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# CHEMISTRY AND CHEMICAL TECHNOLOGY

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## RECOVERY OF THE RECOVERY ZINC CONCENTRATE IN A WEAKLY REDUCING GAS ATMOSPHERIC ENVIRONMENT

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**Abstract:** *This article provides information on the formation of substances resulting from the roasting of sulfide-zinc concentrates, which negatively affects the course of subsequent stages. The resulting calcine was sent for reduction roasting in a weakly reducing inert gas atmosphere. Based on this, it can be assumed that the impact on the calcine of "weak" energetic inert gases the reduce minimises or formation of ferrites and zinc silicates. Since the principal primary using agent is gaseous  $H_2$ , (hydrogen) in a mixture of gases with a weak reducing environment, all redox reactions occurring in total reduction were studied. The course of chemical reactions of hydrogen at high temperatures of oxides is considered. The normative thermodynamic values of reagents are determined accord particular to exceptional standards for certain thermodynamic analyses of substances with hydrogen. Research results show that zinc ferrites and silicates can be significantly reduced by reduction in an atmosphere of weak reducing gases. This, in turn, leads to a decrease in the formation of the numbert of cakes fonumberuring the hydrometallurgical leaching of the calcine, and an increase n the zinc concentration in the solution.*

**Keywords:** *zinc, ferrites, silicate, inert gas, oxide, hydrogen, thermodynamics, roasting, calcine, leaching, cake, hydrometallurgy, reduction, hematite, magnetite, Gess's law, Gibbs energy.*

**INTRODUCTION.** Metallic zinc is widely used in many industries, including metallurgy, chemicals and the light industry. The zinc is produced according to the following scheme using traditional technology. Roasting, le—roastinggrification, electrolytic separation. The roasting process produces zinc oxide, hematite, zinc ferrite and silicates. These ferrites and zinc silicates are inevitably formed during the roasting process, dependzinc concentrate's amount of iron and silicon concentrate[1,2,14]. The formed ferrites and zinc silicates do not pass partially or completely into the solution during the leaching of zinc concentrates. As awholly or partially the zinc using into the cake is sent to a process that is not considered energy a,nd resou,rce efficient [3,4].

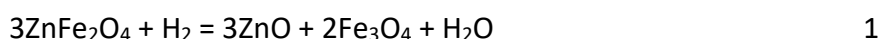
In this case, Zn, Cd and Pb metals are reduced by reducing firing at a temperature of 1100-1200 °C. However, this process indicates the need to create ve technology due to its high energy intensity and stringent requirements for the dust collection system and low metal recovery rate [5,6,7]. When carrying out reduction firing, the results of chemical reactions of hydrogen reduction according to Gess's law were calculated under standard conditions and the results are given.

When carrying out selective reduction reactions, they determine the magnitude of reactions occurring under endothermic standard and their free energy, and whether these reactions proceed under standard conditions. The temperature corresponding to the initial point of the zinc ferrite reduction process has been determined. What temperatures are necessary for the occurrence of these reactions and the results of thermodynamic analyses.

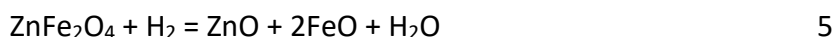
**MATERIAL AND METHODS.** Currently, new pyro and hydrometallurgical methods have been proposed for processing cakes formed during zinc leaching, etc., zinc reduction [1,8,15]. An in-depth analysis of the zinc concentrate of these developed technologies has led to a number of follow-up studies. The chemical composition of zinc concentrate, %: Zn-47.69, Fe-4.46, S-28.83, SiO<sub>2</sub>-4.2, Pb-4.6, Cu-0.87. Zinc calcine obtained by roasting the zinc concentrate was calcined in an inert low reducing medium. The energy gases of the Angren coal mine were used as an inert reducing medium. Average chemical composition of energy gases %: CO — 4.6, CO<sub>2</sub> — 22.1, H<sub>2</sub> — 19.2, CH<sub>4</sub> — 3.0, H<sub>2</sub>S — 0.5, N<sub>2</sub> — 50,1, O<sub>2</sub> — 0.5, C<sub>n</sub>H<sub>m</sub> — 0.2. Restorative firing was carried out in a special laboratory furnace "Boiled Bed".

