Prospects for the use of waste cement industry in the production of clinker-free concrete

M Sh Salamanova¹,²*, S-A Yu Murtazayev¹,², A Kh Alaskhanov¹, and M S Saydumov¹,³

¹GSTOU – Grozny State Oil Technical University named after acad. M.D. Millionshchikov, 100, KH. Isaev avenue, Grozny, 364051, Russia
²CI RAS – Kh. Ibragimov Complex Institute of the Russian Academy of Sciences, 21, Staropromyslovskoe highway, Grozny, 364051, Russia
³Academy of Sciences of the Chechen Republic, 13, M. Esambaeva avenue, Grozny, 364051, Russia

E-mail: madina_salamanova@mail.ru

Abstract. The production of Portland cement clinker is accompanied by huge dust release and the accumulation of huge amounts of aspiration and clinker dust in the dust collection system. The rational use of this high-quality corrected fine-dispersed resource is an urgent task not only in technological, but also in ecological terms. Aspiration dust cannot be returned to the technological cycle. It is taken out of the cement plant, disrupting the ecological situation of valuable agricultural land and mountainous landscape. Taking into account the fact that it can be used in its natural form, without an additional mechanical intervention, this will expand the material and raw material base for the production of alkaline cements. This paper presents the results of studies of the particle size distribution of particles in samples of dispersed material and the determination of the shape and size of cement dust particles. The reactivity of the investigated powders of technogenic nature has been proved. These characteristics of cement dust electrostatic indicate feasibility of these powders dispersed as component binders ligaments alkaline activation.

1. Introduction

The world community has long been faced with the problems of ecological safety of the earth's civilization. Considering these issues, everything rests on the huge industry of building materials, the development of which is associated with large-scale consumption of energy and mineral natural raw materials, pollution of urban systems and problems of rehabilitation of anthropogenically disturbed territories [1-9].

The cement industry is considered one of the most energy- and material-intensive in construction. Monitoring of the state of the construction market showed that from year to year it is the Portland cement that occupies a leading position in production and sales. Certainly, the expediency of increasing production volumes is undeniable, but it is also necessary to take into account the negative consequences of carbonate technology associated with huge emissions of highly dispersed clinker dust and carbon dioxide into the environment and atmosphere.

Therefore, a reasonable technological approach to the presented problem will undoubtedly be the search for new binding systems that do not require high-temperature treatment, which include
alkaline-mixed cements. Those cements of alkaline mixing can be produced both on the basis of wastes of ferrous metallurgy and energy complex, if they are available in the corresponding region, and with the use of aluminosilicate additives of natural and technogenic origin. Clinkerless technology will save expensive and energy-intensive Portland cement, at least in those areas of construction where there is no need for the manifestation of its highly functional properties [3, 6, 8].

In the process of firing clinker raw materials in the dedusting systems of rotary kilns, a large amount of fine dust is captured. This dust is not returned to the technological cycle again, in order to avoid deviations from the set parameters of the mixture. It is extracted from the electrostatic precipitators and stored in the nearby territories with the plant, occupying land suitable for agricultural needs. Therefore, the rational use of these technogenic products containing a significant proportion of a valuable raw material resource is an urgent task for the cement industry.

2. Materials and methods
The study of the cement industry waste in the form of aspiration and clinker dust was carried out with the aim of further obtaining alkaline binders. Aspiration and clinker dust is a man-made product that is extracted in large quantities from the dust collection system of a rotary clinker kiln. In furnaces operating according to the wet method, dust emission is 10–20% of the furnace productivity. In furnaces using the dry method with cyclonic heat exchangers is 25–30%. Aspiration dust was collected in the heating and dehydration zone of the wet clinker kiln at a temperature of 300 - 400 °C. It is a full-fledged raw mixture of slightly fired clay minerals and non-decomposed calcite. Clinker dust was sampled in the cooling zone and corresponds in mineralogy to the finished clinker [4 - 6].

In order to find a rational use for the waste of the cement industry, the task was set to determine the size and shape of particles of aspiration and clinker dust. Also, to establish the particle size distribution of particles in the samples of dispersed material. The study was carried out using a Lasentec D600L laser particle size analyzer with a V819 laser video microscopy system (particle size measurement range 500 nm - 1000 μm). Water was used as a dispersion medium, which was constantly stirred during the analysis; the sample temperature was 23.3 ± 0.3 ºC; measurement duration was 30 minutes, measurement was taken every 10 seconds, the number of measurements for one analysis consisted of 180.

3. Results and discussion
The shape of particles of samples of dispersed material was investigated (Figures 1, 2).
Figure 1. Particle shape in a clinker dust sample.

Figure 2. Particle shape in aspiration dust sample.

The results of the particle size analysis of the dispersed material samples are shown in Table 1 and Figure 3; the symbols for Figure 3(a, b) are shown in Table 2.

