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Processing of converter sludges on the basis of thermal-oxidative coking with coals

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Abstract. The paper deals with the solution of an important problem related to the recycling of converter sludge. High moisture and fine fractional composition of waste causes the application of their deep dehydration and lumping. To reduce environmental emissions the non-thermal method of dehydration is considered – adsorption-contact drying. As a sorbent, the pyrolysis product of coals from the Kansko-Achinsky basin – brown coal semi-coke (BSC) obtained by the technology “Thermokoks”. Experimental data on the dehydration of high-moisture wastes with the help of BSC showed high efficiency of the selected material. The lumping of the dried converter dust was carried out by thermo-chemical coking with coals of grades GZh (gas fat coal) and Zh (fat coal). As a result, an iron-containing product was obtained – ferrocoke, which is characterized by almost complete reduction of iron oxides, as well as zinc transition into a vapor state, and is removed with gaseous process products. Based on the results of the experimental data a process basic diagram of the utilization of converter sludge to produce ferrocoke was, which can be effectively used in various metallurgical aggregates, for example, blast furnaces, converters and electric arc furnaces. In the basic technological scheme heat generated by ferrocoke cooling and the energy of the combustion products after the separation of zinc in the gas turbine plant will be used.

1. Introduction
In the converter production of steel, depending on the technology used and the design of the unit, from 12 to 25 kg of dust per 1 ton of steel is formed. After dust passes through the wet gas cleaning, high-moisture sludge is formed. Converter sludges are a valuable iron-containing technogenic raw material which contains up to 57 – 65% of iron, the main part is represented by Fe₂O₃ oxide. According to the R&D Company “Energostal” the degree of cleaning of waste gases from dust exceeds 80%, and the degree of utilization is 72 % [1, 2].

Currently, the recycling of most types of disperse metallurgical wastes is carried out by using them in the composition of agglomeration burden. However, for technological reasons the application of some of them is limited or impossible. In addition, at the sinter plants without a stockhall the use of technogenic raw materials of different composition without the possibility of its controlled dosing negatively affects the stability of the agglomerate composition and quality [3]. In terms of recycling of iron-containing dispersed wastes the process of their lumping might serve as an alternative.

The use of composite charge materials includes the production of ferrocoke and ferrocoke briquettes [4 - 6]. The concept of ferrocoke production was developed in the 30’s of the last century and aimed at sintering iron ore dust unsuitable for smelting in blast furnaces with fatty or bituminous coal in coke oven batteries. Ferrocoke can be classified as an iron-carbon composition treated by heat
outside the melting unit. Ferrocoke is a composition material containing mainly reduced iron and carbon. However, before ferrocoke production iron-containing dusts and sludge from gas-cleaning units must be dehydrated in advance.

A number of methods for dehydrating sludges are known consisting, as a rule, of cumbersome energy-intensive technological schemes involving preliminary removal of moisture (up to <20-25 %) by mechanical methods (thickening and filtration) and then followed by thermal drying [7, 8]. The latter allows the material to be drained to an essentially dry state, but the intensity of high temperature exposure is strictly limited by the requirements for fire and explosion hazard prevention. Thermal drying requires financial costs for the construction of separate facilities, fuel costs [9]. Currently, innovative non-thermal methods for deep drying of wet materials using adsorption processes are gaining popularity. One of the key factors in adsorption is the developed specific surface of adsorbents.

The authors developed an original technology for recycling of converter sludges, the conceptual basis of which is their adsorption dehydration in combination with thermo-chemical lumping [10, 11]. The symbiosis of these methods of converter sludges processing provides the technology with competitive advantages in terms of energy saving (reduction of energy consumption for moisture removal) during drying of high-moisture sludges and in terms of resource-saving (there is no need to use the binder) during lumping.

2. Methods of research

To study the adsorption dehydration of sludge the experiments were carried out with a high-moisture (\(W_r = 50.0\) %) converter sludge of JSC “EVRAZ ZSMK”. The chemical composition of dry sludge is given in table 1.

| Element | Mass fraction of the element, % wt |
|---------|-----------------------------------|
| FeO     | 46.81                             |
| Fe2O3   | 64.05                             |
| Fe      | 1.82                              |
| MgO     | 4.59                              |
| CaO     | 16.68                             |
| SiO2    | 5.75                              |
| K2O     | 0.19                              |
| V2O5    | 0.069                             |
| Cr2O3   | 0.10                              |
| C       | 0.63                              |
| S       | 0.24                              |
| ZnO     | 1.11                              |
| CuO     | 0.061                             |
| PbO     | 0.11                              |
| MnO     | 1.08                              |
| Al2O3   | 1.93                              |
| Na2O    | 0.88                              |
| P2O5    | 0.32                              |
| Fe2O3   | abs.                              |
| TiO2    | 0.21                              |

The content of zinc and lead in the slutty is different and depends not only on the composition of the raw material but also on the dust dispersion. Evaluation of the granulometric composition of thermally dried sludge was performed on a laser size-distribution device MALVERN-2000 in the Materials Science Center of Siberian State Industrial University (Novokuznetsk, Russia).

