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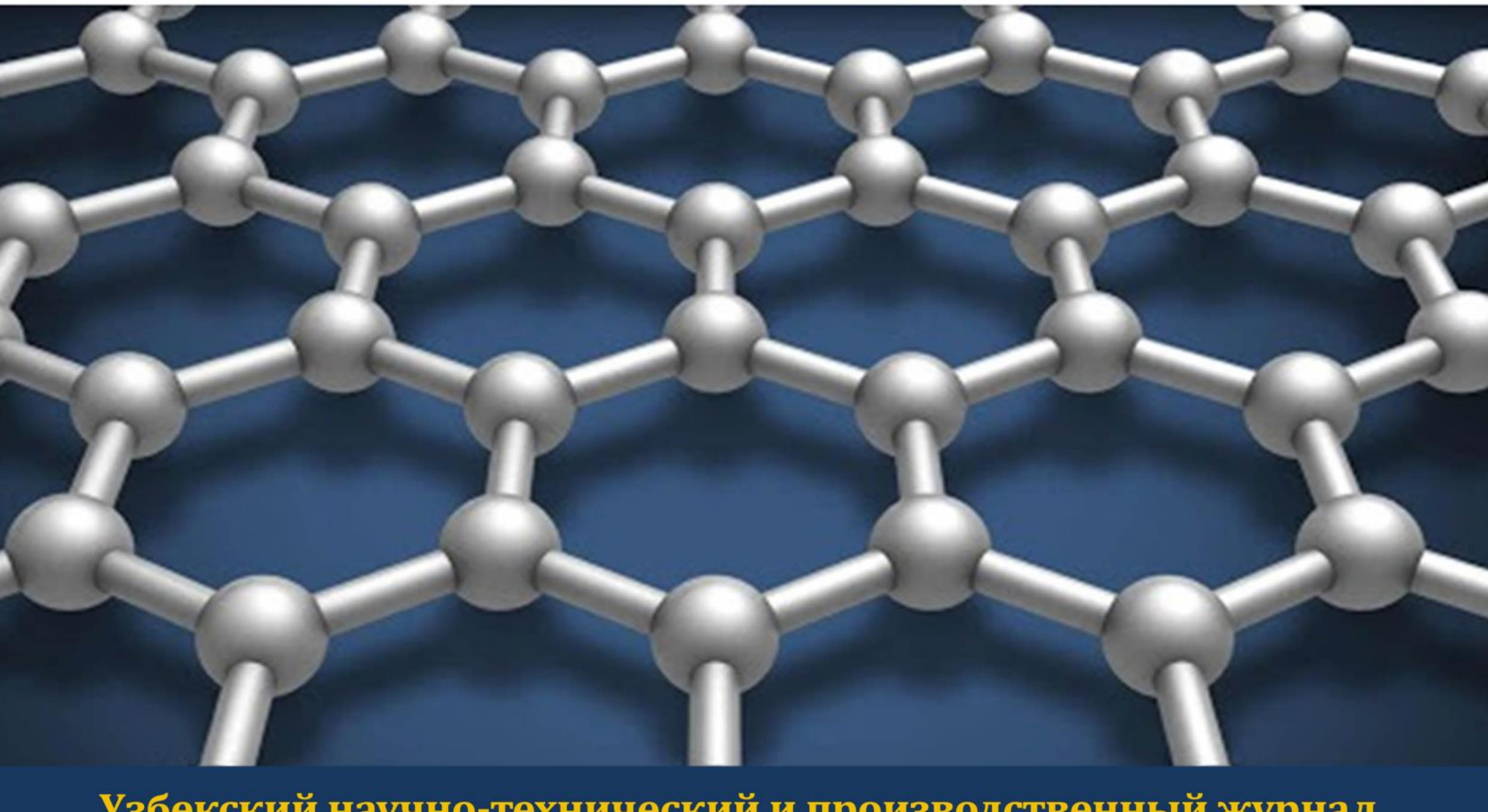

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THERMODYNAMICS OF ORE THERMAL RECOVERY OF COPPER SLAG

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Abstract: In the article - studying the thermodynamic possibilities of reactions of carbon exposure of slag components at several temperatures using the Ellingham method.

