Study of the separation of mineral phases of Waelz clinker for its disposal

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Abstract. The article presents the results of technological studies on the enrichment of a sample of Waelz clinker from zinc cakes from the Chelyabinsk Zinc Plant by magnetic and flotation methods. The phase and chemical composition of the Waelz clinker of various enterprises is considered, the analysis of the main components of the clinker is carried out. Clinker is a large tonnage solid waste of the zinc sub-industry of non-ferrous metallurgy, has a complex multicomponent composition and is characterized by high contents of iron (36.41%), non-ferrous (Cu 5.28%, Zn 0.93%) and noble (Au 3.8 g / t, Ag 332.2 g / t) metals. Apart from that, there is noticeable content of waste rock, including free carbon (cok breeze), silicone dioxide, calcium oxide, magnesium oxide, alumina. It is shown that, in principle, Waelz-clinker can be separated according to the magnetic flotation scheme without recycle operations to produce four products: a non-magnetic carbon-containing product (βC = 21.7%), copper middlings (βCu = 11.39-11.69%), flotation coal product (βC = 22%) and an iron-containing concentrate in the form of flotation tailings (βFe = 60.23%).

1. Introduction
Utilization of metallurgical waste is a prerequisite for improving the safety of the technosphere and the rational use of natural resources. Already in the coming decades, an increasing shortage of natural raw materials of many base metals will lead to a sharp increase in their value, as a result of which, for example, today relatively inexpensive copper and iron can become valuable metals in the near future [1]. The modern development of the mining and metallurgical industry in Russia and abroad [2] is characterized by a decrease in the content of metals in ores and a simultaneous increase in the volume of solid waste with which a significant amount of non-ferrous metals and iron are lost. This category of waste includes zinc clinker from Waelz process (Waelz clinker) [2-4]. Zinc cake is obtained after leaching of zinc cinder - a product of roasting of zinc concentrates in fluidized bed furnaces at a temperature of 950-1000°C. The Waelz process on zinc cakes is carried out in rotary furnaces. Zinc cake contains about 20% zinc, and, besides that, indium, cadmium, lead, copper. To extract these metals, it is mixed with coke breeze and heated to 1250-1350 ° C in a Waelz kiln [5]. As fluxing additives, limestone and foundry sand are used. The products of Waelz process are Waelz oxide and...
copper clinker, with mass fraction of copper up to 5-7%. Effective processing of such waste in economically acceptable ways is within the framework of the concept of sustainable development.

2. The relevance and scientific significance of the issue

An analysis of the publications showed that at the present time, the Waelz clinker is used mainly in the construction field: in the production of bricks, cement, concrete [6–13]. In [6–8], it is said that an increasingly widespread world practice is the use of Waelz clinker in road construction both for coatings and for structural layers. However, in the presence of a high content of heavy metals in it, it is a hazardous waste and cannot be used in road construction, and when using clinker as the base of the pavement, the limiting characteristic is the total sulfur content for which the maximum concentration is established [14].

There are few works devoted to clinker recycling in metallurgy. This is due to the difficulty of processing it to obtain a low content of impurities in the products.

The clinker, according to the conditions of its formation, is the product of two stages of high-temperature roasting of zinc raw materials and leaching with electrolyte. This determines its complex multicomponent composition and presence of most of the valuable metals in the form of solid solutions, which are hard to separate. Clinker is, on the one hand, a large-tonnage solid waste of the zinc sub-industry of non-ferrous metallurgy, and, on the other hand, technogenic mineral raw material with high concentrations of iron, non-ferrous and noble metals [15]. For example, in the Waelz clinker of the Chelyabinsk Zinc Plant and the Vladikavkaz Electrozinc Plant, there are high mass fractions of copper (2.47-3.61%), zinc (0.7-2.19%), iron (24.1-28.1%), carbon (coke breeze) (12.8-28.8%), gold (3.5-7.0 g / t), silver (127-363 g / t). Despite this, nowadays clinker is only used as a raw material for carbon extraction and obtaining an iron-containing product.

