



ON THE MECHANOACTIVATION OF METALLURGICAL WASTE

Prof. Anvar Ishanovich Adilkhojaev 1PhD,
Ilhom Abdullaevich Kadirov 1

Assistant, Bekzod Sherzodovich Kudratov1
Tashkent State Transport University, Tashkent, Uzbekistan

Article history:	Abstract:
Received: April 12 th 2021 Accepted: April 23 rd 2021 Published: May 20 th 2021	The grindability of metallurgical slag in a ball mill under shock-imperious grinding mode has been estimated. Specific surface area, average particle diameter, aggregation phenomena and particle size distribution have been determined. In addition, polynomial mathematical models have been obtained that describe the entire grinding process with high reliability.
Keywords: Metallurgical slags, mechanical activation, ball mill, aggregation, Kozeny-Karman method, specific surface area, average particle diameter.	

INTRODUCTION.

The problem of resource saving is especially relevant in construction, as this industry consumes about one third of the total mass of material production. Material costs of construction from all types of costs can reach up to 85% [1-3].

The solution to the problem of resource and energy conservation in construction is possible through the widespread use of secondary material resources [1-3].

The use of secondary raw materials in the production of building materials allows us to solve several important problems simultaneously: to ensure the saving of natural raw materials and fuel and energy resources, to increase production efficiency, to improve the ecological balance of each region of the country, to reduce the allocation of economically usable land for quarries and dumps for storing waste from local production [4-6].

The most common wastes used in the manufacture of building materials include electro-thermophosphorus and blast furnace slags, whitewash and other sludge, ashes and slags from thermal power plants, production wastes from chemical industry, ferrous and non-ferrous metallurgy, pulp and paper production and many others. The use of wastes allows reducing the power demand by 20-40% [7-8].

It has been proved that mineral additives react chemically with cement constituents to form new strong compounds that compact and strengthen cement structures by reducing capillary pores and binding calcium hydroxide $\text{Ca}(\text{OH})_2$. It should be noted that all processes aimed structure formation occurs at the optimum dispersity of mineral additives. It is also important that the majority of manmade wastes have different activity (or no pozzolanic activity). An important technological technique to achieve the required surface activity and dispersibility of mineral powders is the grinding process (mechanical activation) [9].

The metallurgical plants in Uzbekistan have accumulated large quantities of waste requiring disposal and are valuable modifiers for improving the physical and mechanical properties of the cement stone.

Considering the above mentioned in this article the results of research on mechanical activation of metallurgical slags of JSC "Uzbekistan Temir Yullari" with the purpose of their further use for the development of effective concrete are presented.

RESEARCH METHODS AND CHARACTERISTICS OF RAW MATERIALS.

The process of grinding of metallurgical wastes was carried out in a laboratory ball mill SHLM- 100 in the shock-grinding mode. The mass and number of balls of the mill is shown in Fig. 1. In the study wastes of metallurgical production were dried to a constant mass at $\pm 105^\circ\text{C}$. The dried raw material was loaded into the drums in the amount required for grinding. The grinding process was carried out until the particles aggregate.