Keywords: slag, ore-thermal reduction, raw materials, copper slags, thermodynamics, Angren coal.

Introduction. When carbon is used as a reducing agent to recover metals from metal oxides, such reactions are called carbothermic reactions in metallurgy. Carbothermic reactions can occur step by step depending on the amount of oxygen in the metal oxide. For example, in the first stage of recovery of the high iron oxide - hematite with carbon, magnetite is formed, in the second stage, wustite, and finally in the third stage, metallic iron is formed. Carbothermic reactions are usually carried out at temperatures of several hundred degrees Celsius. Such processes are used to extract elemental (pure matter) forms of many metals. The carbothermic method cannot be used for oxides of some active metals, such as alkali and alkaline-earth metals. The reason for this is that for carbothermic reactions to proceed, the oxygen affinity of the metal in the oxide must be less than the oxygen affinity of the reducing carbon. For example, the oxides of sodium, potassium and calcium metals cannot be reduced by carbon. Because the affinity of these metals for oxygen is relatively greater than that of carbon. Therefore, such chemical reactions do not occur in practice. The ability of metals to participate in carbothermic reactions can be understood in more detail through Ellingham diagrams [1,2].

Research objects and methods. "Almalik KMK" JSC copper smelting slag, Angren mine coal were selected as research objects.

Modern analytical and experimental methods and equipment were used to determine the physico-chemical properties of the structure of steel and copper production slags, to determine the technological and physico-chemical properties of slags, which provide high accuracy and reliability. Metallographic analysis of slag was performed using a 5XB-PC compound microscope with a magnification of ×400. The composition of the produced materials was studied in a NEXT CG X-ray spectrum analyzer and a JEOL IT200 electron microscope.

Experimental methodology. Evaluation of the probable direction of carbothermic reactions occurring between oxidized compounds and carbon in the slag was carried out by changing the thermodynamic values of the system. Thermodynamic analyzes were carried out taking into account the temperature dependence of isobaric-isothermal potentials (Gibbs free energy). The Gibbs free energy change (ΔG) is generally calculated using the following formula:

$$\Delta G_{reak} = \Delta H_{reak} - \Delta S_{reak} T \qquad (1)$$

Here: ΔH_{reak} - is the enthalpy of the corresponding chemical reaction, KJ/mol;

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

T- is the absolute temperature of the system, K.

Depending on the value of the Gibbs energy of the system, it can be concluded as follows whether the reactions will proceed spontaneously or not and the direction of the reaction under standard conditions:

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

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

c) if $\Delta G_{298}=0$, then the system is in chemical equilibrium. It is necessary to change the parameters of the system (P, T, C, V) to shift the equilibrium in the direction of the desired reaction.

The thermodynamic analysis of the process of recovery of metal oxides in slag with carbon was carried out through the following studies [3].

Carbothermic recovery reactions between liquid slag and carbon have been constructed and are as follows:

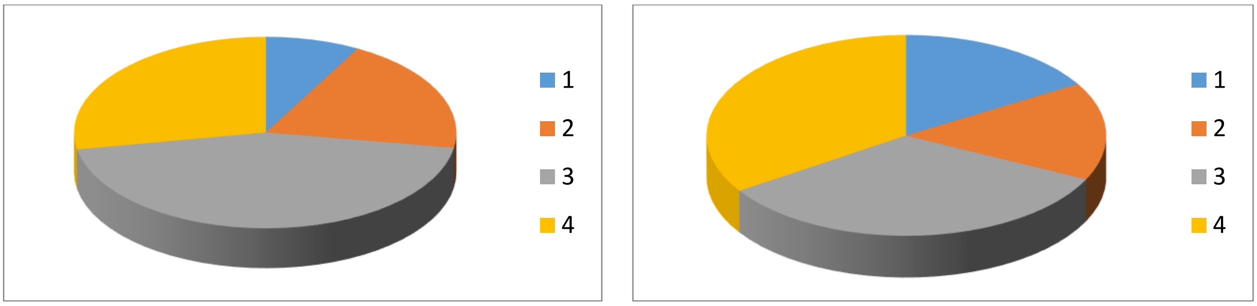
$$Cu_2O + C = 2Cu + CO\uparrow \qquad (1)$$