An analysis of research work [3] shows that the development of alternative clinker processing technologies is carried out in the following areas:

- enrichment separation according to magneto-gravitational [16] and magneto-flotation schemes;
- hydrometallurgical extraction of valuable components from clinker without pretreatment, after oxidative roasting or preliminary mechanical disintegration activation, as well as from products of magnetic separation of clinker by direct and sorption cyanidation or sulfuric chloride solutions [17-19];
- combined hydrometallurgical-flotation schemes [20].

Research is underway on the use of microwave treatment to improve Waelz clinker separation [21].

The developed schemes make it possible to obtain the following products in different combinations: copper-containing, carbon-containing, iron-containing and gold-containing. Usually, only the initial clinker is subjected to magnetic separation. However, there is an example when in a magnetic flotation scheme after the second magnetic separation the magnetic product is crushed and, together with the copper flotation tailings, is sent to the third magnetic separation. The flotation separation of copper clinker is carried out in two ways: with the release of coke breeze (coal flotation operation) in the first flotation or with the release of coke breeze after preliminary flotation of copper.

Due to the insufficiently complete separation of the technogenic phases of the clinker, products obtained by enrichment schemes are characterized by a high content of impurities. For example, the copper content in the carbon-containing concentrate is from 1.64 to 3.25%, and in the iron-containing concentrate is from 2.3 to 4.73%. Extraction of copper in a copper concentrate does not exceed 67% and it is not possible to obtain a concentrate, that would comply with the standard [3].

Clinker processing by hydrometallurgical methods is not effective enough due to the high sorption activity of carbon contained in the clinker, its enrichment and pre-treatment products. For complex processing of zinc clinker, an autoclave or pyro-hydrometallurgical technology is recommended, which ensures the complete and selective separation of the main valuable components into independent products, oxidative catalytic opening [4]. But, in our opinion, such a scheme will be characterized by high capital and operating costs and can hardly be implemented in the near future.
A significant amount of clinker is formed at the metallurgical enterprises that are part of UMMC-Holding, therefore, in the context of a shortage of ore raw materials and the need to reduce the amount of stockpiled waste, it is of interest to develop a technology for processing clinker to produce copper concentrate or industrial product and maximize the use of available technical and technological capabilities of the concentration plant.

3. Research Methods
Technological studies were carried out on a clinker sample of the Chelyabinsk Zinc Plant with the separation of technogenic phases by magnetic separation and flotation methods. Standard laboratory equipment used for enrichment studies was used.

4. Results and discussion
The results of the chemical composition of the sample (Table 1) indicate a high content of iron and non-ferrous and noble metals in the clinker.

| Element, phase | Content (% g/t) | Element, phase | Content (% g/t) |
|----------------|------------------|----------------|------------------|
| Cu (with roasting) | 5.28 | Au* | 3.8 |
| Zn (with separation of Pb) | 0.93 | Ag* | 332.2 |
| S | 5.92 | CaO | 8.85 |
| Fe total | 36.41 | MgO | 18.28 |
| Fe₂O₃ | 13.03 | Pb | 0.05 |
| SiO₂ | 10.03 | Sb | 0.18 |
| C | 14.5 | Al₂O₃ | 1.22 |

* According to the results of assay

According to the results of phase analysis, 69.79% rel. of copper is represented by secondary compounds, 29.04% rel. by primary, 1.07% rel. by oxidized and only 0.09% rel. by sulfidic. The bulk of zinc in clinker, in contrast, is in the primary compounds - 91.80% rel., while 7.68% rel. is in oxidized compounds, and 0.53% rel. is in sulfidic.

Macroscopically, the clinker sample is a material with a grain size of -30 + 0 mm, dark brown, consisting of porous pieces and pieces of alloy. Mineralogically, the clinker sample is represented by metallic iron, magnetite, ferrates, iron oxides (goethites, hydrogetites, hematites), silicates, including copper minerals. Copper minerals are represented by chalcopyrite, bornite, metallic copper and rarely chalcocite. They are present in clinker in the form of xenomorphic, sometimes rounded precipitates of chalcopyrite-bornite solutions in silicates or ferrites; emulsion (less than 1 μm), poikilite (2-5 μm), rounded and xenomorphic inclusions (5-60 μm) of chalcopyrite and chalcopyrite-bornite solutions in metallic iron; complex magnetite-bornite solutions; complex chalcopyrite-bornite-magnetite-metal iron-silicate associations; thin (less than 1 micron) veins in magnetite, small (2-7 microns) grains of metallic copper in silicates and ferrites, rare grains of chalcocite up to 10 microns.