Solid pyrolysis residue of brown coal – fine-grained BSC was used as an adsorbent which is currently produced according to the technology of “Termokoks-KS” at the pilot plant of open-pit mine Berezovsky-1. According to [12], BSC has a highly developed and well-accessible porous structure and, accordingly, high adsorption capacity and energy properties. The micropores volume of the porous BSC structure is tenfold higher than the volume of micropores in the structure of coal coke. In this regard the adsorption capacity of BSC is close in this indicator to traditional activated carbons. In terms of adsorption capacity BSC is slightly inferior in activity to the sorbent brand ABG-D (TU600209591-443-95) and significantly exceeds the sorbent brand DAK (TU0321002-51577712).

At the same time, it should be noted that the density of BSC particles even if the entire porous space is filled with adsorbed moisture (1.42 g/cm3) will be more than 2.5 times lower than the density of converter sludge particles (3.8 g/cm3). The general BSC characteristics are given in table 2.

As it follows from the data in table 2 BSC is a low-ash and low-sulfur high-calorie product with a highly developed and well-accessible porous structure.
Table 2. Characteristics of BSC from open pit coal mine Berezovsky-1.

| Indicators                              | Unit of measurement | Value indicator |
|-----------------------------------------|---------------------|-----------------|
| Total moisture                          | %                   | 3.0             |
| Ash, dry condition                      | %                   | 9.7             |
| The yield of volatile substances        | %                   | 9.9             |
| Elemental composition, combustible mass:| %                   |                 |
| Carbon                                  |                     | 92.8            |
| Oxygen                                  |                     | 4.45            |
| Hydrogen                                |                     | 1.52            |
| Sulfur (dry state)                      |                     | 0.24            |
| Phosphorus (dry state)                  |                     | 0.026           |
| Highest heat of combustion              | kcal/kg             | 7830            |
| Lower heat of combustion, working state | kcal/kg             | 6700-6800       |
| Adsorption activity of iodine           | %                   | not less than 42|
| Total pores volume                      | cm³/g               | 0.47            |
| Specific surface of pores               | m²/g                | 500             |
| Density                                 |                     |                 |
| absolute                                | kg/m³               | 1880            |
| apparent                                |                     | 974             |
| Bulk density                            | kg/m³               | 550             |

The results of dehydration were evaluated according to the free-flowing index of material (GOST 25139-93). The basis for BSC ratio determination: sludge, which is necessary for the production of a free-flowing mixture, is data on sludge moisture and adsorption capacity of BSC.

After gaining free-flowing properties, the mixture of sludge and BSC is supposed to be subjected to pneumatic separation, after which the BSC is sent for technological and energy use, the sludge – for thermo-chemical lumping.

During the experiments on the study of thermo-chemical lumping of converter sludges two series of samples were used. Samples of series No. 1 concentrate CPP Kuznetskaya GZh + Zh – 50 % wt + 50 % by weight converter sludge and samples of series No. 2 concentrate of coal grade Zh of the Mezhegeyskoye deposit – 50 % wt + 50 % wt converter sludge (to obtain a material containing carbon, coal concentrates are added in excess). The characteristics of coal concentrates are given in table 3. The choice of such ration of mixture components is based on the notion that in this case the sludge is an additive to coking coal with a high volatile yield and for the production of a strong lump material it is necessary to have a certain level of mixture sintering.

Table 3. Characteristics of coal concentrates.

| Sample     | Technical analysis, % | Plastometry, mm | Petrography |
|------------|------------------------|-----------------|-------------|
|            | Wr | Ad | Vt   | Sf | X  | Y  | Vt, % | S_r | R   |
| GZh+Zh     | 10.5 | 7.8 | 38.0 | 0.56 | 17 | 24 | 85.0 | 0.56 | 0.864 |
| Zh         | 8.6 | 8.1 | 38.2 | 0.67 | −2 | 34 | 93.0 | 0.045 | 0.853 |

The study of sludge lumping by the thermo-chemical method was carried out in two stages. In the first stage the mixtures were heated in the unit of plastometric analysis to temperature 730 °C. In the second stage the samples subjected to plastometric analysis were heated in a Tamman furnace for 30 minutes to the temperature of completion of coking process (1050-1100 °C).
Determination of the mechanical compressive strength of briquettes from coke batch and mixtures containing coals from the Mezhegeysky and Kuznetsky deposits with converter sludge was carried out in accordance with GOST 21289-75 “Coal briquettes. Methods for determination of mechanical strength”. The hydraulic press 2PG-10 was used for the test.

