Possible solutions to problems in the cement industry

M Sh Salamanova¹,², S A Aliev², S-A U Murtazaev¹,², M S Saidumov² and I A Gabazov²

¹ Integrated Research Institute named after Kh.I. Ibragimov, Russian Academy of Sciences of the Chechen Republic, 21A, Staropromyslovsky ave., Grozny, 364051, Russia
² Grozny State Oil Technical University named after M.D. Millionshchikov, korp. 1,100, prosp. Husejna Isaeva, Grozny, 364068 Russia

E-mail: madina_salamanova@mail.ru, asa-fenix@mail.ru, s.murtazaev@mail.ru, saidumov_m@mail.ru, asa-fenix@mail.ru

Abstract. In this paper, we substantiate approaches to the transition to clinker-free binders and building composites with their use to replace resource-intensive cement, at least in those areas of construction where its high technical functional properties are not needed. The optimal formulations and properties of alkaline activation binders based on mineral powders are revealed and the theoretical foundations of the formation of the structure and strength of cement stone based on an alkaline activator are revealed. The results of the studies are of practical value for the construction industry, as the obtained formulations of clinker-free cements will partially replace expensive and energy-intensive Portland cement in the production of concrete and reinforced concrete structures. This work was carried out as part of research on the implementation of scientific project No. 05.607.21.0320. “The development of technology for new building composites on clinkerless alkaline binders using substandard natural and secondary raw materials” that received support from the Federal target program “Research and development in priority areas for the development of the scientific and technological complex of Russia for 2014–2020”.

1. Introduction

For many years, the modern construction industry has considered concrete and reinforced concrete to be the leader in the construction market, despite the enormous costs associated with their production. And these costs, in the first place, are associated with the use of energy – and resource-intensive binder component. Therefore, the question of creating an alternative solution to this costly material is of increasing interest and is relevant.

At the moment, there are developments proposed by the school of Professor V.D. Glukhovsky, slag-alkali cements and concrete based on them, received universal vocation in the 70s of the last century. The production of these composites requires the presence of granular blast furnace slag of ferrous metallurgy in a finely divided state, for the activation of which it is necessary to use alkaline solutions such as liquid glass, soda ash, caustic soda, sodium metasilicates. There are many results confirming the effectiveness of this area, but nevertheless, we do not observe the large-scale implementation of these developments, since there is a lot of research that has not been investigated in this technology that requires further study [1–5, 24, 25].

This paper presents its view on the development of clinker-free technology. Considering the fact that in many regions of our vast country there are no reserves of ferrous metallurgy wastes, and transportation of this valuable raw material over long distances is economically disadvantageous, our efforts were aimed at finding mutually substituting, blast furnace granulated slags, materials. And this is no coincidence, the slags of ferrous metallurgy...
in their chemical composition are identical to the composition of clinker minerals, therefore, the processes of structure formation of cement stone will be similar for both types of binder [3, 4, 6, 9]. Due to the lack of slag, we made attempts to obtain alkaline mixing binders using finely dispersed mineral powders of various origins.

And this is possible, since the North Caucasus has huge natural potential for the development of the cement industry. In mountainous regions, reserves of cement marls, limestones, flasks, dolomites, large deposits of building and glass sands, limestone, shell limestone, sandstones, natural sand dunes in the Terskaya Lowland are concentrated [16, 21–23].

2. Methods and materials
To develop clinker-free alkaline activation cements, finely dispersed mineral powders were prepared from sedimentary and igneous rocks: silica marl and quartz sand of the Vedeno deposit, limestone of the Yarysh-Mardynsky quarry, sand dunes of the Shelkovskoye deposit, volcanic tuff from the Kabardino-Balkarian Republic.