Table 1. The results of the particle size analysis.

| No. of sample | <1 | 1–5 | 5–10 | 10–50 | 50–250 | 250–500 | 500–1000 | >1000 |
|---------------|----|-----|------|-------|--------|---------|----------|-------|
| 1             | 0.00 | 4.64 | 7.87 | 64.76 | 22.64 | 0.09 | 0.001 | 0.00 |
| 2             | 0.00 | 10.61 | 13.79 | 52.33 | 22.91 | 0.34 | 0.01 | 0.00 |

*sample No. 1 is a clinker dust; sample No. 2 is an aspiration dust.
Figure 3. Dependence of the size and number of particles on the measurement time for samples of clinker (a) and aspiration dust (b).

Table 2. Symbols.

| Color | Name                                      | Y Axis          |
|-------|-------------------------------------------|-----------------|
|       | Median, No Wt (Fine)                      | microns         |
|       | Mean, Sqr Wt (Fine)                       | microns         |
|       | counts, No Wt, <1 (Fine)                  | counts (fines)  |
|       | counts, No Wt, 1-5 (Fine)                 | counts (fines)  |
|       | counts, No Wt, 5-10 (Fine)                | counts (fines)  |
|       | counts, No Wt, 10-50 (Fine)               | counts (fines)  |
|       | counts, No Wt, 50-250 (Fine)              | counts          |
|       | counts, No Wt, 250-500 (Fine)             | counts          |
|       | counts, No Wt, 500-1000 (Fine)            | counts          |
|       | counts, No Wt, >1000 (Fine)               | counts          |

Thus, the size of the particles was determined, the particle size distribution was established, and the shape of the particles in the samples of dispersed material was investigated. Granulometric analysis of the particle size showed that the properties of dispersed systems are not changed over time. The only exception is the initial period of time, which averages 5 minutes and is characterized by the stabilization of the dispersed system. This time period is not taken into account in the calculations. All samples of dispersed material are dominated by particles in the size range of 10–50 µm. The study of the shape of the particles showed that in all samples there are particles characterized by an irregular geometric shape (angular and grainy) and an average degree of sphericity and roundness.
Investigations of characteristic sizes, morphological features and local chemical analysis of particles of reactive powders with determination of the quantitative content of elements of the presented samples were carried out using a QUANTA 3D 200i scanning electron microscope with an integrated microanalysis system Genesis Apex 2 EDS from EDAX, in a high vacuum mode with an electron beam accelerating voltage of 30kV and magnification in 100-500 times.

An Everhart-Thornley detector (ETD) of the scintillator type with a photomultiplier that senses secondary (SE) and backscattered electrons (BSE) excited by the primary beam during its interaction with the sample was used to obtain the image. The spectra were processed using the EDAX TEAM EDS software.

All investigated objects are polydisperse powders with particles of various sizes. For each sample, the task was set to fix their size, surface homogeneity and chemical composition. A layer of reaction powder of the required thickness for research was obtained on a special double-sided sticky carbon tape, which was applied to a portable table, to gain it.

Studies of the morphology, size and chemical composition of clinker dust of electrostatic precipitators are presented in the form of micrographs of the particle surface at magnifications from 100 to 5000 times. The sizes of these particles are also shown (Figure 4). It can be seen from the micrographs that clinker dust consists of particles and their aggregates, which have various shapes and sizes in a wide range from 20 to 250 microns. Table 3 shows the average concentrations of chemical analysis of clinker dust particle areas (Figure 4).

![Figure 4. Aggregates of particles in the sample clinker dust.](image)

Energy dispersive analysis of polydisperse clinker dust showed that on aggregates with sizes of more than 200 μm and on particles with sizes less than 100 μm, the results of chemical composition showed similarity in the type of oxides and concentration, while the total content of CaO, SiO2, and CO2 oxides was more than 90% of the total masses.

| Oxides | Particles >200 microns | Particles <100 microns |
|--------|------------------------|------------------------|
| CO2    | 7.29                   | 7.25                   |
| MgO    | 0.87                   | 0.71                   |
| Al2O3  | 2.20                   | 1.07                   |
| SiO2   | 16.30                  | 16.20                  |
| SO3    | 0.50                   | 0.60                   |
| K2O    | 1.00                   | 0.92                   |
| CaO    | 70.90                  | 70.10                  |
| Fe2O3  | 3.74                   | 2.64                   |

Table 3. Chemical composition of clinker dust particles, %.
Studies of the morphology, size and chemical composition of aspiration dust of electrostatic precipitators are presented in the form of micrographs of the surface of aspiration dust particles at various magnifications in Figure 5. On the surface of the sample, there are no particles that differ from the main massif. As shown in Figure 5, the particles of the sample have rough surfaces of the same type and dimensions of tens of microns. The entire surface of large particles is covered with microparticles less than 3 microns in size, which are shown in the photographs at high magnifications.

Figure 5 shows sections of the sample where the chemical composition was determined. The average values of the chemical composition were determined on the surface of a large particle, as well as on particles less than 100 μm in size. Table 4 shows the average values of the concentrations of chemical elements. In the analysis of the results of the energy-dispersive composition of aspiration dust, it can be noted that a definite dependence of the concentration of basic oxides on the grain size is not observed.