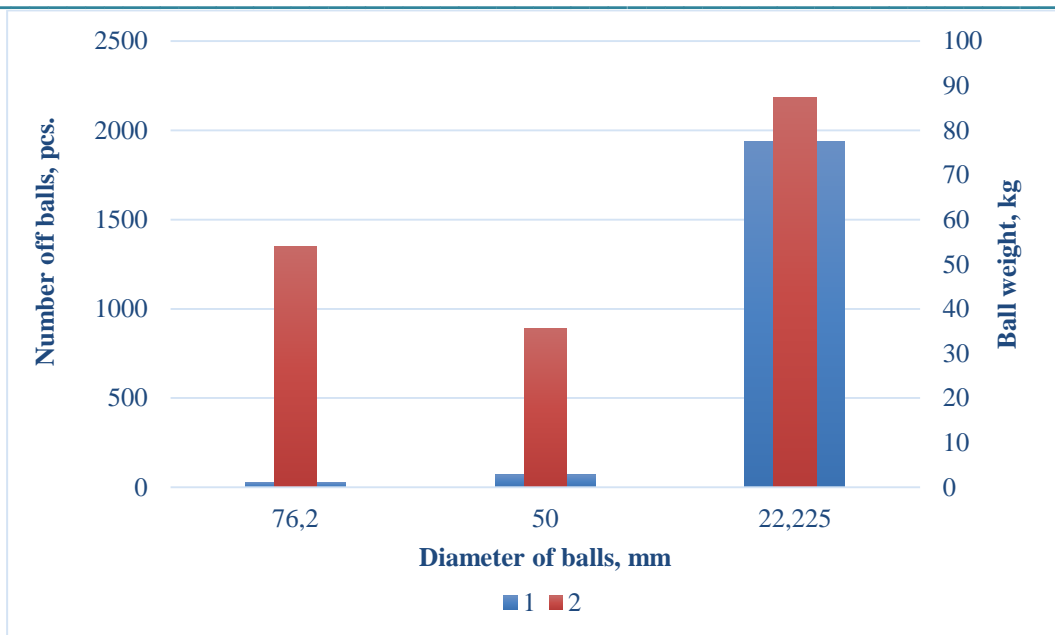


Fig. 1. Number and diameter of balls when loading into a ball mill:
1-number of balls; 2-mass of balls.

Grinding fineness was assessed by specific surface area on a PSX-11A surface gauge. The aggregation phenomenon was determined on sieve #008. The particle size distribution of the milled material was defined on the SS-300 laboratory sieve with the following sieve sizes, mm: 0,5; 0,425; 0,355; 0,3;0,25; 0,212; 0,18; 0,15; 0,125; 0,106; 0,09; 0,075; 0,063; 0,035. The chemical composition of the waste is given in Table 1.

Table 1: Chemical composition of metallurgical waste

Compounds, %	SiO2	Al2O3	MnO	FeO2	MgO	SaO	TiO2	ZnO
Steelmaking slag	48,21	19,27	17,62	7,63	5,99	0,27	0,651	0,133
Foundry and moulding waste	91,56	4,58	0,232	1,12	0,1	0,2	0,061	0,022

RESULTS AND DISCUSSION.

The main wastes of the Foundry Mechanical Plant of JSC "Uzbekistan Temir Yullari" are steelmaking and foundry and moulding slags. The American standard for materials testing (ASTM C125) refers to steelmaking and foundry and moulding slag as non-metallurgical waste which mainly consists of silicates and aluminates [9].

Cement concretes with steelmaking and foundry slag aggregates have a number of advantages over conventional concretes. Research [9] found that the steel-smelting and foundry-forming slag in the Portland cement serve as the active centre, i.e., its surface layer reacts with calcium hydroxide, released during hydrolysis of alite to form an additional amount of calcium hydrosilicates, which create an extremely strong bond of aggregate with the cement matrix and subsequently contribute to reducing the structural defects that are formed due to shrinkage or compaction of the cement matrix. In addition, the use of the aforementioned additives significantly increases corrosion resistance compared to concretes of traditional compositions. This is the reason why metallurgical wastes are widely used in the USA, Japan and other industrialized countries [9].

The main challenge in the production of complex binders from metallurgicalwaste is to increase their surface activity.

Increasing the surface activity of waste enables the full potential of waste to be unlocked, while at the same time solving several important problems: increasing the physical-mechanical and performance characteristics and reducing the binder consumption in the products.

A number of indicators have been proposed which are based on the ratio of the oxides contained in the waste and which allow an indirect assessment of the hydraulic activity of the waste. These evaluation criteria include, first of all, the basicity modulus (M_o) and activity modulus (M_a).

The basicity modulus of slag is the ratio of the sum of Ca and Mg oxides to the sum of Si and Al oxides (w/w %) [9]:

On this basis, depending on the nominal value, the waste modulus can be basic when the basicity modulus is greater than 1, or acidic when the basicity modulus is less than 1.

Another criterion for assessing the activity of waste is the activity modulus

$$M_o = \frac{CaO + MgO}{SiO_2 + Al_2O_3}$$

[9]:

$$M_a = \frac{Al_2O_3}{SiO_2}$$

The activity of waste in most cases increases with increasing basicity and activity modulus [9].

According to the modulus of basicity the values of steel-smelting and foundry and moulding wastes are less than unity 0,09 and 0,003 respectively and belong to acidic ones. The activity modulus for steelmaking wastes is 0,39 and for the foundry and moulding wastes is 0,05. The received data testifies that these kinds of wastes do not possess hydraulic activity and for entering into chemical reaction with the binder it is required to provide the increase of their surface activity.

An analysis of earlier work [1-5] shows that a significant increase in the surface activity of slags can be achieved by mechanical activation.

