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Development of Technology for Processing Zinc Cakes Based on the Use of Petroleum Coke

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Abstract— The article discusses the method of processing cakes of zinc plants with petroleum coke. It has been established that the middling product of the greatest interest from the standpoint of the complexity of the use of raw materials is zinc cakes obtained after leaching of calcined zinc concentrate, the yield of which is from 25 to 45% by weight of the cinder. It has been revealed that one of the most promising methods for processing cakes is the Waelz method, as a result of which zinc passes into sublimates. It was revealed that the main mass of sulfates, zinc carbonates, zinc hydro-zincates decomposes to oxide during the process of Waelzization, which is further reduced to metal when the material is heated. It has been determined that one of the most important characteristics of metallurgical and petroleum coke is its carbon content, which is usually 83-90%. Research has determined that the high ash content of the coke used leads to its high consumption and a decrease in the parameters of the Waelzization process. It has been established that the ash content of petroleum coke (0.39%) is much lower than the ash content of metallurgical coke (9-12.7%) and its use in the Waelz process can improve the process performance in terms of reducing fuel consumption. The comparison of the chemical, mechanical and physicochemical properties of metallurgical and petroleum coke, as well as the results obtained during the Waelzization of zinc cakes with the addition of petroleum coke to the charge, led to the conclusion that it is possible to completely or partially replace metallurgical coke with petroleum coke of the Fergana Oil Refinery.

Keywords— zinc, cake, petroleum coke, reduction process, high temperature.

1. INTRODUCTION

Almost all elements of Mendeleev's periodic system have been found in Uzbekistan. Today, more than 2.7 thousand deposits and promising ore occurrences of various minerals have been discovered, including about 100 types of mineral raw materials, of which more than 60 are already involved in production. More than 900 fields have been explored, in which proven reserves are estimated at 970 billion US dollars. At the same time, it should be noted that the total mineral resource potential is estimated at more than 3.3 trillion US dollars [1-6].

For a number of important minerals, such as gold, uranium, copper, natural gas, tungsten, potassium salts, phosphorites, kaolins, Uzbekistan, in terms of proven reserves and promising ores, occupies leading positions not only in the CIS, but also throughout the world [7].

Uzbekistan is the world leader in the production of copper and zinc, for example, the capacity of the AMMC for the production of copper is 100 thousand tons per year and for zinc 110 thousand tons per year [8-13].

Despite the presence of the richest mineral resources, in order to increase the competitiveness of products manufactured by metallurgical enterprises, it is necessary to reduce production costs and reduce the cost of production due to the localization of production, i.e. involvement in processing instead of consumables imported for foreign currency, local materials [14-18].

In particular, this also applies to the production of zinc, carried out at the AMMC zinc plant according to the hydrometallurgical scheme. This scheme includes the following main sections:

- oxidative roasting of sulfide zinc concentrates;
- sulfuric acid leaching of zinc cinders;
- electrolytic deposition of zinc;
- Waelzization of zinc cakes.

During oxidative roasting of zinc sulfide concentrate, due to the presence of iron compounds, some of the zinc binds into the form of poorly soluble ferrites and silicates, which remain in the cake after sulfuric acid leaching. The yield of cakes, depending on the quality of the concentrate, is 30-40%, and the zinc content in the cakes is 19-20%. To further extract zinc from cakes, the AMMC zinc plant currently uses the Waelz method, the use of which allows, due to the reduction of zinc, to convert it into sublimates. Metallurgical coke imported from abroad for foreign currency is used as a reducing agent in Waelz [19-20].

In this regard, the development of the technology of Waelzization of zinc cakes using local materials as reducing agents is very relevant [21].

2. MATERIALS AND METHODS

2.1. Materials

The output of zinc cakes after sulfuric acid leaching was 34% of the mass of the original cinder. The chemical composition of the obtained zinc cakes is given in Table 1.

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Table 1. Chemical composition of zinc cakes by main components

Compounds	Content, %
Zn	19,4
including:	
ZnO	1,72
$ZnSO_4$	0,74
ZnS	1,66
$ZnO·Fe_2O_3$	15,3
Pb	5,8
including:	
PbO	0,54
$PbSO_4$	0,21
PbS	0,45
$PbO· Fe_2O_3$	4,52
Cd	0,20
including:	
CdO	0,019
$CdSO_4$	0,007
CdS	0,015
$CdO· Fe_2O_3$	0,154
Cu	1,57
including:	
CuO	0,144
$CuSO_4$	0,052
CuS	0,12
$CuO· Fe_2O_3$	1,25
S	7,7
Fe	23,2
CaO	2,7
MgO	1,0
Al_2O_3	2,2

As mentioned earlier, petroleum coke in the amount of 40% by weight of the charge was added to the Waelz charge as a reducing agent and fuel.