3. Results and discussion
Evaluation of the granulometric composition of both samples revealed the similarity of the composition of converter sludge and BSC (figure 1).

![Figure 1. Granulometric composition of sludge (a) and BSC (b).](image)

From these data it follows that the grain-size distribution of the solid part of the materials is represented by small particles in the range 0.5-1000 μm, and the maximum of the grain-size distribution curve is about 500 μm. Experimental observations confirmed the correctness of the calculated adsorption capacity of semicoke (table 4).

| Table 4. Quality and bulk properties of sludge and sludge mixture with BSC. |
|-----------------------------|-----------------|----------------|
| Product                     | Moisture contents, W, % | Free-flowing, g/s |
| Initial sludge (mud-like condition) | 50.0            | 0.0            |
| BSC                         | 3.0             | 25.28          |
| Thermally dried sludge      | 1.35            | 0.0            |
| Sludge + BSC*               | 16.55           | 33.34          |

*Mixing time – 2 min.

When mixing BSC with the wet waste it absorbs moisture giving the mixture a high free-flowing, which is important for transportation of the product in process streams. At the same time the moisture
adsorbed in the pores passes into a bound state and becomes an active participant in oxidation-reduction processes.

As a result of laboratory experiments on thermo-chemical lumping it was established that the thickness of the plastic layer for the samples in series No. 1 was 10 mm, for the samples in series No. 2 – 17 mm. Heating of the experimental mixtures in the apparatus of plastometric analysis to a temperature of 730 °C was accompanied by the removal of volatile substances from the coal portion of the samples, while the content of sludge in the samples increased to 56-57 % by weight. An increase in the FeO content in the chemical composition of the sludge from 1.82 to 14.3 % wt and the appearance in the amount of 2.03 % wt of Fe_{met} were established. The zinc oxide content in the samples was 0.48 % wt. The results of plastometric analysis confirmed the results of thermodynamic modeling [13]. At temperatures of heating the test mixtures up to 730 °C the iron reduction, even in the presence of excessive carbon, practically does not occur.

Calcination in the Tamman furnace was accompanied by solid-phase reduction of iron. In particular, the degree of reduction to Fe_{met} in the samples of series No. 1 was 84.9 % wt, in the samples of series No. 2 – 94.4%.

The product of ferrocoke (figure 2) obtained as a result of a series of experiments contains 35-39 % of Fe_{met} and 45-49 % of C, content of ZnO does not exceed 0.017 %, the compressive strength is 2.8 MPa.

![Figure 2. Samples of ferrocoke (a, b).](image)

Based on the results of experimental studies, a technological scheme for recycling of high-moisture wastes was developed that includes non-thermal adsorption dehydration of converter sludges in combination with the subsequent thermo-chemical lumping (figure 3).

The converter sludge from the sludge reservoir 1 enters the thickener 2 and is then transferred to the mixer-adsorber 5 to contact with BSC serving as a moisture adsorbent. Then the mixture of products is transferred to the separation into pneumatic classifier 7, from where the lighter BSC through the dust separating system (cyclone 6, bag filter 8) enters the hopper 9, from where it is taken for energy-engineering needs, and the dust-free air is discharged into the atmosphere. The heavier sludge from the pneumatic classifier 7 passes through the dispenser into the mixer 12, into which the coking coal from the hopper 11 is also fed through the dispenser. The mixture formed in the specified ratio is subjected to thermo-oxidizing coking in the rotary hearth furnace 13. The ferrocoke obtained at a final temperature of 1100-1150 °C is cooled in the dry quenching unit 15 with a waste heat boiler 17 and sorted into classes 0-10 mm, 25-10 mm and +25 mm. Heat for coking is formed by burning above the bed of charge in the furnace with a rotating hearth of evolved gaseous products. The combustion products from the furnace are forwarded for later use in a gas turbine plant 14.
4. Conclusions
The results obtained in this paper indicate that on the basis of principles of conditioning of wet converter sludges by adsorption dewatering and thermo-chemical lumping it is possible to develop an efficient technology for their utilization with the production of ferrocoke. Ferrocoke is a composite material containing mainly reduced (metallic) iron and carbon. Such product has a wide field of
application as an iron and carbon-containing charge component. In addition to its use in blast furnace production, its application for converter melting technology, including with the liquid-phase reduction elements, is of practical interest.

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