Many scientists in the field of fracture mechanics and solid-state chemistry have noted that the activation of substances during comminution is due to dislocations in the solid and the amorphisation of the crystal lattice, which in turn accumulate and move in certain quantities and contribute to the destruction of the material.

Changes in the structure, composition and properties of minerals during mechanical activation are most often caused by the following phenomena (fig. 2).

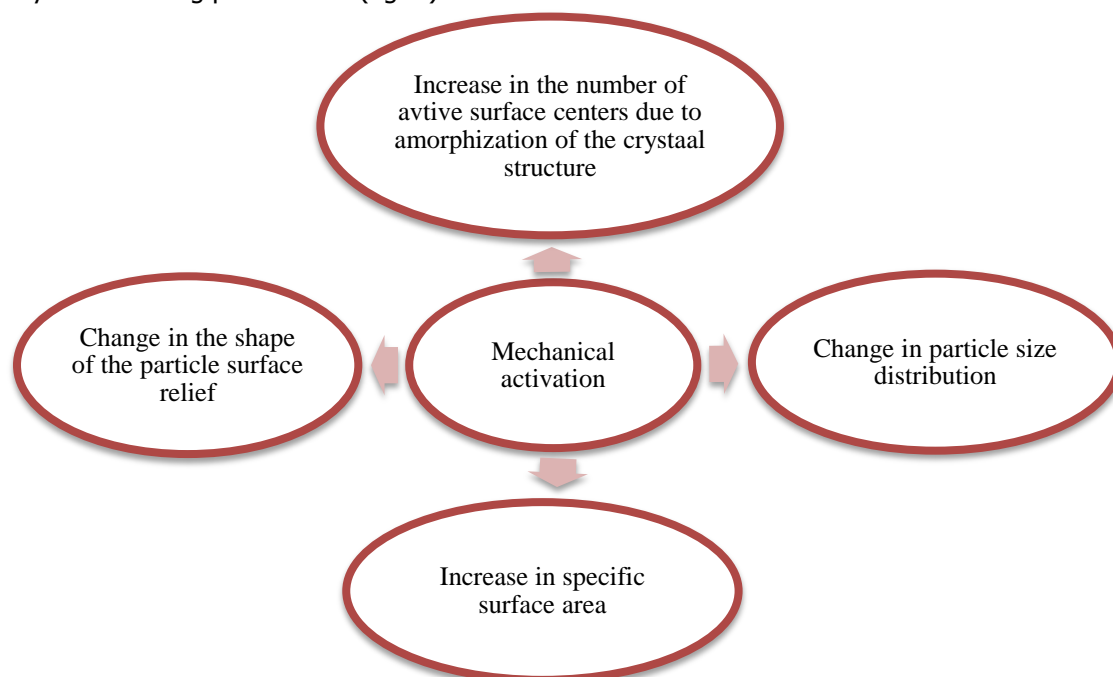


Figure 2. Main parameters characterising the reactivity of materials during mechanical activation

The grinding process increases the specific surface area of the material, changes the shape and topography of the particles and amorphises the crystallattice with the formation of active centres.

Studies [1-7] have established that with increasing dispersibility of mineral materials the number of Brensted active adsorption centres on the surface of the formed powders, responsible for their reactivity, increases. However, this tendency is observed up to a certain value of specific surface (S_{ud}), after which the process slows down

considerably. Therefore, when using freshly milled filler it is important to determine a rational value of S_{ud} , above which the surface activity of the particles increases only slightly and further milling is, therefore, not expedient. The results of the milling studies for metallurgical waste are shown in Figs.3-5.

