# The Research of Fluxed Sinter Production with Sufficiently High Strength and Improved Technological Properties

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#### Abstract

This article is dedicated to utilization of substandard phosphorite fines and simultaneously producing of fluxed sinter.

Optimal technological parameters of the sintering process of phosphate fines with addition of the substandard underoxidized nickel-cobalt-containing ore and the internal overburden of coal mining industry were established. The addition of the nickel-cobalt ore and internal overburden containing nickel, cobalt, silicon and aluminum in the charge composition permits to produce the fluxed sinter with improved technological properties, with acidity module 0.90-1.08, with the high impact, abrasion and compression strength. Decrease of the fines output (less than 6 mm) on 10-15% (relatively) in comparison with the existing (traditional) sintering technology is explained with a content of carbon (up to 50%) in the internal overburden and increase of eutectic liquid phase amount at the expense of fusible components of the nickel-cobalt ore.

The result of this process is the fluxed sinter with sufficiently high strength and improved technological properties. At the subsequent electro thermal sublimation of phosphorus from the fluxed sinter with high strength properties the ferrophosphorus alloy forms which contains the alloying metals such as Ni, Co, Cr and others. These additions containing silicon and aluminum create an exothermic effect, which leads to decreasing of fuel and energy consumptions.

The suggested technology allows to decrease a melting point of the charge on 100°C due to presence of fusible compounds in the sintering mixture and to reduce the fuel and energy consumption for the sinter production.

Found that the introduction of nickel-cobalt ore and internal overburden of coal industry in the sinter charge provides a fluxed sinter phosphorite with module of acidity 0.93-1.08 sufficiently high strength and improved technological properties, in addition, at subsequent electric sublimation of phosphorus from fluxed sinter the ferro alloy alloyed with nickel and cobalt is formed, which is a valuable raw material for the steel industry.

According to the research it is assumed that the replacement of natural quartzite used as a flux to the nickel-cobalt-chromium containing ore and internal overburden, which include about 45% of silicon, as well as transition of nickel, cobalt and chromium ore into ferrophosphorous alloy with subsequent sales of its steel industry to a higher price will significantly improve the technical and economic indices of phosphorus production.

# 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

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the preparation of raw materials for the yellow phosphorus production, is 55-60% of the mined ore mass [1, 2, 3] 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 abovementioned 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 [4, 5, 6].

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.

### Research

We have identified aims and objectives for improvement of the technology of phosphate fines agglomeration by force of introduction of various additives that create the exothermic and strengthening effect, for identification of the most rational raw materials, analysis of their chemical and mineralogical compositions. It is known that the obtained in the industrial conditions sinter has low strength properties and a yield of the sinter with the class + 6 mm is about 45-50%.

Traditionally a silicon-containing raw material such as a quartzite ore is used as a fluxing agent in the yellow phosphorus production. The introduction of silica excess in the charge leads to its sublimation into the gas phase that worsens a quality of the raw phosphorus.

Therefore an aim of the research of the sintering process is the reduction of a quartzite ore amount in the charge, decrease of the fuel and energy costs and the production of the fluxed sinter with a sufficiently high resistance to abrasion and dropping, and also improvement of technological properties.

#### **Experimental**

For the research carrying out we developed and installed a laboratory plant, including a sintering bowl for the phosphate fines agglomeration, which is shown in Fig. 1.

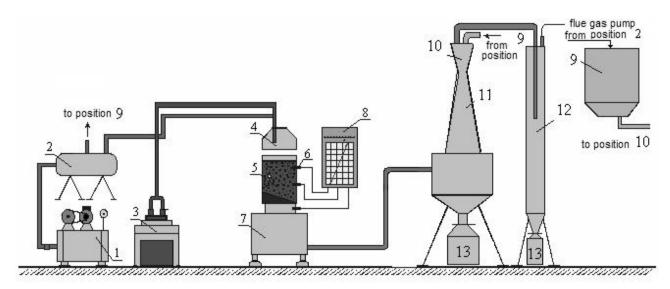


Fig. 1. Laboratory plant for production of fluxed phosphate sinter: 1 – compressor, 2 – spreader, 3 – fuel unit,
4 – ignition furnace, 5 – sintering cylinder, 6 – thermocouple, 7 – vacuum gage, 8 – coordinate recording potentiometer,
9 – water storage, 10 – Venturi tube; 11 – scrubber, 12 – spray catcher, 13 – receiver for sludge.