Since the process of reduction in an atmosphere of gases with weak reducing properties of zinc calcines proceeds under difficult reaction conditions, an analysis of the main chemical reactions that can occur in the process facilitates the concstudy's conclusion a mixture of gases with a weak reducing environment, hydrogen (H<sub>2</sub>), carbon monoxide (CO) and methane (CH<sub>4</sub>) gases act as the main reducing agents, therefore, all redox reactions occurring during the general reduction process were studied, dividing into 3 classes [15]. In this study, reduction processes involving only hydrogen were presented.

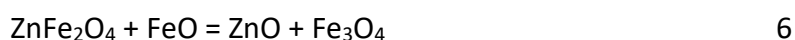
Due to the large proportion of hydrogen in the mixture of gases with a weak reducing medium, the number of collisions of gaseous hydrogen with the components of the calcine is also large, and therefore the reduction reactions of oxides with hydrogen are assigned to class 1. Chemical reactions of oxides of zinc production stub with hydrogen at high temperatures are as follows:



The remaining chemical reactions are intermediate reactions that occur at intermediate stages of the corresponding mechanism of the chemical reaction, depending on the formation of the product [8,9,13]. For example, in the formation mechanism of zinc oxide (ZnO) and magnetite (Fe<sub>3</sub>O<sub>4</sub>) as a chemical reaction product (1), the oxidation potential of Fe<sub>2</sub>O<sub>3</sub> (ferric oxide or hematite) in the zinc ferrite spinel in this region is high and attracts hydrogen [10,11,12] . As a result, ferric oxide is reduced from hydrogen to ferrous oxide (FeO) by accepting one electron:



At the second stage of the process mechanism, FeO molecules formed at the first stage displace zinc oxide from neighboring zinc ferrite molecules and combine with Fe<sub>2</sub>O<sub>3</sub> to form iron oxide (magnetite):



**RESULTS AND DISCUSSION.** The standard thermodynamic values of the substances involved in the reaction are determined from special reference books for the

thermodynamic analysis of the processes of reduction of a zinc butt with hydrogen and are presented in Table 1.

Table 1

Corresponding thermodynamic quantities of substances (25 °C)

№	Substance	$\Delta H^\circ$ , kJ/mol	$\Delta G^\circ$ , kJ/mol	$\Delta S^\circ$ , J/(mol·K)
1	ZnFe <sub>2</sub> O <sub>4</sub>	-1182	-1077	153,3
2	ZnO	-350,62	-320,66	43,64
3	FeO	-272	-251,46	60,75
4	Fe <sub>3</sub> O <sub>4</sub>	-822,2	-740,32	87,4
5	H <sub>2</sub> O	-228,597	-242,827	188,724
6	H <sub>2</sub>	0	0	130,52
7	Fe	0	0	27,15
8	Zn	0	0	41,63
9	CO <sub>2</sub>	-393,51	-394,38	213,67
10	CO	-110,52	-137,14	197,54
11	CH <sub>4</sub>	-74,81	-50,82	186,31
12	Fe <sub>2</sub> O <sub>3</sub>	-822	-740	87

Using the values given in Table 1, the results of Gess' reduction chemistries with hydrogen under standard conditions were calculated and are presented in Table 2. As a result of thermodynamic calculations performed for the standard conditions presented in Table. 2, reaction 2 can proceed independently under exothermic and standard conditions (only the activation energy needs to be specified). However, 1,3,4-reactions showed positive values of free energy under endothermic and standard conditions.

This means that these reactions do not proceed spontaneously under standard conditions. These reactions require high temperatures.

