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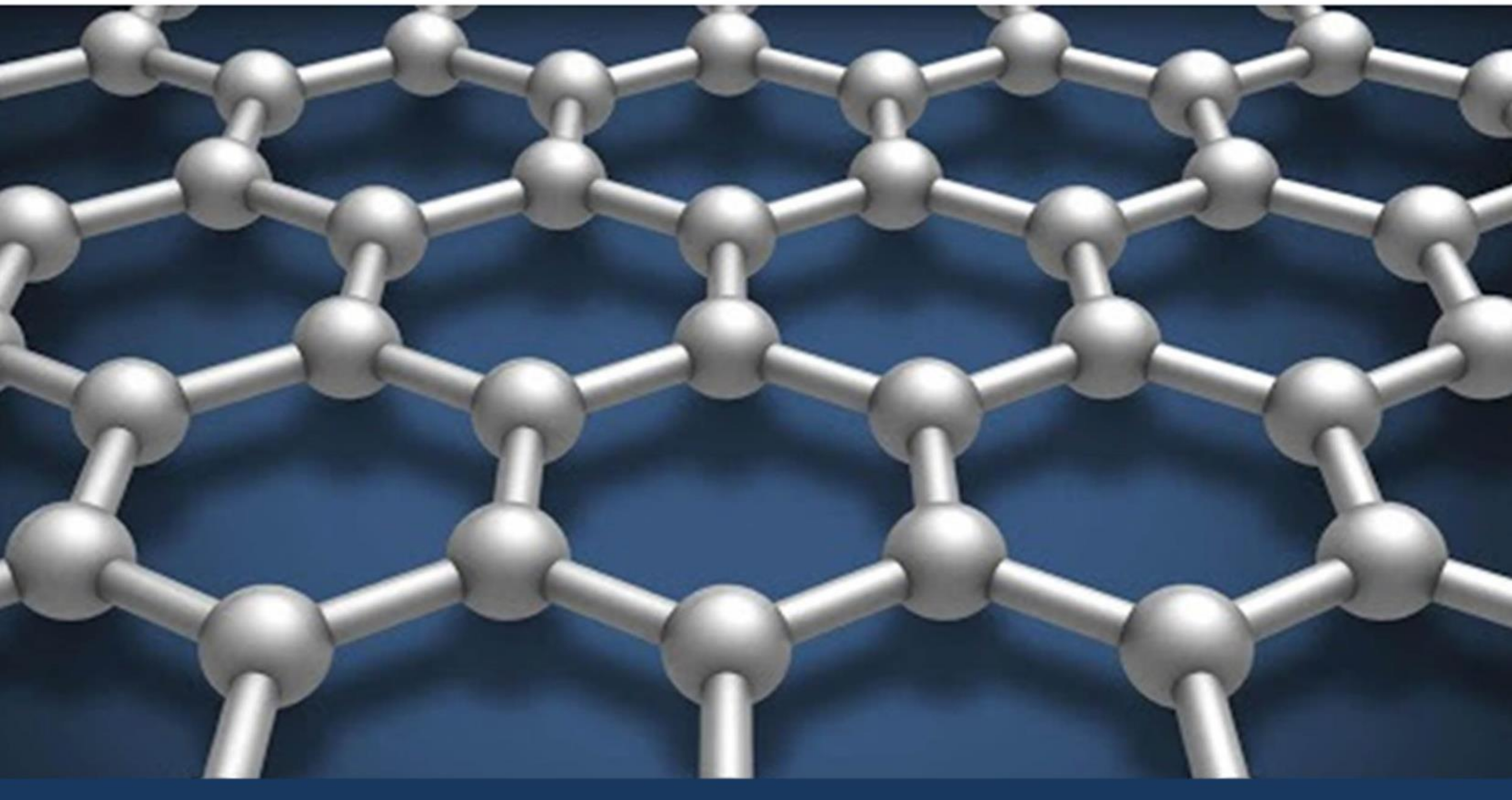

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THERMODYNAMICS OF THE PROCESS OF REDUCING IRON-CONTAINING COMPONENTS IN COPPER SLAG USING CARBON OXIDE

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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. Most types of copper slag are in oxide form. However, some sulfides may also be present in the slag phase due to incomplete separation at the matte/slag interface. Some of these may be associated with the silicate phase or form an independent phase. All compounds in the slag are chemically sustainable [1].

