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# THERMODYNAMIC RESEARCH OF THE POSSIBILITY OF PHOSPHATIC AND SILICEOUS FINES SINTERING WITH THE FLUXING ADDITIVES

**Annotation.**The research of thermodynamic possibility of the most possible reactions course in the sintering process of phosphatic and siliceous fines in the presence of fluxed additives is conducted. Sub-standard nickel-cobalt ores and internal overburdens are used as fluxed additives.

It is established that for course of reaction of Ni and Co containing components it is necessary to increase the temperature due to the presence of carbon in internal overburdens and a coke fines. It is revealed that presence of fluxing additives in sintering charge 10% to phosphorite weight in some provided chemical reactions given in article decreases the melting temperature on 3230 K – 3730 K and makes favorable impact on structure of the received sinter, increasing his strength characteristics by 10-15%.

**Keywords:** thermodynamic research, Gibbs energy, temperature, possible reactions, fluxed sinter, fluxing additives.

**Introduction.** Production of the elemental yellow phosphorus, which is the main raw material for manufacture of feed phosphates, many mineral acids, various grades of salts, detergents and other products, relates with the reduction of natural phosphates in the round and closed ore-thermal furnaces of the ORC type.

In the process of mining and preparation of commercial phosphorites to the electro thermal sublimation a significant amount of ore fines is formed. The total amount of sub-standard fines, formed at the preparation of raw materials for the yellow phosphorus production, is 55-60% of the mined ore mass [1,2] depending on the geological structure of various sections of a phosphorite deposit, their mechanical properties and composition.

Phosphorus industrial enterprises, designed for the lump phosphate processing, recycle only a small amount of phosphate fines. But the above-mentioned fines of 0-5 mm class, formed during the mining and preparation of lump phosphate raw material, transportation for the technological processing, do not provide a favorable and uniform gas-dynamic mode and exit of gases from the furnace bath at the insignificant hydrodynamic resistance in the phosphoric furnace.

In addition, in conditions of the forced industrial-innovative development of the country there is a question of the complex and rational use of industrial wastes of various industries which allow to decrease a consumption of material and energy resources at the yellow phosphorus production [3-5].

Based on the foregoing, the use of fines of phosphate raw material mined on the Karatau field deposits in the electrothermics of phosphorus is the basic economic and environmental problem. The solution of this problem is connected with the improvement of existing methods of thermal preparation of

a raw charge and the development of new processes and devices for the preparation and processing of phosphate rock in the phosphorus production.

**Methods of the research.**The researches are conducted by the full thermodynamic analysis with use of the program HSC-5.1 complex Finnish metallurgical the Outokumpu [6] companies, the minimum of energy of Gibbs [6] based on the fundamental principle taking into account that

$$G(x) = \sum_{a=1}^{f} \cdot \sum_{j=1}^{ia} Xj \left( Cj + \ln\left(\frac{Xj}{Xa}\right) + ln\gamma j \right) \rightarrow G(x)min$$

(1)

at restrictions in a look:

$$\left. \begin{array}{l} \sum_{j=1}^{m} aijXj = bi \\ \sum_{j=1} Xj = Xa \end{array} \right\}$$

(2)

where f – the total number of phases of system; bi – the total number of moths of an independent component i in system; Cj – empirical thermodynamic function; Xa – the total number of moths of a phase and in system; Xj/Xa – a molar share of dependent j-of a component in a phase and.

At carrying out of given researches the subprogrammes as "Reaction Equations", "Equilibrium compositions" were used.

**Experimental part.** We have offered a way of sitering of phosphatic raw materials [6, 7] which allows to receive fluxed phosphoritic sinter with high technological properties.

