



Research in the field of production of fine-grain concrete from metallurgical waste

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Abstract

To examine existing methods for processing and recycling metallurgical waste and to describe their classification. To address the negative impact of the metallurgical industry, particularly the waste generated by its operations, on geosystems. This article assesses the potential for recycling solid industrial waste in the ferrous metallurgy industry. The applicability of dry converter dust as a substitute for natural iron-containing materials is analyzed. It is shown that, based on its composition, the dust can be considered an effective substitute for sinter ore and concentrate. Methods for preparing dust for recycling in metallurgical production are discussed.

Keywords: Recycling, industrial waste, elemental clarkes, slags, sludge, converter dust, agglomeration, agglomeration, briquetting

Introduction

According to the WWF conservation organization, humanity consumes 20% more natural resources than the Earth can reproduce. At the same time, the ecological imperative (or the amount of land needed to meet the vital needs of one person) is 21.9 hectares, while the biological capacity of the Earth provides an average of only 15.7 hectares per person.

In addition, according to environmentalists, a third of the Earth's resources have been lost due to their irrational use, and the main cause of global warming is the greenhouse effect caused by household garbage and industrial waste dumps.

In order to attract the attention of government bodies, businessmen, the public and individuals to the problems of environmental pollution by both household garbage and industrial waste. World Recycling Day is celebrated annually on November 15 in many countries (from the English recycling, recycling and waste utilization) reuse or return to circulation of useful components of household garbage or industrial waste.

Currently, the large- and medium-sized metallurgical industry ranks second in terms of harmful atmospheric emissions in the world. The production capacity of large metallurgical plants processing metal and metal ingots (molten metal blanks) is at a standstill due to the use of raw materials with very limited useful component content. For this reason, metallurgical plants receive very large volumes of ore for processing into finished products, which, accordingly, generates large quantities of waste, including secondary products such as slag and exhaust gases from unused components. Thus, air and soil pollution are among the main causes of environmental problems arising from the activities of the large- and medium-sized metallurgical industry. Effluents from metallurgical production facilities, discharged through waste pipes and storm water drainage systems from open waste disposal sites, pollute the soil (the fertile topsoil) and create man-made wastelands around the perimeters of large factories and metallurgical facilities. For this reason, metallurgical operations have a detrimental impact not only on the air, but also on water and soil ^[1].

Discussion

The implementation of technological operations with waste involves converting them into secondary raw materials, energy or products with certain consumer properties. The most common are both secondary and multiple processing on one scale or another of such materials as glass, paper, scrap non-ferrous and ferrous metals, asphalt, fabrics and various types of plastic. Organic waste has also been used in agriculture since ancient times. Production waste is recycled to a lesser extent.

Accumulations of mineral substances on the Earth's surface or in mine workings, representing waste from mining, processing, metallurgy and other industries and suitable in quantity and quality for industrial use, which becomes possible as their processing technology develops and economic conditions change, are considered as technogenic deposits.

The content of some useful components in technogenic waste is commensurate with their share in the ores of natural deposits.

For example, according to the data of work ^[1], ferrous (Cr, Mn), alloying (Ti, V, Ni, Co, Mo, W), non-ferrous (Cu, Zn, Pb, Hg, Sb, Bi), noble (Ag), rare (Li, Be, Sr, Y, La, Yb, Nb, Cd, Sc, Ba, Ge) metals and non-metals (P, F) are present in the rocks of the coal-bearing strata, coals and coal ash of Donbass. The concentration of some elements is relatively high (Ge, Be, Li — 2–3 concentration clarkes — the ratio of the average content of a given chemical element to the clarkes of the lithosphere or its part, Yb up to 8 c. c.). His calculations showed that the ash formed annually in the Donbass contains various elements worth several billion US dollars.

Blast furnace and steelmaking slags also have a high content of useful components. As a result of our spectral analysis of steelmaking slag samples from the dump of a metallurgical plant, it was found that in addition to the main elements (Fe, Ca, Si, Mg, Al and Mn), the slag contains more than 50 elements for most of which the concentration clarkes are higher than one, including noble metals.

Currently, technologies for extracting rare and noble metals from man-made waste are ineffective. However, given the elemental composition of man-made deposits, they are a

potential source for the extraction of these metals. The main distinguishing features of man-made deposits are

- a fairly large volume of stored waste
- location near industrial enterprises
- a fairly high socio-economic efficiency of their use.