That is, the clinker is represented by hard-to-open, resistant to processing mineral components with complex thin sprouting into each other.

A study of the distribution of valuable clinker components (copper, zinc, iron, carbon, gold, silver) in different size classes showed that about 50% of copper and precious metals are concentrated in large-grained classes with grain size from -30 mm to +3 mm, which will require a long time of grinding to open them. Carbon predominates to a greater extent (up to 64.45%) in small-grained classes -1 + 0 mm and will be crushed with long-term grinding. 64.32% of iron is concentrated in small-grained classes -1 + 0 mm, its content in all classes of particle size is quite high and ranges from 37.96 to 43.11%.
In the process of technological research, it was found that clinker is an intractable material due to the presence of metallic iron in it, which is malleable and practically does not crush, together with highly sludging non-metallic part. Clinker enrichment was carried out according to a scheme that included magnetic separation of the initial clinker and flotation of the magnetic product to produce only copper concentrate or coal and copper concentrates.

Magnetic enrichment of clinker shredded to 100% of particles less than 3 mm (Table 2) showed that in this case, only sufficiently selective separation of coke breeze into the non-magnetic fraction (carbon extraction of 70.65%) and iron into the magnetic fraction (recovery of 84.53%) is possible. Despite the fact that the extraction of non-ferrous and noble metals into the magnetic fraction is high, the mass fraction of metals in the magnetic fraction compared to the initial clinker increases insignificantly.

| Product name     | Yield (%) | Mass fraction (%) | Extraction (%) |
|------------------|-----------|-------------------|----------------|
|                  |           | Cu | Fe | C | Au | Ag | Cu | Fe | C | Au | Ag |
| Magnetic fraction| 64.30     | 6.52 | 36.58 | 2.75 | 3.10 | 303.6 | 78.70 | 84.53 | 29.35 | 87.47 | 77.60 |
| Non-magnetic fraction | 35.70 | 3.18 | 12.06 | 27.70 | 0.80 | 157.80 | 21.30 | 15.47 | 70.65 | 12.53 | 22.40 |
| Clinker          | 100.0     | 5.33 | 27.83 | 14.0 | 2.28 | 251.55 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

Magnetic flotation enrichment of clinker was carried out according to the scheme: crushing up to 100% into size class minus 3 mm, magnetic enrichment, grinding magnetic fraction up to 86% into size class minus 0.071 mm, copper “head” with purification of concentrate, copper flotation with fractional removal of foam product. Flotation was carried out in an open cycle at pH = 11.5, alkalinity 280 g / cm3 St. CaO, with a total consumption of potassium butyl xanthate 300 g / t, T-92 - 234 g / t. As a result of magnetic flotation enrichment (Table 3), quite satisfactory results were obtained on the transition of copper compounds to coarse copper concentrate, and coke breeze - to a non-magnetic fraction.

| Product name                  | Yield (%) | Mass fraction (%) | Extraction (%) |
|-------------------------------|-----------|-------------------|----------------|
|                               |           | Cu | Fe | C | Cu | Fe | C | Cu | Fe | C |
| Concentrate Cu «heads»        | 0.54      | 13.91 | 30.52 | 12.00 | 1.40 | 0.48 | 0.57 |
| Tailings of Cu head cleaner   | 5.43      | 13.61 | 34.92 | 10.20 | 13.73 | 5.45 | 4.88 |
| Cu concentrate fr. 1          | 11.74     | 12.91 | 38.51 | 7.20 | 28.19 | 13.00 | 7.45 |
| fr. 2                         | 7.00      | 9.32 | 38.09 | 5.90 | 12.13 | 7.67 | 3.64 |
| fr. 3                         | 2.98      | 5.72 | 36.39 | 6.40 | 3.17 | 3.12 | 1.68 |
| Coarse Cu Concentrate         | 27.69     | 11.39 | 29.70 | 7.47 | 58.62 | 29.70 | 18.23 |
| Flotation tailings            | 32.31     | 2.18 | 59.68 | 1.83 | 13.12 | 55.43 | 5.24 |
| Magnetic fraction             | 60.00     | 6.42 | 49.24 | 4.44 | 71.74 | 85.15 | 23.46 |
| Non-magnetic fraction         | 40.00     | 3.80 | 12.91 | 21.70 | 28.26 | 14.85 | 76.54 |
| Clinker                       | 100.0     | 5.38 | 34.79 | 11.34 | 100.0 | 100.0 | 100.0 |