For the research carrying out we developed and installed a laboratory plant, including a sintering bowl for the phosphate fines sitering, which is shown in figure 1 [8].
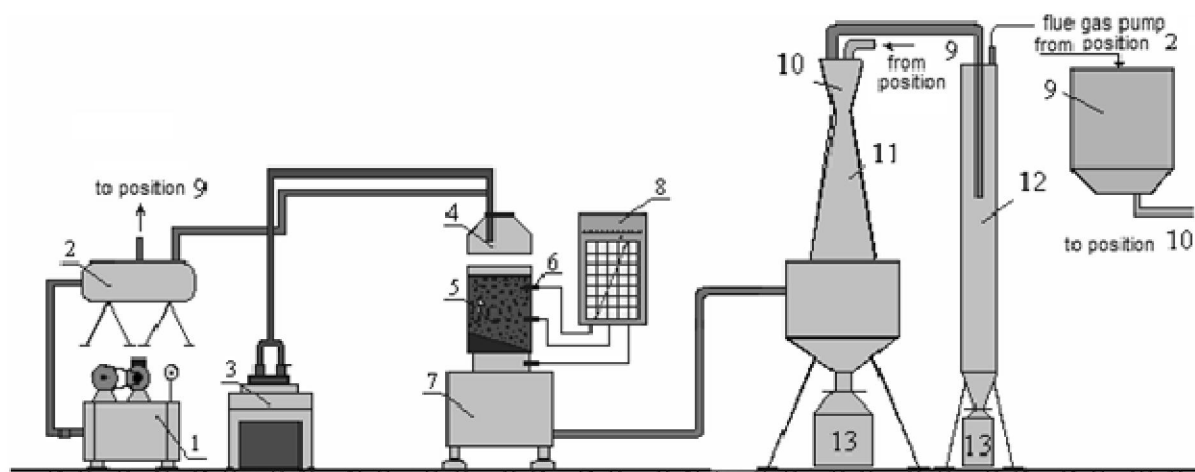


1 - compressor, 2 - spreader, 3 - fuel unit, 4 - ignition furnace, 5 - sintering cylinder, 6 - thermocouple, 7 - vacuum gage, - coordinate recording potentiometer, 9 - water storage, 10 - Venturi tube; 1 - scrubber, 12 - spray catcher, 13 – receiver for sludge.
Figure 1 - Laboratory plant for production of fluxed phosphate sinter

The laboratory plant has a system of temperature and pressure control at work of the sinter bowl.

In the sintering process the off-grade nickel-cobalt-containing ore (NCO) and the internal overburden (IO) - waste of the coal mining industry – are used as an fluxing agent and an additional fuel [9-15].

Addition to the charge up to 10% of the internal overburden and the nickel-cobalt ore permit to decrease a consumption of the solid fuel (coke) on 15-20%, to receive more durable sinter and at the further synthesis of phosphorus from the fluxed sinter to produce the alloyed with valuable elements ferroalloy.

These effects are achieved at the expense of:

- content of free carbon up to 50% in the internal overburden;

- obtaining of the eutectic liquid phase in the sintered material layer on 10-12% (relatively) higher than at the existing technology due to the content of fusible minerals in NCO and IO.

For this problem solving we made the sampling of internal overburden formed at the brown coal mining of the Lenger deposit (Kazakhstan, South Kazakhstan Region) and the nickel-cobalt-containing off-grade ore of the Kempirsay deposit (Kazakhstan, Aktobe region) and also we carried out a research of the sintering process of the Zhanatas deposit phosphorite fines in combination with the above additives.

The chemical composition of the charge materials (in %):

- the internal overburden of Lenger brown coal deposit: $Cr_2O_3$ – up to 0.1; $Fe_2O_3$ – 2.6-11.9; $Al_2O_3$ – 6.5-9.5; $SiO_2$ – 48-52; $CaO$ – 0.5-2.5; $MgO$ – 0.9-2.9; Cfree- 25-35; $K_2O$ – 0.4-0.7; $Na_2O$ – 0.3-0.5; etc. up to 100;

- nickel-cobalt-containing ores: $NiO$ – 0.88; $CoO$ – 0.05; $Cr_2O_3$ – 1.4; $Fe_2O_3$ – 20.4; $Al_2O_3$ – 6.4; $SiO_2$ – 31.6; $CaO$ – 0.6; $MgO$ – 6; Cfree – 1.1;