Table 2

Values of reactions of hydrogen-thermal reduction under standard conditions (25 °C)

№	Chemical reactions	$\Delta H_{\text{react}}$ , kJ	$\Delta G_{\text{react}}$ , kJ	$\Delta S_{\text{react}}$ , J/K
1	ZnFe <sub>2</sub> O <sub>4</sub> + H <sub>2</sub> = ZnO + 2FeO + H <sub>2</sub> O	58,783	10,593	70,044
2	Fe <sub>3</sub> O <sub>4</sub> + H <sub>2</sub> = 3FeO + H <sub>2</sub> O	-222,397	-256,887	153,054
3	FeO + H <sub>2</sub> = Fe + H <sub>2</sub> O	43,403	8,633	24,604
4	ZnO + H <sub>2</sub> = Zn + H <sub>2</sub> O	122,023	77,833	56,194

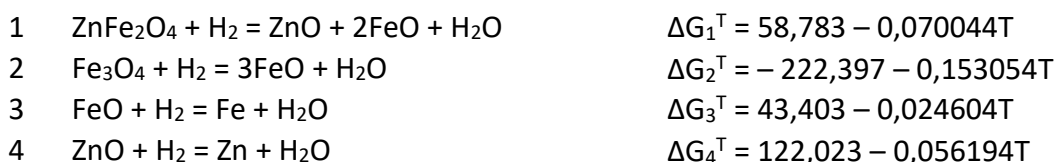
Thermodynamic analyzes were carried out taking into account the dependence of isobaric-isothermal potentials (Gibbs free energy) on temperature. The change in Gibbs free energy ( $\Delta G_{\text{react}}$ ) is usually calculated using the following formula:

$$\Delta G_{\text{react}} = \Delta H_{\text{react}} - \Delta S_{\text{react}}T \quad 7$$

Where:  $\Delta H_{\text{react}}$  – is the enthalpy of the corresponding chemical reaction, kJ/mol;

$\Delta S_{\text{react}}$  - is the entropy of the corresponding chemical reaction, J/(mol K);

T - is the absolute temperature of the system, K. Using the thermodynamic values under standard conditions given in Table 2, the general formulas for the temperature dependence of the Gibbs energy change for all hydrothermal chemical reactions are written as follows:



Based on the equations of the temperature dependence of the free energy of the above four hydrothermal chemical reactions, the values of the free energy of oxide reduction reactions during combustion at several temperatures were calculated, and these values are presented in Table 3. In this case, the values of the Gibbs energy were calculated when the temperature in the system changed every 50 units .

Table 3

Gibbs energy values for hydrothermal reduction reactions at different temperatures

No	T, °C	$\Delta G_1^T$	$\Delta G_2^T$	$\Delta G_3^T$	$\Delta G_4^T$
1	75	34,408	-275,660	34,841	102,467
2	125	30,905	-283,312	33,611	99,658
3	175	27,403	-290,965	32,380	96,848
4	225	23,901	-298,618	31,150	94,038
5	275	20,399	-306,271	29,920	91,229
6	325	16,897	-313,923	28,690	88,419
7	375	13,394	-321,576	27,460	85,609
8	425	9,892	-329,229	26,229	82,800
9	475	6,390	-336,881	24,999	79,990
10	525	2,888	-344,534	23,769	77,180
11	575	-0,614	-352,187	22,539	74,370
12	625	-4,117	-359,839	21,309	71,561
13	675	-7,619	-367,492	20,078	68,751
14	725	-11,121	-375,145	18,848	65,941
15	775	-14,623	-382,798	17,618	63,132
16	825	-18,125	-390,450	16,388	60,322
17	875	-21,628	-398,103	15,158	57,512
18	925	-25,130	-405,756	13,927	54,703
19	975	-28,632	-413,408	12,697	51,893
20	1025	-32,134	-421,061	11,467	49,083

Using a thermodynamic analysis of all reduction reactions presented in Table 3, an Ellingham diagram was constructed for all chemical reactions occurring during the processing of calcine oxides in the presence of hydrogen gas, as shown in Figure 1. Since the slowest (limiting) reaction of all hydrogen hydrothermal reactions in the oxide-hydrogen system is the reduction of zinc oxide with hydrogen, the optimum system temperature for the complete reaction is determined by the reduction temperature of this zinc oxide. However, since the aim of the study was to reduce zinc burnouts in an atmosphere of weakly reducing gases, it was not expected that zinc oxide and iron (II) oxides in the system would be reduced to their original metallic state.