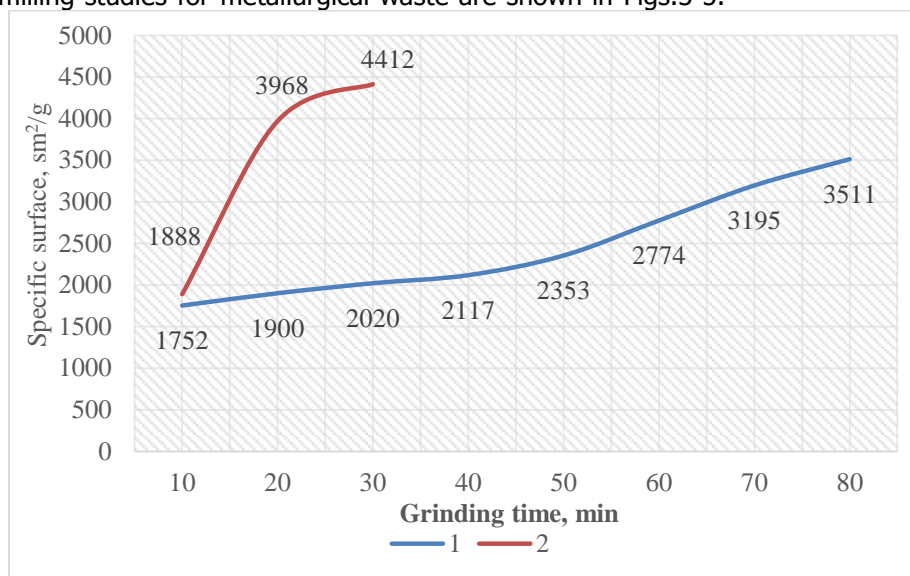


Fig. 3. Effect of grinding time on specific surface area of (1) steelmaking slag and (2) casting and moulding wastes
 The results of changes in specific surface area show that, after 80 minutes of milling steelmaking slag, the specific surface area reaches 3511 cm²/g. With foundry and moulding wastes it is possible to reach $S_d=4412$ cm²/g within 30 minutes.

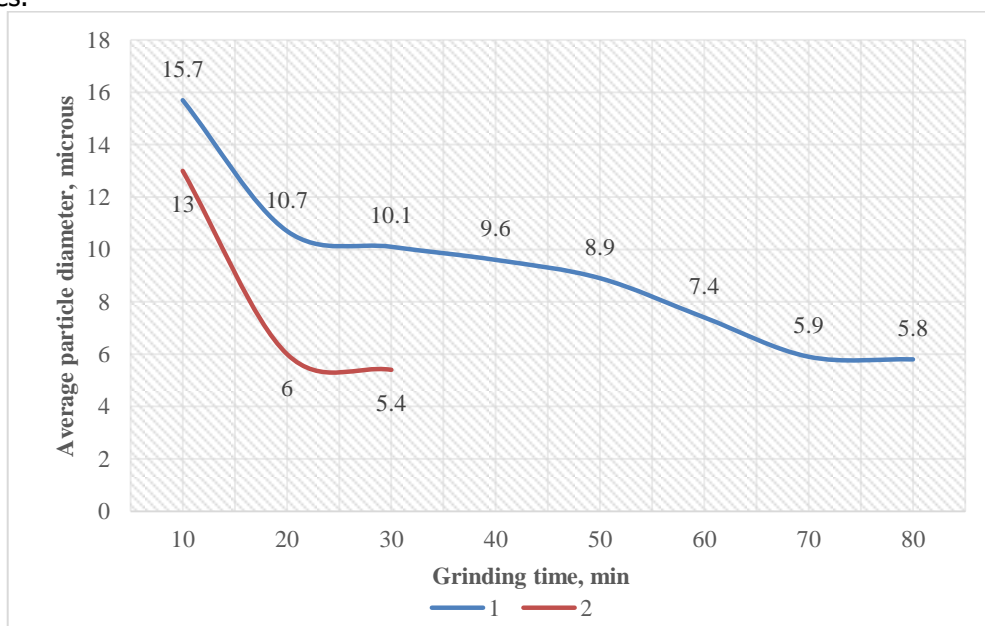


Fig. 4. Effect of grinding time on average particle diameter of (1) steelmaking slag and (2) casting and moulding wastes

At the same time the average particle diameter of steelmaking slag (SS) decreases from 15.7 μm to 5.8 μm . In turn, the average particle diameter of foundry moulding waste (SFW) decreases to 5.4 μm .

As the size of each particle decreases, the total surface of the milled material increases rapidly, while the volume of the particle remains constant when the pieces are added together. The surface increasing rapidly with grinding, has a reserve of surface energy, which is further consumed in the formation of products from the mixture with the flow of reactions on the interfaces. Once a certain dispersibility limit is reached, the potential surface energy may increase, often leading to spontaneous aggregation of particles with a reduction of the specific surface area and an increase in the heterogeneity of the initial product.