In addition, the comprehensive development of man-made deposits will significantly improve the ecology of the environment in industrial areas, reduce damage to nature, and clear significant areas for new economic activity.

The largest share in the volume of man-made deposits of ferrous metallurgy is occupied by slag dumps (blast furnace, steelmaking and ferroalloy production) and sludge ponds.

Until the middle of the 20th century, metallurgical slags and sludges were considered mainly as production waste and were stored in special dumps. But in the second half of the century, ferrous metallurgy slags began to be considered an independent product of metallurgical production. They began to be used in civil and road construction, for the production of cement and cinder blocks, cast products, slag wool, and as fertilizers.

For all metallurgical slags, hazard class IV is established ^[2] - low-hazard, leading to moderate disruption of the ecosystem

and requiring at least 3 years for its restoration. This means that these metallurgical wastes are harmful to the environment and require the choice of the correct method of their recycling.

The method of recycling slags and sludge from both blast furnace and steelmaking production is determined by their chemical composition. Their main components are oxides SiO₂, CaO, Al₂O₃, MgO, FeO and CaS. In addition to the listed oxides, slags from steelmaking production contain metallic iron in an amount of 10-15% in the form of beads and large scrap, which reinforces the slag, due to which its processing is very difficult. The content of these components is determined by the composition of the raw material, the type of smelted metal and the smelting process. The most important quantitative ratio for characterizing slag properties is CaO/SiO₂ (basicity (B)). According to the basicity value, acidic (B is less than one), neutral (B is equal to one or close to it) and basic (B is more than one) slags are distinguished. The composition of slags of different basicity differs significantly.

The approximate chemical composition of slags and slimes of metallurgical enterprises of Donbass is presented in Tables 1.

Table 1: Chemical composition of slags and sludge

Component Content, %											
Chemical composition of slags											
	Fe	FeO	Fe ₂ O ₃	SiO ₂	CaO	MgO	Al ₂ O ₃	MnO	P ₂ O ₃	S	B
Domain	1–1,5	1–2	–	30–45	35–48	5–6	5–10	2–6	–	<2	0,7–1,6
Marten	8–16	<1	11–22	14–18	36–43	11–18	5–7	5–23	1,5–2	<0,5	2,0–3,1
Converter Furnace	15–20	9–16	3–5	8–17	42–51	6–9	2–4	9–12	4–5	<0,5	2,5–6,4
Electric steelmaking	1–2	<0,2	1–3	17–22	42–55	14–16	4–9	1–4	0,4–1,5	<0,45	1,9–3,2
Chemical composition of sludge											
Agglomeration	50,5	12,5	8,1	9,0	0,9	0,8	0,6	0,03	0,025	3,0	6,9
Domain	45,9	10,1	7,6	10,9	1,0	1,7	1,1	0,08	0,02	10,2	15,3
Steelmaking	50,8	8,3	4,3	7,5	6,1	0,7	1,5	0,01	0,02	1,5	4,9

The chemical composition of blast furnace slag does not allow its recycling in metallurgy, which is due to the practical absence of metallic iron, fluxing ability close to zero and high sulfur content.

At the same time, the high content of SiO₂, CaO, MgO, Al₂O₃ in these slags allows them to be widely used in construction, for the production of granulated slag, crushed stone, pumice, slag wool, cement, clinker, and also as a source material for stone casting. According to numerous estimates by statistical specialists, over 90% of blast furnace slags of current production are currently processed.

Until the early 70s of the last centuries, open-hearth slags were used in small quantities - they were mainly considered as a source of crushed stone. The main reason is the difficulties associated with crushing slag due to the presence of metallic iron in it. Currently, many enterprises operate installations for the separation of metallic iron from slag, the production of enriched slag with subsequent recycling in agglomeration, as well as in the smelting of iron and steel.

Converter slag is also of certain technological interest due to the presence of calcium, magnesium, iron oxides and other elements valuable for metallurgical processing. After appropriate preparation (crushing), it can be used in agglomeration and blast furnace production.

Electric steelmaking slags contain less iron, and the proportion of basic oxides and alloying elements in them is higher.

Sludge from metallurgical production is also a valuable material and can be returned to the metallurgical process by means of agglomeration. The main characteristic feature of sludge is its high dispersion. The average diameter of sludge particles is close to the size of iron ore concentrate particles and is about 0.05 mm. Therefore, it can be introduced into the agglomeration batch instead of expensive traditional process raw materials. The main disadvantage of sludge is its high humidity (up to 30%), which requires their preliminary drying (to a humidity of 8–9%).