The energy dispersive microanalysis of the powders under study, performed using a Quanta 3D 200 i scanning electron microscope, showed a significant difference in the chemical composition of the mineral additives:

- quartz sand, %: MgO = 6,32; Al$_2$O$_3$ = 14,99; SiO$_2$ = 73,83; K$_2$O = 1,83; CaO = 0,60; Fe$_2$O$_3$ = 0,97; TiO$_2$ = 1,32; SO$_3$ = 0,14.
- volcanic tuff, %: MgO = 0,20; Al$_2$O$_3$ = 13,57; SiO$_2$ = 73,67; K$_2$O = 6,00; CaO = 1,79; Fe$_2$O$_3$ = 1,52; TiO$_2$ = 2,85; il = 0,40.
- limestone, %: MgO = 0,72; Al$_2$O$_3$ = 1,55; SiO$_2$ = 5,05; K$_2$O = 0,60; CaO = 90,14; Fe$_2$O$_3$ = 1,40; SO$_3$ = 0,49.
- silicified marl, %: MgO = 1,64; Al$_2$O$_3$ = 6,42; SiO$_2$ = 28,6; K$_2$O = 1,33; CaO = 16,90; Fe$_2$O$_3$ = 1,08; TiO$_2$ = 0,47; SO$_3$ = 0,29; il = 43,2.
- barchan sands, %: MgO = 2,41; Al$_2$O$_3$ = 7,81; SiO$_2$ = 59,54; K$_2$O = 1,44; CaO = 17,52; Fe$_2$O$_3$ = 2,60; Na$_2$O = 1,35; SO$_3$ = 0,21; il = 7,12.

To prepare fine powders from the studied rocks, coarse ones were preliminarily crushed in a jaw crusher, and then, like fine grains, they were subjected to fine grinding in a VM-20 laboratory vibratory ball mill. At certain intervals, samples were taken from the mill to determine the specific surface of the powders and to conduct a comparative analysis (using the PSX-12 device).

3. Results
The specific surface of the obtained powders varied from 210 to 1120 m$^2$/kg depending on the grinding time (Fig. 1).

![Figure 1. The dependence of the specific surface of fine powders on the duration of grinding](image-url)

The main binder – in the proposed compositions is an alkaline activator, shuttling them with the studied powders, we get a cement paste, which hardens with time, forming an alkaline cement stone [7–11]. It should be noted that the properties of cement stone will depend both on the nature of the mineral powder and on the type of grout [8, 12–20].
To study the effect of the specific surface area of the obtained mineral powders on the properties of the cement paste, molding mixtures were prepared from the studied components, and they were activated by various alkaline solutions: salable liquid sodium glass, caustic soda and soda ash. At the first stage, it was necessary to trace how the specific surface of mineral powders will change the normal density of alkaline cement paste. The normal density of the alkaline cement paste was determined according to the standard method, on a Vika instrument, replacing the needle with a pestle, the results are shown in table 1.

| No. | Mineral powders | Na$_2$SiO$_3$ | Alkaline solution | NaOH | Na$_2$CO$_3$ |
|-----|-----------------|----------------|-----------------|------|-------------|
| 1   | Quartz sand     | 25             | Ssp = 250 m$^2$/kg | 26   | 27          |
| 2   | Volcanic tuff   | 24             |                 | 24   | 25          |
| 3   | Siliceous Marl  | 24             |                 | 25   | 26          |
| 4   | barchan sands   | 28             |                 | 29   | 29          |
| 5   | Limestone       | 27             |                 | 28   | 28          |
| 6   | Quartz sand     | 26             | Ssp = 500 m$^2$/kg | 27   | 28          |
| 7   | Volcanic tuff   | 25             |                 | 27   | 27          |
| 8   | Siliceous Marl  | 25             |                 | 26   | 26          |
| 9   | barchan sands   | 29             |                 | 29.5 | 30          |
| 10  | Limestone       | 27             |                 | 29   | 29          |
| 11  | Quartz sand     | 27             | Ssp = 900 m$^2$/kg | 29   | 29          |
| 12  | Volcanic tuff   | 26             |                 | 28   | 27          |
| 13  | Siliceous Marl  | 26             |                 | 27   | 28          |
| 14  | barchan sands   | 33             |                 | 34   | 35          |
| 15  | Limestone       | 29             |                 | 31   | 31          |

The results of the study showed that the normal density of all the studied compositions of alkaline cement paste does not differ significantly depending on the alkaline solutions used, the use of caustic soda and soda ash slightly increase this indicator. A significant influence is exerted by the nature of the mineral powder and the degree of dispersion, as we observe, with an increase in the specific surface, the normal density of the alkaline cement paste increases. This indicator is especially high for highly dispersed sand dunes, the explanation for this is the presence of clay particles in the sand. I analyze the results of studies, it can be assumed that with an increase in the specific surface, the demand for powders in an alkaline solution increase. Therefore, to obtain binders of alkaline mixing, there is no need for long-term grinding of mineral additives, Ssp = 250 m$^2$/kg is quite enough.