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

In the sintering process the off-grade nickelcobalt-containing ore (NCO) and the internal overburden (IO) - waste of the coal mining industry – are used as a fluxing agent and an additional fuel.

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-cobaltcontaining 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;  $C_{free}$  - 25-35;  $K_2O$  - 0.4-0.7;  $Na_2O$  - 0.3-0.5; etc. up to 100;

 $- \mbox{ nickel-cobalt-containing ores: NiO } - \mbox{ 0.88; } CoO - 0.05; Cr_2O_3 - 1.4; Fe_2O_3 - 20.4; Al_2O_3 - 6.4; \\ SiO_2 - 31.6; CaO - 0.6; MgO - 6; C_{free} - 1.1; \\$ 

phosphorites of the Zhanatas deposit: P<sub>2</sub>O<sub>5</sub> 21.2; SiO<sub>2</sub> - 24.1; CaO -36.8; MgO - 2.1; Al<sub>2</sub>O<sub>3</sub> 1.6; Fe<sub>2</sub>O<sub>3</sub> - 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; solid fuel (coke breeze) -3-5% with a size 0-3 mm. 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.

The charge sintering after the ignition is carried out for 35-45 minutes at evacuation 800-1000 millimeters of water. Obtained cake is cooled and crushed for the separation of suitable sinter with a size 8-70 mm.

Specific productivity of the sinter plant according to the suitable sinter is calculated by the formula:

$$Q = \frac{P_{\tilde{A}} \, 60}{\tau 1000 \cdot S} \, (\text{t/m}^2 \, \text{hour}),$$

where:

 $P_{\tilde{A}}$  – mass of the suitable sinter, kg;

 $\tau$  – time of sintering, min;

S – cross-section area of a layer, m<sup>2</sup>.

Obtained fluxed sinter has:

- compression strength - 120-220 kg/piece;

- impact strength - 80-85% (by yield of a class +5 mm);

- abrasion strength - 5-8% (by yield of a class less 0.5 mm).

The mechanical compression strength of the sinter was determined on a mechanical press, and the impact and abrasion strength was defined according to GOST 15137-77 in a standard drum [7]. The suitable sinter output was determined according to amount of the sinter fraction with a size of the material over 6 mm on standard sieves. Total amount of fines output over the research period ranged from 46% to 50.4%, averaging 48.3%, that is on 10-15% (relatively) less in comparison with the existing technology of phosphorite fines sintering (54%). Produced fluxed sinter at the optimum characteristics of the charge had the acidity module from 0.81 to 0.99. The chemical composition of produced fluxed sinter was: (%)  $P_2O_5 - 23.2$ ; SiO<sub>2</sub> -26.8; CaO - 37.1; MgO - 2.6; Al<sub>2</sub>O<sub>3</sub> - 2.7; Fe<sub>2</sub>O<sub>3</sub> -1.4;  $CO_2 - 0.5$ ;  $C_{general} - 0.31$ ; NiO - 0.14; CoO -0.001; and  $Cr_2O_3 - 0.113$ .

Examples on determination of the sintering process effectiveness depending on a quantity of additives are shown in the Table 1, and the sinter strength at different parameters of the sinter bowl work is shown in the Table 2.

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#/#		The cha	rge comp	osition, %	Acidity mod-	Yield of fines	Specific	
of experi-	Phosphorite	NCO	IO	Solid fuel	Sinter re-	ule, a.m.	with a class less	productivity,
ments					turn		than 5 mm, %	t/m <sup>2</sup> ·hour
1	2	3	4	5	6	7	8	9
2	61.0	5	15	3.4	15	1.08	25	0.76
3	61.0	10	10	4.0	15	1,03	24	0.765
4	60.5	15	5	4.5	15	0.98	25	0.76
5	60.0	17	3	5.0	15	0.96	25	0.76
6	66.0	5	10	4.0	15	0.90	27	0.73
7	66.0	7.5	7.5	4.0	15	0.93	26	0.75
8	67.0	7.5	7.5	4.0	14	0.93	25	0.75
9	65.0	7.5	7.5	4.0	16	0.96	27	0.74
10	60.0	10	10	4.0	16	1.1	26	0.75
11	62.0	10	10	4.0	14	1.04	24	0.78
12*	70-75	-	-	5-6	20-25	0.7-0.85	25-28	0.65-0.78