The efficiency of using sludge in agglomeration is largely determined by the method of their introduction into the agglomeration batch ^[6]. In the conditions of a metallurgical plant, all sludges are fed into one sludge settling tank, therefore their composition differs significantly from the compositions given in Table 1. The metallurgical value of metallurgical plant sludges is assessed in ^[7], and the features of the agglomeration process and its efficiency when introducing a large amount of sludge into the charge are analyzed in ^[8].

In the converter production, in addition to the main gas cleaning, there are a number of aspiration units that ensure dust collection at all stages of the technological process, up to the production of a continuously cast billet ^[9].

Dusts from converter steel production are characterized by a high content of iron oxides, increased basicity and low silica content, which determines the feasibility of their utilization

in the metallurgical cycle itself. Table 2 shows the chemical composition of dusts in different areas of its collection and a mixture of all dusts, taking into account their actual amount formed per unit of production. In addition to the content of the components specified in Table 2, the dusts contain phosphorus (about 0.2%)

and sulfur (on average 0.33%). The metallurgical value of the dusts listed is due to the presence of metallic iron in their composition, a fairly high content of total iron, and high basicity. The value of metallurgical iron ore raw materials is significantly reduced by the presence of harmful impurities such as zinc and lead.

Table 2: Chemical composition of dust collected from various areas of the converter shop

№	Fe	Fe _{met}	FeO	Fe ₂ O ₃	SiO ₂	CaO	MgO	Al ₂ O ₃	MnO	TiO ₂	Zn	Pb	п.п.п.
1	42,1	0,88	8,23	49,9	2,7	21,8	3,5	0,59	1,52	0,11	0,21	0,03	9,19
2	57,1	2,3	10,8	66,4	1,74	7,92	2,29	0,26	0,14	0,051	0,087	0,01	6,43
3	66,4	28,5	34,8	15,6	6,38	8,32	0,77	1,36	0,78	0,03	0,036	0,006	1,45
4	-	-	-	5,84	3,75	60	9,5	0,7	1,9	0,027	-	-	18,1
5	30,5	2,92	6,1	32,7	7,27	20,5	6,13	2,68	4,1	0,12	0,9	0,055	11,5
6	44,7	29,7	15,9	3,72	3,16	32	6,68	0,6	0,28	0,066	0,007	0,004	7,55
7	50,5	4,47	17,8	46,1	1,35	18,5	3,6	0,23	0,32	0,029	0,036	0,008	6,24
8	-	-	-	5,17	4,34	61,5	9,9	0,81	1,78	0,029	-	-	16,3
9	50,65	10,51	20,28	35,37	3,08	18,73	3,27	0,62	0,64	0,03	0,05	0,01	5,97

According to the data given in Table 2, high zinc content is observed in dust samples from sections 1 and 5, 0.21% and 0.9%, respectively. However, the share of dust from these sections in the mixture is small (3.4% and 0.9%), which ensures that the zinc content in it is only 0.05%. The lead content in the dust mixture is also insignificant (0.01%). Such content of the considered harmful impurities in dust does not exceed their permissible content in the agglomerate.

Despite the intensive search, the question of a rational method of dust recycling remains open.

Usually, small technogenic waste, depending on its chemical composition and physical characteristics, is included in the agglomeration batch instead of sinter ore or concentrate.

Industrial waste is, on the one hand, one of the main sources of environmental pollution, and on the other, a valuable mineral raw material that can be used for the production of building materials in the construction industry [11]. The use of metallurgical waste makes it possible to adjust the technological properties of the concrete mixture, in particular, to change the properties of concrete, as well as to ensure the production of finished products of the required quality by saving fillers and Portland cement.

In modern industrial and civil engineering, hydrothermal fasteners are used, in particular fine-grained, heavy, etc. for various purposes. concrete is widely used. In addition to heavy concrete, fine-grained concrete is used in industrial and private construction, the construction of hydraulic structures, road construction and the production of decorative coatings. Successful scientific research in the field of concrete products has proved that a favorable factor for the composition of fine-grained concrete is the possibility of using ferrous metallurgy waste as a blast furnace slurry. Blast furnace sludge is an artificial waste formed in the form of suspensions of dispersed particles during the production of metals. Its peculiarity is that this secondary raw material has already undergone high-temperature treatment, crystalline structures have formed in the waste and they do not contain organic waste. The use of the solution will solve the problem of processing man-made waste, as well as reduce the cost of manufacturing concrete products.