For the study, samples of petroleum sulphurous calcined coke grade KPS-3 of the Fergana oil refinery were taken (the main characteristics of petroleum coke are given in Table 2).

The granulometric composition of petroleum coke grade KPS - 3 FOPP is given in Table 3.

Table 2. Indicators of petroleum coke brand KPS - 3 FOPP

№	The name of indicators	Value
1	Mass fraction of carbon, %	85,5 – 90,0
2	Ash content, %, no more	0,39
3	Mass fraction of sulfur, %, no more	2,67
4	Mass fraction of total moisture, %, no more	0,16
5	Mass fraction of active elements, %, no more	0,08 0,08 0,03
6	Silicon	2,02
7	Gland	30,0
8	Vanadium	0,86
9	Actual density, g/cm^3	8,3

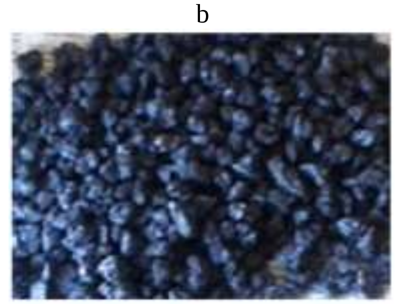
Table 3. Granulometric composition of petroleum coke FOPP

Fraction	+ 10	+7	+5	+3	+2,5	Total
%	39,1	6,3	5,1	2,8	3,0	100
Fraction	+2	+1,7	+1,5	+1,2	Residue	
%	4,1	2,5	3,4	2,4	31,3	

The appearance of petroleum coke grade KPS - 3 of the Fergana refinery is shown in Fig.1.

a

b



c

Fig.1. Petroleum coke FOPP: a – lumpy (+25 mm); b – “nut” (-25 + 6 mm); c – a trifle (- 6 mm)

2.2. Methods

Waelzization of zinc cakes with the addition of petroleum coke from the Fergana Oil Refinery to the charge was carried out on a laboratory installation of a tubular rotary kiln (Fig.2).

The installation consists of a compressor, a tubular rotary electric furnace with an internal diameter of 53 mm, a length of 517 mm, a cooling and trapping system.

The furnace has removable covers with internal bearings that are rigidly fixed on the supports, which are put on at both ends of the furnace. In the center of the lids there are holes that serve for loading and unloading material, supplying steam, as well as for removing firing sublimes.

The furnace is mounted on support rollers and is driven by an electric motor at a speed of 6 rpm. To move the material inside the working space of the furnace, the furnace is set at an angle of 5-10 degrees.

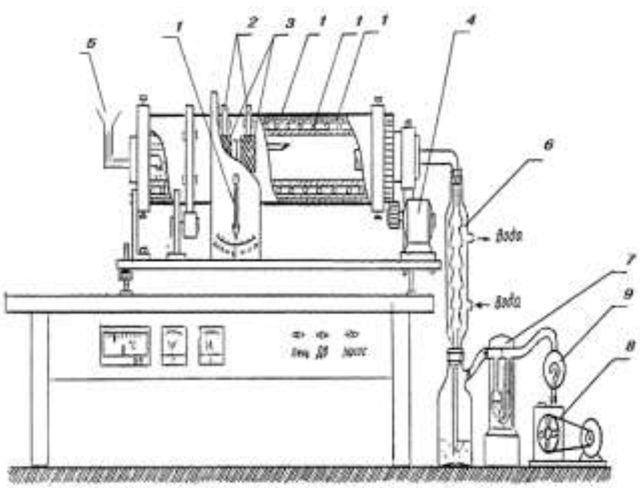


Fig.2. Laboratory facility for Waelzization of zinc cakes 1- Tubular Rotary Kiln (RTF); 2 - contact ring; 3 – graphite contact; 4- electric motor; 5- funnel for charge loading; 6 - refrigerator; 7 - pressure gauge; 8 - air pump; 9 - glass ball to stabilize suction; 10 - oven tilt indicator; 11 - quartz tube; 12 - nichrome spiral.