At the next stage, the task was set to determine the setting time of binders for alkaline activation, on the basis of the studied powders with a specific surface Ssp = 250 m$^2$/kg, the preference for this degree of dispersion was given for the rational use of technological equipment and energy saving. The research results are shown in table 2.

The results obtained confirm that the setting time of the binders of alkaline mixing varies depending on the type of activator, the use of sodium metasilicate leads to a quick setting of the mixture, sodium hydroxide and soda ash lengthens this indicator for 5–7 minutes. It should also be noted that limestone mineral powders trapped with an alkaline solution are characterized by a slower start and setting time, and of course the reason for this is the petrographic composition of these rocks, it is likely that the calcite mineral prevailing in the present case reacts much later with an alkaline activator.

As we know, compositions based on liquid glass belong to the category of air binders, but the aim of these studies was to obtain durable waterproof materials that can exhibit hydraulic properties. To confirm this hypothesis, beam samples of 20x20x100 mm in size were prepared from a molding
mixture consisting of the studied powders $S_{sp} = 250 \text{ m}^2/\text{kg}$ mixed with an alkaline solution, and coarse quartz sand with a particle size of 2.8 was used as a filler. After a day, and some samples on the second day, were redistributed. Some of the samples were placed periodically for several hours in an oven at a temperature of 40 °C. After heat treatment, part of the samples were stored in water for 28 days, and the other part of the samples hardened under normal conditions at a temperature of 18–20 °C. We studied the kinetics of a set of strength binders for alkaline activation, under various conditions of hardening. The composition of the solid components in the compositions was constant, only the consumption of the alkaline hardener changed, depending on the normal density of the mixture: mineral powder 500 kg/m$^3$, fine aggregate 1500 kg/m$^3$. The research results are shown in table 3.

### Table 2. Influence of the nature of mineral powders and alkaline solution on the terms of gripping binders of alkaline activation (start of crossing / end of crossing)

| No. | Mineral powders | $\text{Na}_2\text{SiO}_3$ | $\text{NaOH}$ | $\text{Na}_2\text{CO}_3$ |
|-----|-----------------|-----------------|--------------|-----------------|
|     | Specific surface area $S_{sp} = 250 \text{ m}^2/\text{kg}$ | 0–30 | 0–35 | 0–36 |
| 1   | Quartz sand     | 0–55 | 0–42 | 0–50 |
| 2   | Volcanic tuff   | 0–20 | 0–25 | 0–30 |
| 3   | Siliceous Marl  | 0–20 | 0–25 | 0–30 |
| 4   | barchan sands   | 0–14 | 0–20 | 0–24 |
| 5   | Limestone       | 0–23 | 0–35 | 0–40 |