- phosphorites of the Zhanatas deposit: $P_2O_5$ – 21.2; $SiO_2$ – 24.1; $CaO$ –36.8; $MgO$ – 2.1; $Al_2O_3$ – 1.6; $Fe_2O_3$ –1.7.
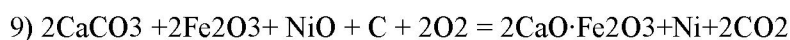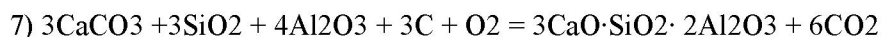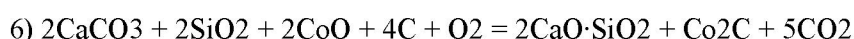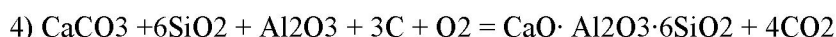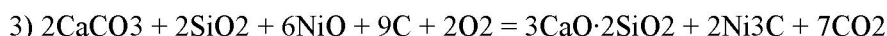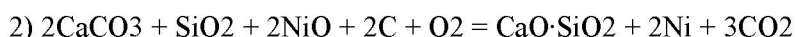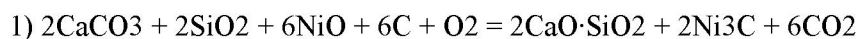
For the sintering process carrying out we used a charge mixture taken in defined ratio with the following composition: phosphate raw material – 55.0-67.0 % with a size 3-10 mm; sinter fines return – 14-16 % with a particle size 0-5 mm, nickel-cobalt ore – 3-17 % with a size 0-5 mm, internal overburden – 3-17 % with a size 0-5 mm; solid fuel (coke breeze) – 3-5 % with a size 0-3mm. The charge is mixed, moistened up to moisture content 6-8 %, pelletized and loaded on a fire grate of the sinter bowl with a height of a layer 200-220 mm over the 10-20 mm "bed" layer from the sinter with a fraction 8-16 mm. Then the fuel contained in the charge is ignited by the blowing of a gas heat carrier, formed at the combustion of natural gas in a burner.
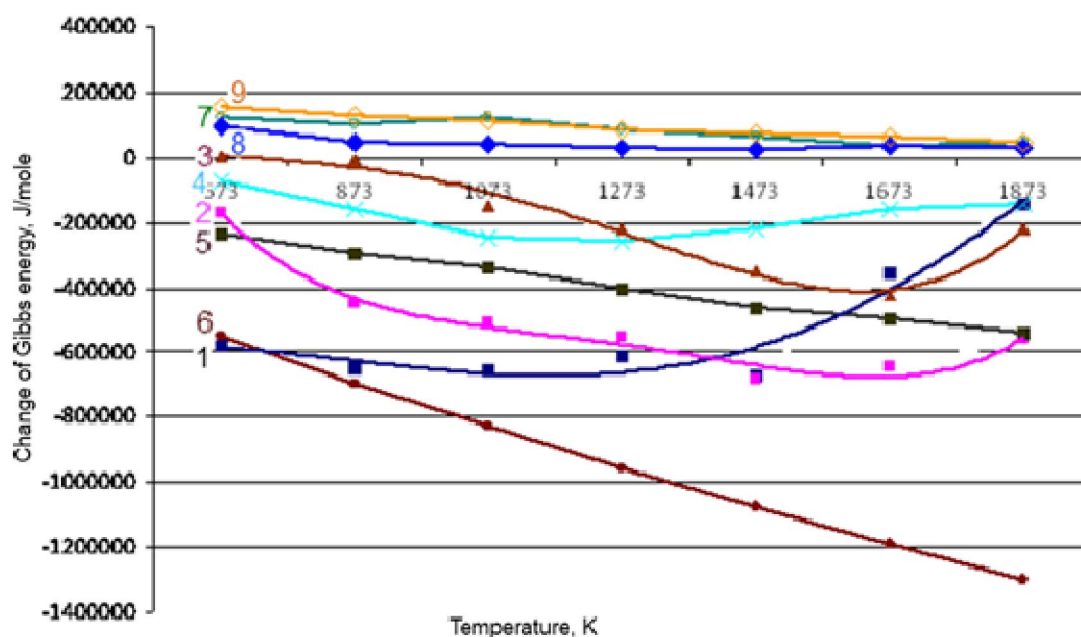
Sitering of an agloshikhta is conducted during 35-45 miknut at preservation of the module of acidity of the oflyusovanny phosphoritic sinter equal 0,93-1,16.

Increase in durability in the course of high-temperature roasting, according to us, happens due to education in system "liquid - firm" the alyumosilikatnykh and phosphorite-nickel-cobalt of calcic connections which when cooling harden, creating the difficult destroyed sheaves between larger melted-off particles of a phosphatic and siliceous fines.

The thermodynamic possiblity of course of the main reactions of solid-phase interaction between components of furnace charge was estimated with use of the program complex based on the fundamental principle of a minimum of energy of Gibbs by calculation and definition of Change of energy of Gibbs for a number of chemical compounds in the range of temperatures 673-1873 °K.