Since the coke breeze contained in clinker has good floatability, and the reagent modes of its flotation are simple, coal flotation was carried out before sulfide flotation of the magnetic product. The results of an open experiment of magnetic flotation enrichment of clinker with coal flotation are
shown in table 4. In coal flotation, the consumption of kerosene amounted to 560 g / t, foaming agent T-92 - 234 g / t. Copper flotation conditions are similar to previous experience.

Table 4. The results of magnetic flotation concentration with coal flotation.

| Product name                      | Yield (%) | Mass fraction (%) | Extraction (%) |
|-----------------------------------|-----------|-------------------|----------------|
|                                   |           | Cu    | Fe    | C    | Cu    | Fe    | C    |
| Coal concentrate                  | 2.41      | 5.32  | 17.99 | 22.00| 2.37  | 1.25  | 4.77 |
| Concentrate Cu «heads»            | 2.54      | 15.10 | 37.87 | 8.20 | 7.09  | 2.76  | 1.87 |
| Tailings of Cu head cleaner       | 9.50      | 12.91 | 37.24 | 7.00 | 22.67 | 10.16 | 5.97 |
| Cu concentrate fr. 1              | 9.14      | 11.91 | 37.88 | 6.20 | 20.10 | 9.94  | 5.09 |
| Cu concentrate fr. 2              | 3.44      | 8.52  | 37.03 | 4.60 | 5.42  | 3.66  | 1.42 |
| Cu concentrate fr. 3              | 2.11      | 6.32  | 35.97 | 3.30 | 2.47  | 2.18  | 0.63 |
| Coarse Cu Concentrate             | 26.74     | 11.69 | 37.39 | 6.24 | 57.75 | 28.71 | 14.98|
| Collective concentrate            | 29.15     | 11.16 | 35.78 | 7.54 | 60.13 | 29.96 | 19.75|
| Flotation tailings                | 30.85     | 2.04  | 60.23 | 0.83 | 11.79 | 55.22 | 2.32 |
| Magnetic fraction                 | 60.00     | 6.49  | 49.43 | 4.10 | 71.92 | 85.17 | 22.07|
| Non-magnetic fraction             | 40.0      | 3.80  | 12.91 | 21.70| 28.08 | 14.83 | 77.93|
| Clinker                           | 100.0     | 5.41  | 34.82 | 11.14| 100.0 | 100.0 | 100.0|

The introduction of coal flotation operations into the enrichment scheme to produce additional coal concentrate increases the mass fraction of copper in sulfide concentrate to 11.69%, but reduces its recovery due to the transfer of 2.37% copper to the coal product.

From an analysis of the results of magnetic and magnetic flotation enrichment of clinker, it follows that up to 72% of the copper in the sample is associated with 85% of the iron in the magnetic fraction. Of these, up to 13% of copper remains in the tailings along with metallic iron, which cannot be grinded. Coarse copper concentrates with a mass fraction of copper of 11.39-11.69% were obtained with a low recovery of 58.62% and 57.75% without coal flotation and with coal flotation, respectively.

5. Conclusion

Thus, it has been shown that it is possible in principle to separate the Chelyabinsk Waelz clinker according to a magnetic flotation scheme without recycle operations to produce four products: a non-magnetic carbon-containing product, a copper middlings, a coal product and an iron-containing concentrate in the form of flotation tailings with an iron mass fraction of over 60%. The resulting products can be processed with the extraction of metals from them, which will ensure the recycling of valuable components.

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