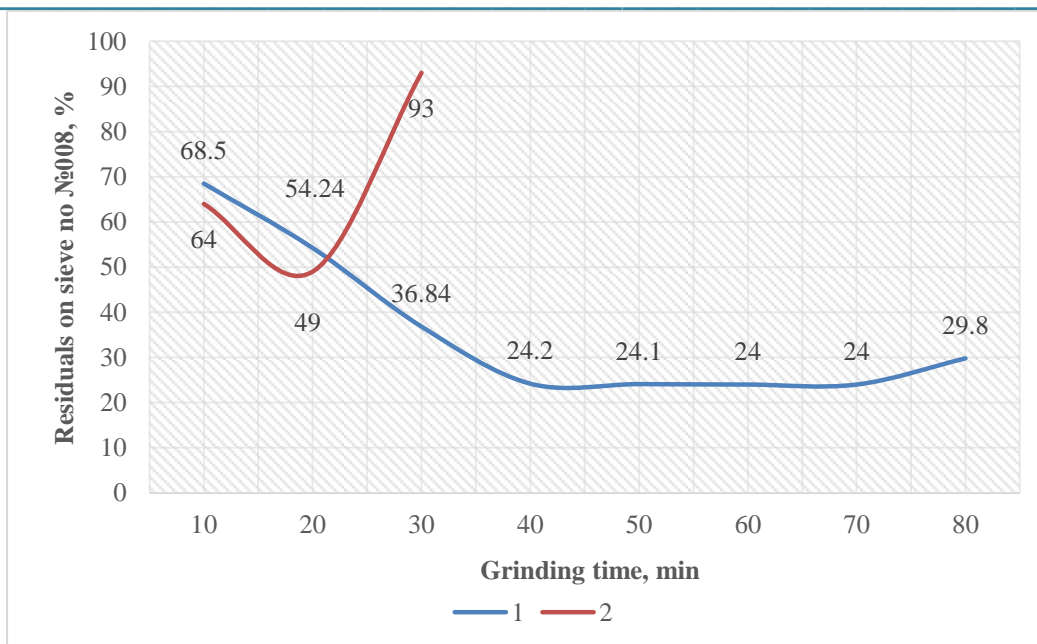


Fig. 5. Effect of grinding time on particle aggregation of (1) steelmaking slag and (2) casting and moulding wastes
 With a grinding time of 70 minutes, aggregation and sticking of the particles can be observed, as shown in Fig. 5. 5. After 40 minutes of grinding the residue on sieve #008 decreases from 68.5 % to 24.2 %. This value is then retained, and the line changes to a horizontal plane and the value of the residue on the sieve remains for a while. After 70 minutes of grinding the Residual amount began to increase and the phenomenon of aggregation of the particles set in. The amount of residue on sieve #008 LFO is reduced from 64 % to 49 %. After grinding for up to 30 min the sieve residue increases sharply to 93%. Further continuation of milling is not practical due to sticking of particles which may subsequently affect the physical and mechanical properties of the cement stone.

In addition to the grinding fineness (specific surface area), the granulometric composition has a significant influence on the technical characteristics of the mineral filler. Data on the particle size distribution of crushed metallurgical slag are shown in Fig. 6,7.