Oxidation-reduction reactions can proceed by different mechanisms both in heterogeneous phases and in homogeneous phases. In most cases, the initial stage of the reaction occurs with the transfer of electrons at the contact surfaces. Oxidation usually occurs in regions of highest electron density, and reduction occurs in regions of least electron density [2]. Due to the high relative electronegativity of oxygen in the oxides of the slag, the valence electrons in the outer layer of the metal atoms move to the side of the oxygen atoms. As a result, the electron density is higher on the oxygen side, creating a negative polarity. Due to valence electrons leaving metal atoms, there is an imbalance between the number of electrons corresponding to the number of protons in the atomic nucleus. Since the number of electrons in the orbital of a metal atom is less than the number of protons in its nucleus, this metal atom has a positive pole. As a result, the electron density in the region of metal atoms decreases [3].

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

Copper slags at JSC Almalyk Mining and Metallurgical Combine contain up to 30% Fe_2O_3 , which can be enriched and subjected to reduction with subsequent production of iron-containing raw materials.The process of reducing magnetite from copper slags is most effectively carried out using coke as a reducing agent, but in Uzbekistan there are no reserves of coal for coking, therefore, low-grade brown and hard coal from the Angren deposit were used as a reducing agent in the study. For the study, two modes were selected: low-temperature at a temperature of 850-1000 ^{0}C and high-temperature at a temperature of 1300-1400^{0}C.

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. The carbothermic recovery reactions between liquid slag and flue gas are as follows:

$$Cu_2O + CO = 2Cu + CO_2\uparrow \quad (1)$$

$$FeO + CO = Fe + CO_2\uparrow \quad (2)$$

$$Fe_2SiO_4 + 2CO = 2Fe + SiO_2 + 2CO_2\uparrow \quad (3)$$

$$Fe_2SiO_4 + 2CaO + 2CO = 2Fe + Ca_2SiO_4 + 2CO_2\uparrow (4)$$

According to Hess's law, the results of the reduction chemical reactions between the silicate slag components with the gas were calculated under standard conditions and are presented in Table 1.

1-table.

Values of reduction reactions with carbon dioxide gas at standard conditions (298 K).

№	Chemical reactions	ΔH_{reak}, kJ	ΔG_{reak}, kJ	ΔS_{reak}, J/K
1	$Cu_2O + CO = 2Cu + CO_2\uparrow$	-109,79	-106,64	-10,57
2	$FeO + CO = Fe + CO_2\uparrow$	-17,99	-13,24	-17,52
3	$Fe_2SiO_4 + 2CO = 2Fe + SiO_2 + 2CO_2\uparrow$	6,42	10,92	-15,13
4	$Fe_2SiO_4 + 2CaO + 2CO = 2Fe + Ca_2SiO_4 + 2CO_2\uparrow$	-125,48	-124,08	-7,1

From the values of thermodynamic calculations presented in Table 1 under standard conditions, it can be seen that the 1st, 2nd and 4th chemical reactions are exothermic reactions, their standard Gibbs energy values are negative, that is, at 298 K, the reaction occurs spontaneously. Only in the 3rd chemical reaction, a certain amount of heat absorption was observed. Although most carbothermic reactions are exothermic ($\Delta H_{reak}<0$), the entropy of the system decreases as a result of the reactions ($\Delta S_{reak}<0$).