![Figure 5. Micrographs of aspiration dust particles.](image)

**Table 4. Chemical composition of aspiration dust particles, %.**

| Oxides | Particles > 200 microns | Particles < 100 microns |
|--------|-------------------------|------------------------|
| CO₂    | 10.70                   | 9.70                   |
| MgO    | 0.73                    | 0.68                   |
| Al₂O₃  | 3.40                    | 3.10                   |
| SiO₂   | 14.60                   | 14.80                  |
| SO₃    | 1.80                    | 3.20                   |
| Cl     | 0.32                    | 0.40                   |
| K₂O    | 6.20                    | 7.50                   |
| CaO    | 57.60                   | 58.10                  |
| Fe₂O₃  | 2.80                    | 2.70                   |

It is known that the aspiration dust of electrostatic precipitators of rotary kilns is collected from the zones of pre-drying, calcining and exothermic reactions. Therefore, its main mass consists of a mixture of baked clay and undecomposed limestone, this is confirmed by the chemical composition, where calcium oxide accounts for 60%, silicon oxide up to 15% and carbon monoxide 10% of the mass.

To determine the binding properties of the studied powders, they were mixed with all kinds of solutions. It should be noted that the aspiration dust showed sufficient activity in combination with an alkaline solution of sodium water glass. The beginning of the setting came in 16 minutes (table 5).
Clinker dust reacted much worse to both alkaline activation and hydration with water, which is due to the higher content of particles with a size of 250 - 500 microns. But the reactivity has been proven, as evidenced by research results.

4. Summary
The above arguments confirm that the granulometry, particle shape and reactivity of the claimed man-made powders will make it possible to use these qualities in the future to create formulations of linker-free binders of alkaline activation, and the expected research results will be of interest to specialists in the construction industry, as an alternative to expensive and energy-intensive Portland cement for creating strong and durable concrete and reinforced concrete composites.

5. References
[1] Bataev D K-S, Murtazayev S-A Yu, Salamanova M Sh, Viskhanov S S 2019 Utilization of Cement Kiln Dust in Production of Alkali-Activated Clinker-Free Binders Proceedings of the International Symposium "Engineering and Earth Sciences: Applied and Fundamental Research" dedicated to the 85th anniversary of H.I. Ibragimov (ISEES 2019). Atlantis Highlights in Material Sciences and Technology (AHMST) 1 457–460
[2] Murtazayev S-. Yu, Salamanova M Sh, Ismailova Z Kh 2019 Features of Production of Fine Concretes Based on Clinkerless Binders of Alkaline Mixing 14th International Congress for Applied Mineralogy (ICAM 2019) (Belgorod: Belgorod State Technological University named after V G Shukhov) pp 385-388
[3] Rakhimova N R, Rakhimov R Z 2009 Properties of the slag-alkaline bindings - specific surface and granulometric of ground blast furnace slags relation 17 Internationale Baustofftagung. Tagungsbericht (Band 1. Weimar) pp 1-0499-0504
[4] Kozhukhova N I, Chizhov R V, Zhernovsky I V, Strokova V V 2016 Structure formation of geopolymer perlite binder vs. Type of alkali activating agent International Journal of Pharmacy and Technology 8(3) 15338–15348
[5] Dombrowski K, Buchwald A, Weil M 2007 The Influence of Calcium Content on the Structure and Thermal Performance of Fly Ash Based Geopolymers Journal of Materials Science 42(9) 3033–3043
[6] Pawlasova S, Skvara F 2008 High-Temperature Properties of Geopolymer Materials Akali Activated Materials 523–525
[7] Khater H M 2015 Effect of firing temperatures on alkali activated Geopolymer mortar doped with MWCNT Advances in Nano Research 3(4) 225–242
[8] Khater H M, El Nagar A M 2016 Ezzat Optimization of Alkali Activated Grog/Ceramic Wastes Geopolymer Bricks] International Journal of Innovative Research in Science, Engineering and Technology 5(1) 37–46
[9] Villa C, Pecina E T, Torres R, Gomez L 2010 Geopolymer synthesis using alkaline activation of natural zeolite Construction and Building Materials 24 2084–2090

Table 5. Properties of binder systems on waste from the cement industry.

| Quality indicators                      | Clinker dust | Aspiration dust |
|-----------------------------------------|--------------|-----------------|
| Normal density of alkaline cement paste, % | Na₂SiO₃ 30.0 | Na₂SiO₃ 72.5     |
|                                          | H₂O 50.0     | H₂O 42.0        |
|                                          | Na₂SiO₃ 72.5 | Na₂SiO₃ 70.0    |
|                                          | H₂O 42.0     | Na₂SiO₃ 70.0    |
|                                          | Na₂SiO₃ 72.5 | Na₂SiO₃ 70.0    |
| Setting time, start / end, hour-min.    | 00-40        | 00-08           |
|                                          | 00-54        | 00-24           |
|                                          | 00-16        | 00-36           |
|                                          | 01-20        | 01-56           |
|                                          | 01-31        | 07-16           |

Clinker dust reacted much worse to both alkaline activation and hydration with water, which is due to the higher content of particles with a size of 250 - 500 microns. But the reactivity has been proven, as evidenced by research results.