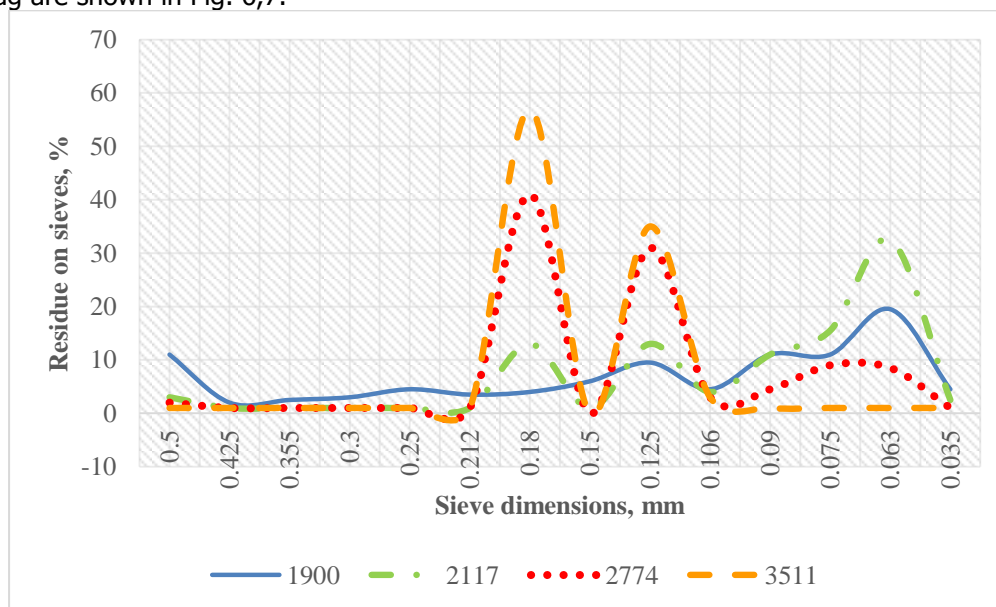


Figure 6. Granulometric composition of mechanically activated slurry

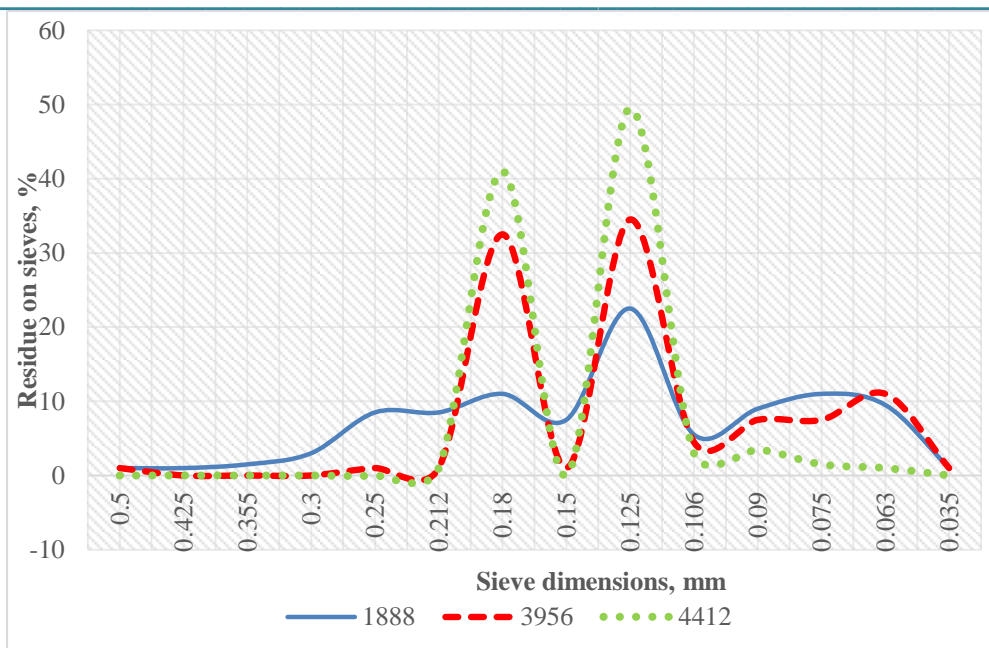


Figure 7. Granulometric composition of mechanically activated LFO

It can be seen that the powder with Sud=1900 cm²/g has a high particle size distribution from 0.5 mm to 0.25 mm. Further milling reduces the coarse particles and increases the proportion of fines, which is confirmed by the particle size distribution with Sud=2117 cm²/g. Fig. 6 shows that increase of Sud=2774 cm²/g to Sud=3511 cm²/g reduces the total fraction of particles with sizes from 0,09 mm to 0,035 mm on average by 10 %. The content of particles between 0.106mm and 0.212mm increases by 31% and 62% respectively.

Analysis of the particle size distribution of LFO showed that the finefraction content for the powder with Sud=1888 cm²/g in the area from 0.09 mm to 0.035 mm was 28 %. Despite the time of grinding the residue on the sieves below ≤0.09 mm for powders with Sud=3968 cm²/g and Sud=4412 cm²/g decreased and the proportion of coarse particles increased. In our opinion this is due to an initial increase in the surface energy of the particles which eventually leads to spontaneous sticking.

The results (Figs. 8-10) of the approximation of the mechanical activation curve for mineral filler versus grinding time are shown below.