From the values presented in Table 1, the corresponding mathematical expressions of the relationship between how the temperature increase in the reaction system affects each recovery reaction were constructed, and they look like this:

1	$Cu_2O + CO = 2Cu + CO_2\uparrow$	$\Delta G_5^T = -109,79 + 0,01057\cdot T$
2	$FeO + CO = Fe + CO_2\uparrow$	$\Delta G_6^T = -17,99 + 0,01752\cdot T$
3	$Fe_2SiO_4 + 2CO = 2Fe + SiO_2 + 2CO_2\uparrow$	$\Delta G_7^T = 6,42 + 0,01513\cdot T$
4	$Fe_2SiO_4 + 2CaO + 2CO = 2Fe + Ca_2SiO_4 + 2CO_2\uparrow$	$\Delta G_8^T = -125,48 + 0,0071\cdot T$

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

2-Table.

Values of Gibbs energy at different temperatures of reduction reactions in the presence of carbon dioxide gas

№	T, K	ΔG_5^T, kJ	ΔG_6^T, kJ	ΔG_7^T, kJ	ΔG_8^T, kJ
1	323	-106,376	-12,331	11,307	-123,187
2	373	-105,847	-11,455	12,063	-122,832
3	423	-105,319	-10,579	12,820	-122,477
4	473	-104,790	-9,703	13,576	-122,122
5	523	-104,262	-8,827	14,333	-121,767
6	573	-103,733	-7,951	15,089	-121,412
7	623	-103,205	-7,075	15,846	-121,057
8	673	-102,676	-6,199	16,602	-120,702
9	723	-102,148	-5,323	17,359	-120,347
10	773	-101,619	-4,447	18,115	-119,992
11	823	-101,091	-3,571	18,872	-119,637
12	873	-100,562	-2,695	19,628	-119,282
13	923	-100,034	-1,819	20,385	-118,927
14	973	-99,505	-0,943	21,141	-118,572
15	1023	-98,977	-0,067	21,898	-118,217
16	1073	-98,448	0,809	22,654	-117,862
17	1123	-97,920	1,685	23,411	-117,507
18	1173	-97,391	2,561	24,167	-117,152
19	1223	-96,863	3,437	24,924	-116,797
20	1273	-96,334	4,313	25,680	-116,442
21	1323	-95,806	5,189	26,437	-116,087
22	1373	-95,277	6,065	27,193	-115,732
23	1423	-94,749	6,941	27,950	-115,377
24	1473	-94,220	7,817	28,706	-115,022
25	1523	-93,692	8,693	29,463	-114,667
26	1573	-93,163	9,569	30,219	-114,312

Table 2 presents the corresponding Gibbs energies of chemical reduction reactions in the presence of greenhouse gases in the temperature range of 50-1300 ^oC, and the values of Gibbs energies in all reduction reactions became positive as the temperature increased. Despite the fact that it is an exothermic process, chemical reaction 1, i.e. reduction of copper oxide with heat gas, and reaction 3, i.e. reduction of fayalite with heat gas in the presence of calcium oxide, are more likely to occur in the given temperature range. But the 4th chemical reaction, i.e., the recovery of the activity itself with carbon dioxide, is unlikely to occur at all given temperature values. The recovery of the 1st chemical reaction, that is, wustite with carbon dioxide, occurs with a very low probability at initial temperatures. Unfortunately, increasing the temperature above 800 ^oC stops the recovery of wustite.

Conclusion. The chemical reactions of metal oxides in the slag of copper production in the presence of carbon dioxide gas and the mechanism of these reactions were established. The effect of temperature increase on Gibbs energy change and equilibrium constant in these carbothermic recovery chemical reactions was investigated. Accordingly, all recovery reactions with solid carbon at 1300 ^oC have positive indicators, that is, all chemical reactions occur practically. However, during the recovery process with hot gas, only reduction reactions took place in the presence of copper oxide and activated lime.

When comparing the values of the results obtained from the thermodynamic analysis of the recovery process of metal oxides in copper production slags and the conclusions obtained from these values with the experimental results obtained from the production practice, it was found that these values fully correspond to each other.

4. Прикладные, экономические и экологические аспект применения композиционных материалов

5. Методы исследовании, приборов и оборудований композиционных материалов

6. Проблемные обзоры