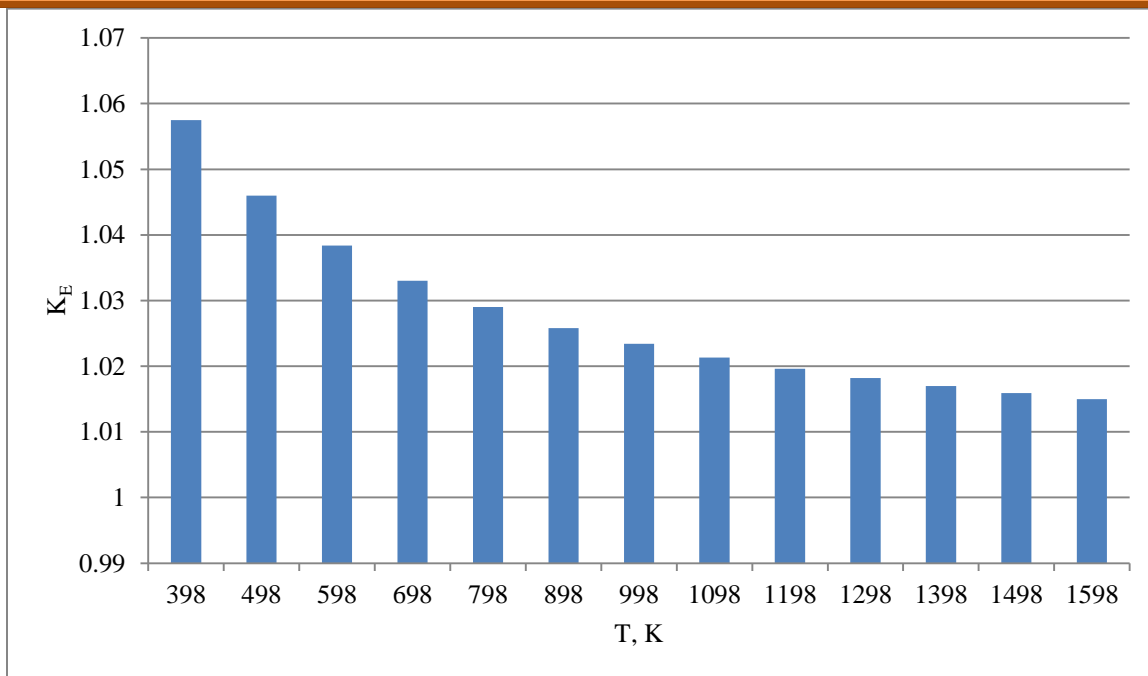


Fig.2. Temperature-dependent change of equilibrium constant during the addition of iron (II) -metasilicate with lime

From the graph shown in the form of the values in Table 5 and the histograms in Figure 2, it can be seen that when the temperature reaches 1598 K (1325 °C) the chemical reaction, (1) value ($K_E = 1,015$).

4. CONCLUSION

Copper production produces large amounts of oxidized waste during flotation enrichment of sulfide copper-molybdenum ores. Chemical analysis of the waste showed that it contained large amounts of oxidized iron compounds. Quantitative analysis revealed that the iron in this material is mainly in the form of iron (II) -metasilicate ($FeSiO_3$).

In order to facilitate the separation of iron from copper concentrator waste, a technology was developed to support iron silicate with lime, as it required the conversion of iron from silicate to oxide.

The results of thermodynamic and kinetic analysis of the process of lime reinforcement of iron (II) -metasilicate showed that the probability of the reaction and the equilibrium constant increase with increasing temperature. when the temperature reaches 1598 K (1325 °C), the reaction rate reaches its maximum value.

The importance of studying this process is that the iron oxide formed as a result of the reaction can be separated by a magnetic method, and the magnetic fraction can be used as a raw material for the production of steel. Due to the fact that the calcium silicate formed as a result of the reaction corresponds to the composition of cement, it is possible to use it as a building material. In addition, the extraction of iron from non-magnetic materials increases the amount of zinc and copper, making it more efficient in production. Because these metals are also oxidized, they can be separated by selective leaching in sulfuric acid. This will allow the introduction of waste-free technology and increase the level of improvement of environmental protection.

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