### Table 3. Kinetics of strengthening of knitting alkali closing

| Alkaline activator | After TO | The limit of compressive strength, MPa per day |
|-------------------|----------|-----------------------------------------------|
|                   | 28       | 90    | 180   | 28      | 90    | 180   | 28      | 90    | 180   |
| quartz sand       |          |       |       |         |       |       |         |       |       |
| $\text{Na}_2\text{SiO}_3$ | 24.7 | 25.6 | 26.1 | 18.4 | 23.5 | 24.7 | 18.4 | 19.0 | 19.6 |
| $\text{NaOH}$     | 20.2 | 21.0 | 22.3 | 16.4 | 17.4 | 18.4 | 16.5 | 17.0 | 17.5 |
| $\text{Na}_2\text{CO}_3$ | 15.3 | 15.7 | 15.9 | 12.7 | 13.6 | 13.9 | 12.1 | 12.9 | 13.2 |
| volcanic tuff     |          |       |       |         |       |       |         |       |       |
| $\text{Na}_2\text{SiO}_3$ | 44.0 | 46.5 | 48.7 | 42.6 | 44.7 | 45.2 | 39.1 | 40.8 | 42.6 |
| $\text{NaOH}$     | 35.3 | 36.8 | 37.9 | 33.2 | 34.9 | 35.7 | 31.5 | 32.3 | 33.6 |
| $\text{Na}_2\text{CO}_3$ | 30.2 | 31.8 | 32.6 | 29.8 | 30.1 | 31.6 | 27.5 | 27.4 | 27.9 |
| silicified marl   |          |       |       |         |       |       |         |       |       |
| $\text{Na}_2\text{SiO}_3$ | 45.4 | 50.0 | 51.3 | 44.1 | 46.3 | 48.6 | 40.0 | 42.2 | 43.4 |
| $\text{NaOH}$     | 36.1 | 37.5 | 39.7 | 34.3 | 37.5 | 39.7 | 33.1 | 35.2 | 36.2 |
| $\text{Na}_2\text{CO}_3$ | 31.0 | 32.6 | 33.8 | 30.7 | 31.6 | 33.5 | 29.2 | 30.3 | 31.5 |
| barchan sands     |          |       |       |         |       |       |         |       |       |
| $\text{Na}_2\text{SiO}_3$ | 46.6 | 47.9 | 49.5 | 44.1 | 45.4 | 46.7 | 42.5 | 43.7 | 44.8 |
| $\text{NaOH}$     | 35.4 | 36.8 | 38.4 | 33.7 | 35.7 | 36.0 | 31.9 | 32.6 | 33.7 |
| $\text{Na}_2\text{CO}_3$ | 34.2 | 34.9 | 35.9 | 31.0 | 31.7 | 32.8 | 30.6 | 31.6 | 32.9 |
| Limestone         |          |       |       |         |       |       |         |       |       |
| $\text{Na}_2\text{SiO}_3$ | 9.7  | 10.1 | 10.7 | 6.4  | 6.5  | 6.5  | 4.5   | 4.6  | 5.6   |
| $\text{NaOH}$     | 8.1   | 8.7  | 9.3  | –    | –    | –    | 4.0   | 4.2  | 4.3   |
| $\text{Na}_2\text{CO}_3$ | 7.0  | 7.6  | 7.9  | –    | –    | –    | 3.4   | 3.9  | 4.4   |

### 4. Conclusion

The results showed that sodium metasilicate is the best activator of mineral powders of various origin, a solution of sodium hydroxide and soda ash is inferior to this mash. Astringent alkaline activation
based on sand dunes and silicified marl showed the highest results; volcanic tuff powder is slightly inferior to them. The effectiveness of the indicated powders can be explained by their aluminosilicate nature, which, when activated by an alkaline solution, allows the formation of a strong heliopolymer stone represented by a three-dimensional aluminosilicate hydrogel. But it is important to take into account the high cost of liquid sodium glass, therefore, in the future, our studies will be aimed at creating a less energy-consuming activator, or using binary alkaline solutions [4, 6, 9].

Substandard sand sands belong to the thin class with a particle size modulus of 0.65, they are unsuitable for use in construction, as they are characterized by a high content of clay particles, but in the proposed technology this can only favorably affect the properties of composites, and besides, it can be used them in their natural form, without subjecting to fine grinding.

The obtained research results will significantly expand the scope of application of clinker-free alkaline mixing cements and become an alternative to energy and resource-consuming Portland cement, and of course, it will be possible to at least partially replace it in the construction industry.