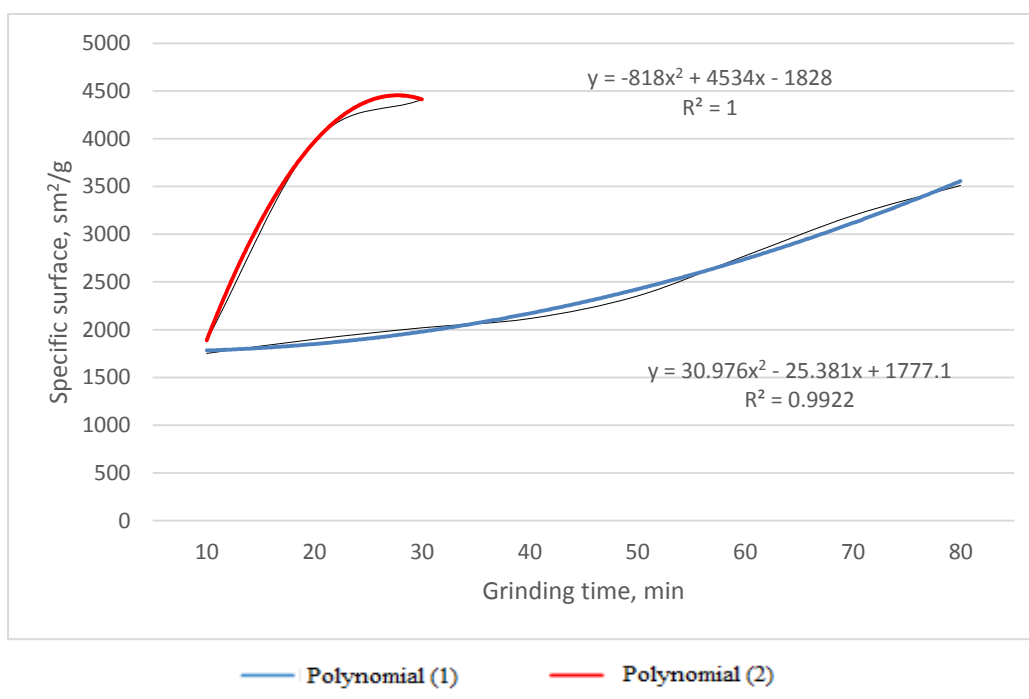


Figure 8. Dependence of change in specific surface area on mechanical activation time (1) SS (2) LFO

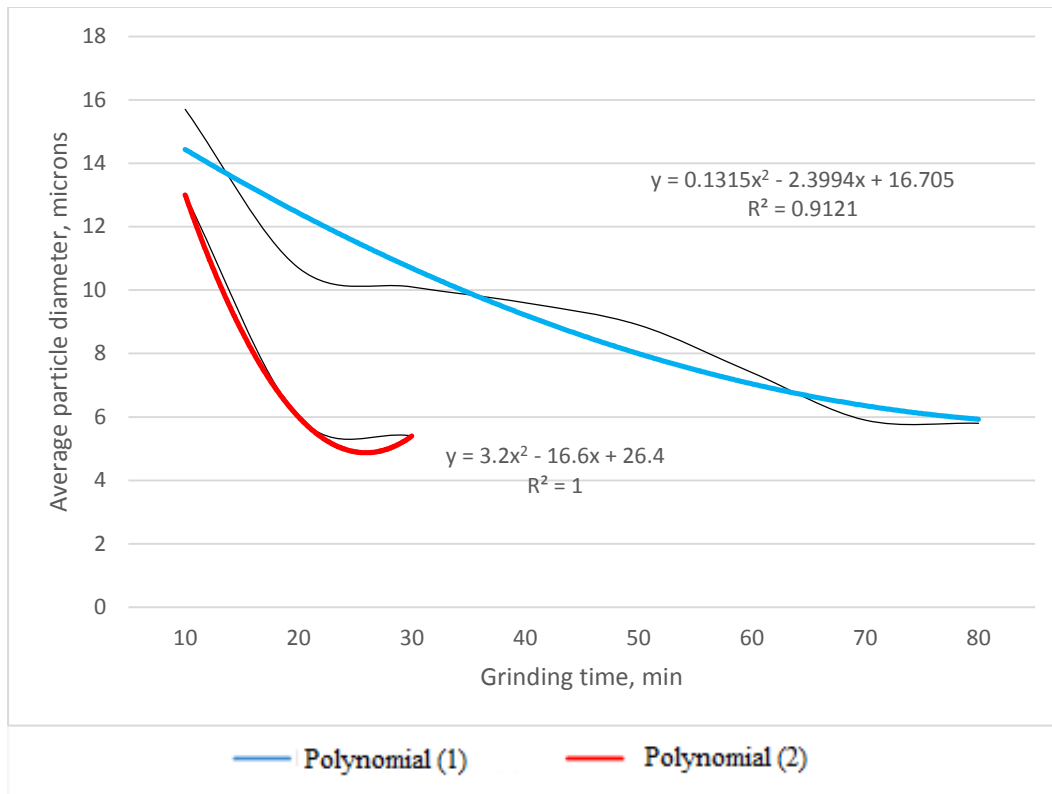


Figure 9. Dependence of change in mean particle diameter on mechanical activation time (1) SS (2) LFO