 Table 1

 A quantitative composition of the raw mixture for selection of the optimal charge composition for the sintering process

Table 2
Dependence of the fluxed sinter strength on parameters of the sinter bowl

#	Height of layer, mm		Consumption		Rate of the top layer sintering, mm/min	Strength of the sinter		
	bed	charge	heat carrier gas,	air, m <sup>3</sup> /		impact	abrasion	compression,
			$m^3/t_{sintering}$	t <sub>sintering</sub>		%,+5	% + 0.5	kg/piece
						mm		
Existing	18.00	180.00	13.50	150.00	11.50	80.00	5.00	120.00
1	20.00	200.00	13.80	152.50	12.00	82.50	6.50	170.00
2	20.40	204.00	13.86	153.00	12.10	83.00	6.80	180.00
3	20.80	208.00	13.92	153.50	12.20	83.50	7.10	190.00
4	21.20	212.00	13.98	154.00	12.30	84.00	7.40	200.00
5	21.60	216.00	14.04	154.50	12.40	84.50	7.70	210.00
6	22.00	220.00	14.10	155.00	12.50	85.00	8.00	220.00

The electrosmelting of fluxed sinter was carried out on a single electrode arc furnace (Fig. 2) with acidity module of the charge 0.9 (the first melting) and with increase up to 0.95 (the second melting) at using of quartzite of the Vysokoye deposit (Tulkubas district, South Kazakhstan region, Kazakhstan). The quartzite content (%):  $SiO_2 - 97.0$ ; CaO - 0.7; MgO - 0.3;  $Al_2O_3 - 0.8$ ;  $Fe_2O_3 - 0.9$ ; others - 0.3.

The phosphorus electro thermal sublimation from the fluxed charge was made during 60 minutes. The general view of fault of crucibles with products of the melting is shown on Fig. 3 [8].



Fig. 2. General view of a single electrode arc furnace.

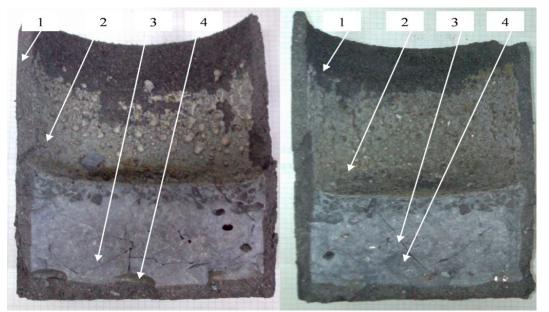


Fig. 3. Fault of the crucible with products after the melting: 1 – carbon-graphite crucible, 2 – sublimates on walls of the crucible, 3 – phosphorus slag, 4 – ferrophosphorus globules containing the alloying metals.

According to the research results it is supposed that the replacement of natural quartzite used as a flux by the nickel-cobalt-chromium-containing ore and the internal overburden, which contains about 45% of silicon, as well as the transformation of nickel, cobalt and chromium from the ore to the ferrophosphorus alloy with its further realization into the metallurgy industry on higher price will significantly improve the technical and economic parameters of phosphorus production.

For more substantiated corroboration of results and preconditions it is necessary to carry out more detailed and long-term researches with the study of mineralogical, petrographic and structural composition of the sinter containing the internal overburden formed at the coal mining, and the underoxidized nickel-cobalt ore with a sample volume more 600 tons and with subsequent processing of the fluxed sinter on industrial ore-thermal furnaces of ORC-80 F-M1 type.

## Conclusions

The submitted data indicate that the addition of the nickel-cobalt ore and internal overburden containing nickel, cobalt, silicon and aluminum in the charge composition permits to produce the fluxed sinter with improved technological properties, with acidity module 0.90-1.08, with the high impact, abrasion and compression strength [9]. Decrease of the fines output (less than 6 mm) on 10-15% (relatively) in comparison with the existing (traditional) sintering technology is explained with a content of carbon (up to 50%) in the internal overburden and increase of eutectic liquid phase amount at the expense of fusible components of the nickel-cobalt ore.

Also a consumption of a solid fuel (coke) in the sintering process is decreased on 15-20%, melting point of the charge is decreased on 100°C, that leads to reduction of fuel and energy costs on 10%. In addition, a result of the phosphorus synthesis according to the traditional scheme from the fluxed sinter is the ferroalloy alloyed with valuable elements.

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