Therefore, the reduction of zinc ferrite and magnetite in the reaction system satisfies the weak reduction condition. From the graph presented in fig. 1, it can be seen that if we compare the free energies of the reduction processes of zinc ferrite and magnetite, taking into account endothermic reactions, then the limiting reaction is the reduction of zinc ferrite

with hydrogen. The starting point of the zinc ferrite reduction process corresponded to a temperature of 575 °C. At this temperature, the probability of magnetite reduction by hydrogen is very high. When determining the optimal process temperature, it is also necessary to know its kinetic characteristics. To do this, it is necessary to determine the equilibrium constants of chemical reactions using the values of the Gibbs energy. The dependence of the reaction equilibrium constant ( $K_M$ ) on temperature and Gibbs energy was determined by the following formula:

Table 4

**Values of equilibrium constants of hydrogen-thermal reduction reactions at different temperatures**

№	T, K	$K_1$	$K_2$	$K_3$	$K_4$
1	75	0,9882	1,1000	0,9880	0,9652
2	125	0,9907	1,0894	0,9899	0,9703
3	175	0,9927	1,0813	0,9913	0,9743
4	225	0,9942	1,0748	0,9925	0,9775
5	275	0,9955	1,0696	0,9935	0,9802
6	325	0,9966	1,0652	0,9942	0,9824
7	375	0,9975	1,0615	0,9949	0,9842
8	425	0,9983	1,0584	0,9955	0,9858
9	475	0,9990	1,0557	0,9960	0,9872
10	525	0,9996	1,0533	0,9964	0,9884
11	575	1,0001	1,0512	0,9968	0,9895
12	625	1,0006	1,0494	0,9971	0,9905
13	675	1,0010	1,0478	0,9975	0,9913
14	725	1,0013	1,0463	0,9977	0,9921
15	775	1,0017	1,0449	0,9980	0,9928
16	825	1,0020	1,0437	0,9982	0,9934
17	875	1,0023	1,0426	0,9984	0,9940
18	925	1,0025	1,0416	0,9986	0,9945
19	975	1,0028	1,0407	0,9988	0,9950
20	1025	1,0030	1,0398	0,9989	0,9955

$$\Delta G = - RT \ln K_M$$

8

Where: R - is the universal gas constant,  $R = 8,31696 \cdot 10^{-3}$  kJ/(deg·mol);  $K_M$  – is the equilibrium constant of the corresponding chemical reaction(2). To determine the equilibrium constant from a mathematical expression, divide both sides of the equation by the product of RT with a negative sign, and then take the logarithm of the following mathematical expression:

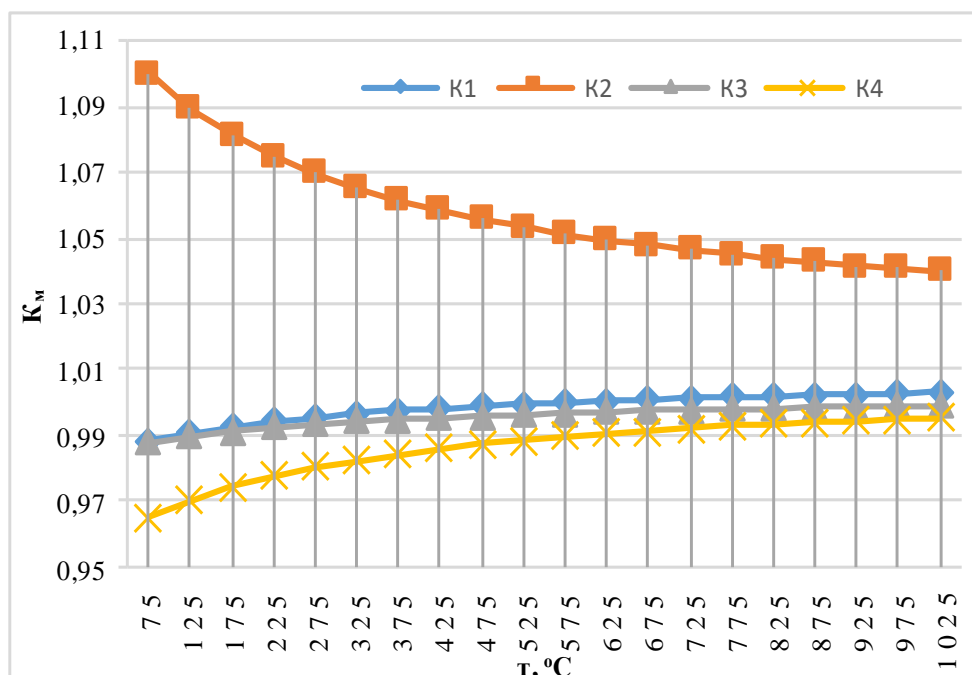
$$K_M = e^{-\frac{\Delta G}{RT}}$$

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Based on the mathematical expression (3) and the free energy values in Table 3, the chemical equilibrium constants at given temperatures for each hydrogen hydrothermal reaction were determined, and these values are presented in Table 4.

From the graph presented in Figure 2, it can be seen that the limiting reaction upon reaching a temperature of 575 °C - chemical equilibrium in the system is achieved when zinc

ferrite is reduced, and when the temperature reaches 1025 °C, the equilibrium constant reaches a high value and the reaction shifts to the right, that is, it goes in the direction of formation product ( $K_M = 1.003$ ).



**Fig. 1.** Temperature-dependent changes in the equilibrium constant of oxides during hydrogen-thermal reduction

The advantage of the hydrogen gas reduction method over other reducing gases is that hydrogen gas molecules are very small in size (hydrogen molecule diameter 27 nm), and therefore hydrogen molecules can easily diffuse into the internal pores of materials larger than 27 nm. Therefore, in powder metallurgy, bulk solids reduction process in the presence of hydrogen is more efficient. In this case, the partial pressure of hydrogen must be maintained during the reduction process in order for the process to proceed optimally.

**CONCLUSION.** The process of reduction of a zinc stub in a weakly reducing gaseous medium, a reduction process under difficult reaction conditions. The chemical reactions occurring in the process (1), (2), (3), (4), (5) and (6) were analyzed by classifying them. This helped draw the final conclusions about the study.

Since the slowest (limiting) reaction of all hydrogen hydrothermal reactions in the oxide-hydrogen system is the reduction of zinc oxide with hydrogen, the optimum system temperature for the complete reaction is determined by the reduction temperature of this zinc oxide. However, since the aim of the study was to reduce zinc burnouts in an atmosphere of weakly reducing gases, it was not expected that zinc oxide and iron (II) oxides in the system would be reduced to their original metallic state. The starting point of the zinc ferrite reduction process corresponded to a temperature of 575 °C. At this temperature, the probability of magnetite reduction by hydrogen was very high. The equilibrium constants of chemical reactions were determined using the values of the Gibbs energy, since when determining the optimal process temperature, it was required to know its kinetic characteristics.

Concluding, in a weakly reducing process in the presence of hydrogen, the reduction of zinc in the ferritic state ( $ZnFe_2O_4$ ) to ZnO is seen, and  $Fe_2O_3$  in the state of  $Fe_3O_4$  from the above reactions, it can be seen that the resulting zinc oxide is recovered by leaching.

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