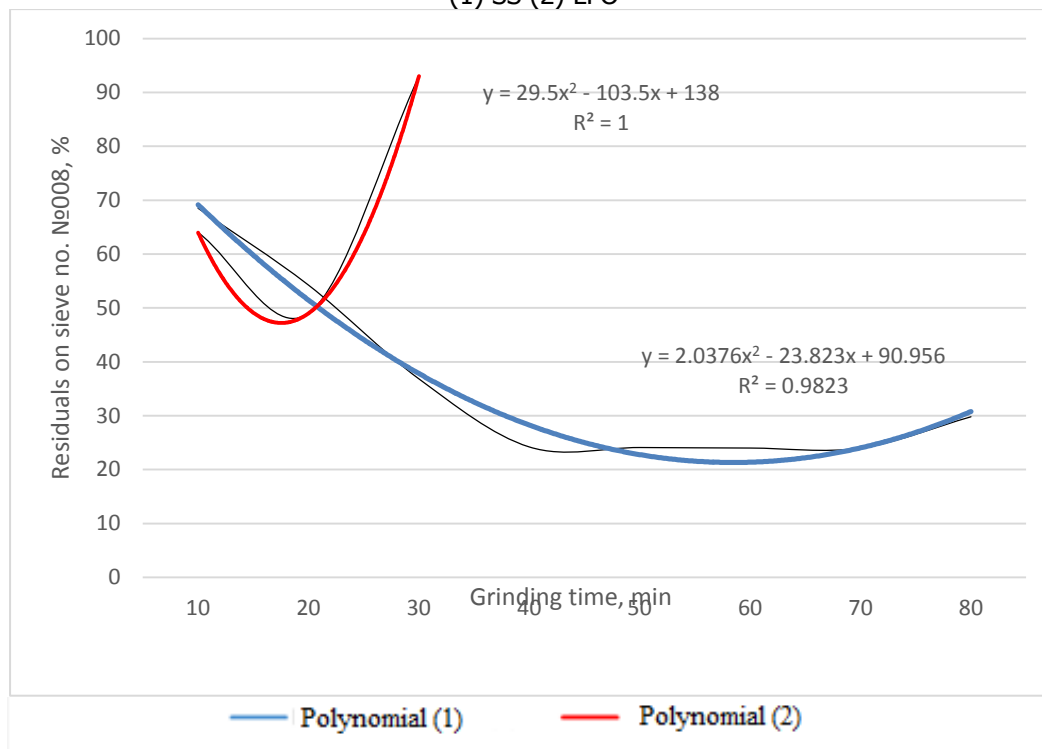


Fig. 10. Dependence of the variation of the residue on sieve 008 on the mechanical activation time (1) SS (2) LFO

The coefficient of determination R^2 of the models obtained is in the region of 0.91-1, which provides high reliability of the polynomial equations obtained.

CONCLUSIONS.

One of the most effective raw materials for use in construction is metallurgical slags. The reactivity of the components of the raw mixture for the production of concrete and mortars is considerably increased by mechanical processing. Mechanical activation of initial or intermediate products changes qualitative characteristics of the final product which allows for obtaining a product of higher quality or new useful properties.

A comparison of the grinding fineness values of the SS and LFO mills showed that the impact grinding mode of the ball mill can grind the SS to a specific surface of 3511 cm²/g and an average particle diameter of 5.8 μm in 80 minutes.

LFO milling in 30 min produces a dispersion of 4412 cm²/g, with an average particle diameter of 5.4 μm.

It was found that after reaching SS specific surface $S_{ud}=3195$ cm²/g, further dispersion increases the amount of residue on sieve #008. The same figure for LFO is $S_{ud}=3968$ cm²/g. Thus, it can be stated that further dispersion process leads to aggregation of material particles.

In addition, polynomial models are derived which adequately describe the whole process of mechanoactivation of metallurgical waste.

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