The purpose of this work was to produce fine-grained concrete using waste from the metallurgical industry.

During the experiment, the fine aggregate in the concrete was partially replaced by blast furnace slurry. The blast furnace sludge was used as recyclable waste. This decision was justified by the fact that the chemical composition of mud is a multicomponent system that enhances chemical reactions with the formation of silicate systems with calcium hydrosilicates of various contents responsible for strength characteristics. The analysis of the X-ray phase of metallurgical sludge is shown in Figure 1.

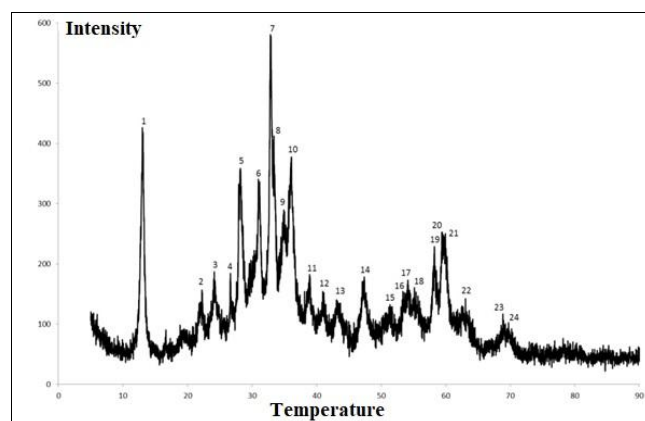


Fig 1: X-ray diffraction scheme of blast furnace silt

From the presented example of X-ray diffraction, it follows that the domna slurry is mainly represented by the following components: iron hydrosilicates ($d = 6.81$ nm peak 1; $d = 1.55$ nm peak 20), calcium hydrosilicates ($d = 2.31$ nm peak), Quartz = 1.6 nm. 5; $d = 2.88$ nm peak 6), carbonate ($d = 2.73$ nm peak 7; $d = 2.68$ nm peak 8; $d = 2.49$ nm peak 10; $d = 1.54$ nm peak 21), carbon ($d = 1.914$ nm).

From the foregoing, it follows that the composition of technogenic waste contains a sufficiently high content of iron-containing compounds (piks 1, 12, 15, 18, 19, 20, 22), it is characterized by carbon (peaks 4, 14, 17, 23), a small amount of calcium phase bottles and amorphous carbonates. The use of silicate systems, characterized by an increase in the iron-containing phase, leads to the formation of an aluminoferrite component. The effect of carbonate-containing additives is that with their participation, during the hydrothermal treatment of fine-grained concrete during the ongoing hydration of cement, as well as during the interaction of calcium hydroxide with sand, calcium

hydrosilicates with carbonate groups (calcium hydrocarbosilicates) are formed, which are close to the composition of the hydrosilicate phases. The formation of these products during the concrete production process helps to increase the strength properties of the resulting material and reduces the likelihood of late formation of similar phases during its service life, which helps to minimize the scale of carbon dioxide corrosion and reduce the shrinkage deformations accompanying this process.

Conclusion

In our opinion, it is advisable to use Portland cement for briquetting converter dust without subsequent firing. Preliminary studies have shown that cement consumption should be 10–15% of the dust mass with a mixture humidity of 8–12%.

With low cement consumption and drying time, it is possible to obtain crumbling briquettes that are suitable for inclusion in the agglomeration batch.

With an increase in drying time, it is possible to obtain a material of the required strength suitable for blast furnaces and oxygen converters. The composition of the mixture for producing briquettes can be absolutely anything, everything depends on the specific requirements for the quality of the material. In this case, large-piece materials can be added to the briquetted mixture as a filler, such as MOS (metallized steelmaking waste) fractions of 10–60 mm^[4], screenings of agglomerate and pellets, and possibly screenings of coke.

The production of briquettes using converter dust is possible on equipment and using technologies for the manufacture of concrete products.

The above shows that recycling of technogenic waste from ferrous metal production is of great national economic importance. Its efficiency depends on the preliminary preparation of the waste.

Converter dust can be used as a substitute for both ore and concentrate in the sintering charge. The most promising method of preparing converter dust for use is its briquetting without firing using Portland cement as a binder.

In the course of further research, it is necessary to

- Study the properties of dust: moisture capacity, variations in chemical and granulometric composition, lumping at different humidity, etc.;
- Establish optimal conditions for obtaining briquettes of a given strength using different binders and different curing times.

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