References

[1] Glukhovsky V D (ed) 1979 Alkaline and alkaline-alkaline earth hydraulic binders and concrete (Kiev: Vishcha school) 232 p
[2] Glukhovsky V D and Pakhomov V A 1978 Slag-alkali cements and concretes (Kiev: Budivelnik) 184 p
[3] Krivenko P V and Pushkareva K K 1993 Durability of slag-alkali concrete (Kiev: Budivelnik) 224 p
[4] Davidovitz J 2008 Geopolymer. Chemistry and applications (St. Quentin: Instit. Geopolymer) 592 p
[5] Duxson P, Fernandez A and Provis J 2007 Geopolymer technology: The current state of the art J. Mater. Sci. 42 2917–33
[6] Murtazaev S-A Yu, Salamanova M Sh, Saidumov M S, Ismailova Z Kh 2017 The influence of active surface centers on the reactivity of mineral additives Modern Sci. and Innovat. 2(18) 168–75
[7] Murtazaev S A Yu and Salamanova M Sh 2018 Prospects for the use of thermally activated raw materials of aluminosilicate nature Volga Sci. J. 2(46) 65–70
[8] Nikiforov E A, Loganova V I and Simonov E E The effect of alkaline activation on the structure and properties of diatomite Bull. of BSTU
[9] Salamanova M Sh and Murtazaev S-A U 2019 Alkaline activation cements: the possibility of reducing the energy intensity of obtaining building composites Build. Mater. 7 31–42
[10] Nesvetaev G, Koryanova Y and Zhitnikova T 2018 On effect of superplasticizers and mineral additives on shrinkage of hardened cement paste and concrete Theoretical Foundation of Civil Engineering (27RSP) MATEC Web of Conf. 27. Ser. 27th R-S-P Seminar (TFoCE 2018) p 04018
[11] Stelmakh S A, Nazhuev M P, Shcherban E M et al 2018 Selection of the composition for centrifuged concrete, types of centrifuges and compaction modes of concrete mixtures Physics and Mechanics of New Materials and Their Applications (PHENMA 2018) p 337
[12] Shuisky A, Stelmakh S, Shcherban E and Torlina E 2017 Recipe-technological aspects of improving the properties of non-autoclaved aerated concrete Modern Trends in Manufacturing Technologies and Equipment MATEC Web of Conf. Ser. Int. Conf. (ICMTMTE 2017) p 05011
[13] Soldatov A A, Sariev I V, Zharov M A and Abduraimova M A 2016 Building materials based on liquid glass Actual problems of construction, transport, engineering and technosphere safety Mater. of the IV annual sci. and pract. Conf. of the North Caucasus Fed. Univer. pp 192–5
[14] Martschuk V and Stark T 1998 Untersuchungen zur Frost-Tausalz-Widerstand von Mochleistungsbetonen. Wiss. Z. Bauhaus – Univ. Weimar 44(1–2) 92–103
[15] Larbi J A and Bijen J M 1990 Effect of water-cement ratio, quantity and fineness of sand on the evolution of lime in set portland cement systems *Cem. and concr. Res.* **20**(5) 783–94
[16] Salamanova M Sh, Aliiev S A and Murtazaeva R S-A 2019 The structure and properties of binders for alkaline activation using cement dust *Bull. of the Dagestan State Techn. Univer. Techn. Sci.* **2**(46) 148–58
[17] Kozhuhova N I, Chizhov R V, Zhernovsky I V and Strokova V V 2016 Structure formation of geopolymer perlite binder vs. Type of alkali activating agent *ARPN J. of Engineer. and Appl. Sci.* **11**(20) 12275–81
[18] Kozhuhova N I, Chizhov R V, Zhernovsky I V and Strokova V V 2016 Structure formation of geopolymer perlite binder vs. Type of alkali activating agent *Int. J. of Pharmacy and Technol.* **8**(3) 15338–48
[19] Larbi J A and Bijen J M 1990 The chemistry of the pole fluid of silica fume blended cement systems *Cem. and concr. Res.* **20**(4) 506–16
[20] Kozhuhova N I, Zhernovskiy I V, Osadchaya M S et al 2014 Revisiting a selection of natural and technogenic raw materials for geopolymer binders *Int. J. of Appl. Engineer. Res.* **9**(22) 16945–55
[21] Udodov S A and Guiche M R 2015 The effect of dosage of redispersible powder on the localization of the polymer and the deformation properties of the solution *Sci. works of the Kuban State Technol. Univer.* **9** 164–74
[22] Salamanova M Sh, Murtazayev S Yu and Ismailova Z H 2018 The Use of Highly Active Additives for the Production of Clinkerless Binders *Engineering and Earth Sciences: Applied and Fundamental Research* vol 177 Proc. of the Int. Symp. (ISEES 2018) pp 355–8 ISSN Part of series: AER, ISSN: 2352-5401, ISBN 978-94-6252-637-2
[23] Salamanova M Sh and Murtazayev S Yu 2018 Clinker-free binders based on finely dispersed mineral components *Internationale Baustofftagung, Tagungsbericht.* 12–14 september 2018, Bauhaus-Universitdt Weimar. Band 1 und 2. Weimar: В 2 pp 707–14
[24] Lesovik V S, Zagorodnyuk L K et al 2015 Designing of mortar compositions on the basis of dry mixes *Int. J. of Appl. Engineer. Res.* **10**(5) 12383–90