3. RESULTS AND DISCUSSION

3.1. Comparative analysis of the properties of metallurgical and petroleum coke

To determine the possibility of using petroleum coke of the Fergana oil refinery instead of metallurgical coke, studies were carried out to compare the properties of the two materials.

For this, the requirements for the quality of metallurgical coke were investigated. The coke loaded into the Waelz furnace performs the functions of a reducing agent and, in part, a heat source. Due to the heat of combustion of natural gas and coke, high temperatures are created in the layer of charge materials, which contribute to the normal course of reduction processes in the working space of the furnace. In addition, coke loosens the charge, improving its gas permeability. The composition of the most commonly used coking coals for zinc cakes is given in Table 4.

Table 4. Main properties of coking coals often used in the waelzing of zinc cakes

№	The name of indicators	Value
1	Mass fraction of carbon, %	85,5 – 89,5
2	Ash content, %	9,0 – 12,7
3	Mass fraction of sulfur, %	0,45 – 2,0
4	Mass fraction of total moisture, %, no more	5,0
5	Mass fraction of active volatile substances,%	until 1,5

The study of the mineralogical composition of coke made it possible to establish that 17.9 - 22.7% of coke sulfur is included in the composition of sulfides, 1.6-7.3% in the composition of sulfates, 71.3-76.7% - in the structure of coal proper substances (“organic” sulfur).

The content of residual volatile substances in coke depends on the temperature and duration of coking. According to the standards, the content of volatiles in coke should not exceed 1.5%. One of the most important characteristics of coke is also the content of non-volatile carbon in it, which is usually 83-88% (based on working fuel).

The physical and chemical characteristics of coke include its flammability and reactivity. The combustibility of coke is determined by the rate of interaction of its substance with oxygen. The reactivity of coke is determined by the rate constant of its interaction with carbon dioxide at 1100 °C.

In appearance, good coke is distinguished by a columnar structure, a silvery sheen on the surface of the piece. Good coke doesn't get your hands dirty. In terms of porosity (45-55%), coke occupies an intermediate position between dense stone (1-10%) and charcoal (75-85%) coals. Bulk weight of coke is close to 450 kg/m^3.

Petroleum coke of the Fergana oil refinery was also studied according to similar indicators. The main properties of petroleum coke are given in table 5.

Table 5. Main properties of petroleum coke of the Fergana Oil Refinery

№	The name of indicators	Value
1	Mass fraction of carbon, %	85,5 – 90,0
2	Ash content, %, no more	0,39
3	Mass fraction of sulfur, %, no more	0,45 – 2,0

4	Mass fraction of total moisture, %, no more	0,16
5	Mass fraction of active volatile substances,%	8,3

Petroleum coke was examined for the content of harmful components, which, during walezation, can turn into sublimates. Chemical analysis determined a rather low content of harmful components,%: 0.01 Cl; 0.0015 - 0.008 F; 0.74 - 1.24 S.

An extremely undesirable component in coke is ash. Increased ash content causes an increase in fuel consumption, and also reduces the productivity of Waelz furnaces. As noted in [11], an increase in the ash content of coke by 1% causes an increase in its consumption by approximately 2.5%. Based on the foregoing and the data given in Table. 4.1 and 4.2. it can be said that the addition of petroleum coke to the Waelz charge, instead of metallurgical coke, is more preferable due to the low ash content (ash content of petroleum coke is not more than 0.39%, metallurgical coke - 9.0 - 12.7%).

Petroleum coke was tested for mechanical strength by abrasion. The results for the attrition of petroleum coke are close to the results of the attrition of standard coke.

The attrition of petroleum coke depends on the yield of volatiles, as well as on the chemical composition and on the production method. Abrasion was determined in a drum with a diameter of 200 mm and a width of 80 mm. There are slots 4 mm wide around the circumference of the drum. A batch of coke with a size of pieces of 50 - 100 mm is loaded into the drum. The drum is driven by an electric motor, the rotation speed is 22 rpm. Abrasion was characterized by the percentage of coke that spilled through the slots after rotating the drum for 2 minutes. Four weights of petroleum coke were subjected to abrasion; the arithmetic mean of the three closest determinations was taken as the test result. The results of determining the coke friability are shown in Table 6.