$$FeO + C = Fe + CO\uparrow \qquad (2)$$

$$Fe_2SiO_4 + 2C = 2Fe + SiO_2 + 2CO\uparrow \qquad (3)$$

$$Fe_2SiO_4 + 2CaO + 2C = 2Fe + Ca_2SiO_4 + 2CO\uparrow \quad (4)$$

In order to visualize the contribution of each chemical reaction in the study of enthalpy and entropy of a reaction, they are depicted in the form of a pie chart in Figure 1.



a) b)

Figure 1. Representation of enthalpy and entropy values of recovery reactions involving carbon in shares: a) contribution of recovery reactions in heat absorption; b) the contribution of each reaction in the change of entropy of the system after recovery reactions

From the pie chart shown in Figure 1a, it can be seen that the largest amount of heat is absorbed in chemical reaction 3. For this reason, the reaction temperature is very high. In Figure 1b, as a result of the 4th chemical reaction, the degree of disorder of the particles in the reaction system increases dramatically.

Based on the conclusion drawn from the values in Table 1, the corresponding mathematical expressions of the relationship between the effect of increasing temperature on each recovery reaction were constructed, and they look like this:

1 $Cu_2O + C = 2Cu + CO\uparrow$ $\Delta G_1^T = 62,68 - 0,1651 \cdot T$
2 $FeO + C = Fe + CO\uparrow$ $\Delta G_2^T = 154,48 - 0,15815 \cdot T$
3 $Fe_2SiO_4 + 2C = 2Fe + SiO_2 + 2CO\uparrow$ $\Delta G_3^T = 351,36 - 0,33621 \cdot T$
4 $Fe_2SiO_4 + 2CaO + 2C = 2Fe + Ca_2SiO_4 + 2CO\uparrow$ $\Delta G_4^T = 219,46 - 0,34424 \cdot T$

Results and discussion. Based on the calculated mathematical expressions, the probability of occurrence of each recovery chemical process was determined when the temperature in the reaction system increased by 50 units. The obtained results are presented in Table 2.

2-Table.

Values of Gibbs energies of reduction reactions in the presence of carbon at different temperatures

№	T, K	ΔG_1^T, kJ	ΔG_2^T, kJ	ΔG_3^T, kJ	ΔG_4^T, kJ
1	323	9,353	103,398	242,764	108,270
2	373	1,098	95,490	225,954	91,058
3	**423**	**-7,157**	87,583	209,143	73,846
4	473	-15,412	79,675	192,333	56,634
5	523	-23,667	71,768	175,522	39,422
6	573	-31,922	63,860	158,712	22,210
7	623	-40,177	55,953	141,901	4,998
8	**673**	-48,432	48,045	125,091	**-12,214**
9	723	-56,687	40,138	108,280	-29,426
10	773	-64,942	32,230	91,470	-46,638
11	823	-73,197	24,323	74,659	-63,850
12	873	-81,452	16,415	57,849	-81,062
13	923	-89,707	8,508	41,038	-98,274
14	973	-97,962	0,600	24,228	-115,486
15	**1023**	-106,217	**-7,307**	7,417	-132,698
16	**1073**	-114,472	-15,215	**-9,393**	-149,910
17	1123	-122,727	-23,122	-26,204	-167,122
18	1173	-130,982	-31,030	-43,014	-184,334
19	1223	-139,237	-38,937	-59,825	-201,546
20	1273	-147,492	-46,845	-76,635	-218,758
21	1323	-155,747	-54,752	-93,446	-235,970
22	1373	-164,002	-62,660	-110,256	-253,182
23	1423	-172,257	-70,567	-127,067	-270,394
24	1473	-180,512	-78,475	-143,877	-287,606
25	1523	-188,767	-86,382	-160,688	-304,818
26	1573	-197,022	-94,290	-177,498	-322,030

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