Calculation in the studied system was carried out only for most for the most possible interactions given below:

1) $2CaCO_3 + 2SiO_2 + 6NiO + 6C + O_2 = 2CaO\cdot SiO_2 + 2Ni_3C + 6CO_2$

2) $2CaCO_3 + SiO_2 + 2NiO + 2C + O_2 = CaO\cdot SiO_2 + 2Ni + 3CO_2$

3) $2CaCO_3 + 2SiO_2 + 6NiO + 9C + 2O_2 = 3CaO\cdot 2SiO_2 + 2Ni_3C + 7CO_2$

4) $CaCO_3 + 6SiO_2 + Al_2O_3 + 3C + O_2 = CaO\cdot Al_2O_3\cdot 6SiO_2 + 4CO_2$

5) $CaCO_3 + SiO_2 + 2CoO + 3C + O_2 = CaO\cdot SiO_2 + Co_2C + 3CO_2$

6) $2CaCO_3 + 2SiO_2 + 2CoO + 4C + O_2 = 2CaO\cdot SiO_2 + Co_2C + 5CO_2$

7) $3CaCO_3 + 3SiO_2 + 4Al_2O_3 + 3C + O_2 = 3CaO\cdot SiO_2\cdot 2Al_2O_3 + 6CO_2$

8) $2CaCO_3 + 2Fe_2O_3 + 3NiO + 2C + O_2 = 2CaO\cdot Fe_2O_3 + Ni_3C + CO_2$

9) $2CaCO_3 + 2Fe_2O_3 + NiO + C + 2O_2 = 2CaO\cdot Fe_2O_3 + Ni + 2CO_2$

Changes of energy of Gibbs of reaction at course of reaction given above are given in the figure 2.
Figure 2 - Results of calculations of change of Gibbs energy at course of reaction on the equations (1) – (9)

It agrees the change of Gibbs energy of reactions (1) – (9) presented in the figure 2 of solid-phase interactions in the oxidizing and deoxidazing environment it is possible to assume the following:

- reactions of interaction (7) - (9) between components of charge mix in the field of the studied temperatures are theoretically impossible as in all interval of the studied temperatures of value of Gibbs energy is ;

- reactions of interaction (1) - (4) between components of charge mix with formation of metal nickel, nickel carbide Ni3C and also silicates 2CaO·SiO2, CaO·SiO2, 2CaO·Al2O3·6SiO2 in the field of the studied temperatures (673-18730 K) thermodynamic are possible because ;

- reactions of solid-phase interaction (3) with formation of silicate of calcium 3CaO·2SiO2 and nickel carbide Ni3C in the range of temperatures 673-18730 K thermodynamic are possible;

- reactions of solid-phase interaction (5) and (6) with formation of silicates of calcium CaO·SiO2, 2CaO·SiO2 and cobalt carbide Co2C in the range of temperatures 673-18730 K thermodynamic are possible.

**Conclusions:**

It is revealed that in the conditions of sintering process the heating of charge materials to the maximum temperatures of a zone of fuel burning is carried out for very short time. At the same time the practical value has the interaction between solid phases in an initial stage. Presence at composition of furnace charge of sintering process nickel-cobalt ore and internal overburden breeds of coal mining in number of 10% to the phosphorite weight on the equations (1) – (7) reduces melting temperature on 323-3730 K and makes favorable impact on structure of the received sinter, increasing its strength characteristics on 10-15%.

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## ФОСФАТТЫ-КРЕМНИЙЛІ ҰСАҚТЫ ФЛЮСТЕУШІ ҚОСПАЛАРМЕН АГЛОМЕРАЦИЯЛАУ МҮМКІНДІГІН ТЕРМОДИНАМИКАЛЫҚ ЗЕРТТЕУ

**Аннотация.** Фосфатты-кремнийлі ұсақты флюстеуші қоспалардың қатысуымен агломерациялау үрдісінде мүмкіндігі аса жоғары реакциялардың жүруінің термодинамикалық мүмкіндігі зерттелді. Флюстеуші қоспалар ретінде кондициялы емес никель-кобальт құрамды кен мен ішкі қазба жыныстыр пайдаланылды.

Ni және Co құрамды компоненттер реакциясының жүруі үшін ішкі қазба жыныстары мен кокс ұсағы құрамындағы көміртектің жануы есебінен температураны көтеру керектігі анықталды. Агломерациялы шихтаның құрамында флюстеуші қоспалардың фосфориттің салмағына қатысты 10 % мөлшерде болуы мақалада келтірілген кейбір реакциялырдың балқу температурасын 3230 К – 3730 К азайтады және оның беріктік қасиетін 10-15%-ға жоғарылата отырып алынатын агломераттың құрылысына қолайлы әсер етеді.

**Түйін сөздер:** термодинамикалық зерттеу, Гиббс энергиясы, температура, болжамды реакциялар, флюстенген агломерат, флюстеуші қоспалар.