From the comparison of the chemical, mechanical and physicochemical properties of standard and petroleum coke, they showed the similarity of their properties, which is a good basis for recommending petroleum coke as an alternative fuel when replacing it in the charge of the Waelz furnace.

Table 6. Results of determining the friability of petroleum coke

Sample number	**Weight of petroleum coke sample, kg**	**Abrasion, %**
1	1,1	4,5
2	1,0	5,0
3	1,2	4,8
4	1,0	5,1

3.2. Study of the influence of petroleum coke on the extraction of zinc into sublimates

Research on the effect of petroleum coke on the extraction of zinc into sublimates was carried out on a laboratory installation, the description of which is given in chapter 2.2 and in Fig.2.

To determine the optimal amount of petroleum coke added to the Waelzization charge, three samples were prepared with different amounts of petroleum coke in the charge:

- composition of the 1st sample, wt %: zinc cake - 55.0; Ferghana petroleum coke - 37.0; limestone - 8.0;
- composition of the 2nd sample, wt %: zinc cake - 50.0; Ferghana petroleum coke - 40.0; limestone - 10.0;
- composition of the 3rd sample, wt %: zinc cake - 44.0; Ferghana petroleum coke - 44.0; limestone - 12.0.

The results of studies on Waelz with the addition of Fergana coke to the charge are given in Table 7.

Table 7. Results of Waelzization of zinc cakes with the addition of Fergana petroleum coke to the charge

Samples	The content of petroleum coke in the charge, in % of the mass of the charge	Zinc content in Waelz oxides, %
1st sample	37,0	48,6
2nd sample	40,0	59,6
3rd sample	44,0	59,8

As can be seen from the data obtained, the highest content of zinc oxide in the Waelz oxides of 59.8% is observed at a consumption of petroleum coke of 44% by weight of the charge. However, we adopted the 2nd batch as the optimal composition of the charge (zinc cake - 50.0; Ferghana petroleum coke - 40.0; limestone - 10.0), since in the 3rd batch (zinc cake - 44.0; Ferghana petroleum coke - 44.0; limestone - 12.0) due to the increase in the share of petroleum coke in the charge, the amount of processed cake is reduced.

In Waelzization of zinc cakes with the addition of petroleum coke at a reducing agent consumption of 40.0% by weight of the charge, the yield of Waelz oxide was 33%, the yield of clinker was 55%. The average zinc content in the Waelz oxide was 59.6%, and in the clinker 1.24%, while the initial zinc content in the cake was 22.0%. The extraction of zinc into Waelz oxide was 89%.

Comparing the results of Waelzization of zinc cakes with the addition of Fergana petroleum coke to the charge with the results of Waelzization with metallurgical coke (Table 8), we can conclude that it is possible to completely or partially replace metallurgical coke with petroleum coke.

Table 8. Comparison of Waelzization indices for zinc cakes

№	Indicators	Waelz sector of Zinc Plant of AMMC	Waelz with the addition of petroleum coke
1.	Yield of oxides from cakes, %	30,0 – 32,1	32,7 – 33,0

2.	Clinker yield from cakes, %	63,0 – 63,1	54,5 – 55,0
4.	Content of zinc in oxide, %	56,0 – 56,5	59,0 – 59,8
5.	Content of zinc in clinker, %	1,2 – 1,78	1,24

4. CONCLUSION

Based on the analysis and comparison of the properties of metallurgical and petroleum coke, the following conclusions can be drawn:

- it was found that the coke loaded into the Waelz furnace performs the functions of a reducing agent and, in part, a heat source;

- it has been determined that one of the most important characteristics of metallurgical and petroleum coke is its carbon content, which is usually 83-90%;

- it was found that the increased ash content of coke causes an increase in its consumption, and also reduces the productivity of Waelz furnaces, for example, an increase in the ash content of coke by 1% causes an increase in its consumption by about 2.5%;

- it has been determined that the ash content of petroleum coke is much lower than the ash content of metallurgical coke and its use in the Waelz process can improve the performance of the process in terms of reducing fuel consumption;

- conducted studies of metallurgical and petroleum coke, established the similarity of their properties, which can be the basis for replacing metallurgical coke with petroleum coke in the wake of zinc cakes.

- it was found that the optimal amount of petroleum coke introduced into the Waelz charge is 40% of the mass of the cake, while the yield of Waelz oxide is 33%, the yield of clinker is 55%, the extraction of zinc into Waelz oxide is 89%.

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