*DOI: https://doi.org/10.32347/2707-501x.2023.51.283-289*

**UDK 691.5**

**V. Zozulynets**,
PhD student TBKV department, junior researcher
ORCID: 0000-0002-8066-2033
**O. Kovalchuk,**
PhD (Eng.), senior researcher
ORCID: 0000-0001-6337-0488
*Scientific research institute for binders and materials named after V. Glukhovskii, Kyiv National University of Construction and Architecture, Kyiv*

## EFFICIENCY OF THE USE OF RED MUD IN THE DEVELOPMENT OF ACID-RESISTANT HYBRID ALKALINE CEMENTS

*The use of secondary industrial products has long been an integral part of the construction industry. The most common man-made raw materials used in the production of building materials, in addition to slag, are fly ash and red mud.*

*This work is devoted to the study of the effectiveness of using red mud as an additional source of an alumina silicate component of man-made origin in the production of alkali-activated cements with increased acid resistance.*

*In conventional cement systems, the use of significant amounts of red mud is not possible due to the high content of alkali metal compounds and heavy elements, but this is not a problem for alkali-activated binders.*

*Red mud obtained by processing bauxite ore using the Bayer process is highly alkaline, and its disposal and reusability are hampered by high sodium concentrations and high pH. That is why, according to the analysis of literature sources, research on the integrated use of red mud is mainly found in only a few areas, among which construction occupies a leading position.*

*In the course of research, the parameters of dough of normal density, hardening terms and strength for the developed systems were determined. Direct determination of the acid resistance index was also carried out using two methods: accelerated and by long-term aging of samples. In this way, the main physical and mechanical characteristics of the developed compounds were determined and the results were analyzed.*

*The obtained results of the study confirmed the possibility of partially replacing alumina silicate components with red mud to obtain acid-resistant alkaline cements. It was found that the introduction of up to 30% of red mud makes it possible to obtain material with an acid resistance coefficient (Ks) in the range of 0.8-0.95.*

***Key words: alkali-activated cements, acid resistance, aggressive environment, industrial waste, red mud.***

**Introduction.** Rapid development of modern technologies requires from industrial complexes rapid renovation and adaptation as for the Ukrainian market needs, so far as for world market. Every day there are creating a lot of goods and services, which are necessary for improvement life level and working conditions. However, there are still exist factures which need attention because of absence of effective materials to realize exploitation characteristics of separate flats of buildings in complex. First of all there are object of food and chemical industries.

Nowadays, the main roles in development of building materials of new generation are given to economical expediency of their production, ecology aspects and effectiveness under exploitation in time. Use of natural raw materials for production of building materials is very attractive from the point of view of safety and stability of obtained materials, including by the absence of extra content of heavy metals and hazardous materials. However, use of natural raw materials only if not attractive from the point of view of sustainable development. The most widely used materials with technogenic origin are blast furnace slag and fly ash. Red mud from alumina production is not widely used, but use of them is very perspective from the chemical point of view.

**Analysis of the studies and publication.** Bauxite residue, known as red mud, is the by-product of alumina production by Bayer process. Nowadays this source is about 4.6 mln tones in the storages. Global storying of red md needs a huge areas, causing huge impact for environment and leading to increasing of ecological risks. Moreover, it contents a lot of sodium, able to easily dissolve in the ground water. That is why it is necessary to provide stable approach for its complex treatment [1].

At present time, complex use of red mud is mainly realized in the following directs: construction industry, chemical industry, environmental protection, agricultural industry, and also industry of mining of rare elements [2-3].

Red muds from Bayer process have high alkalinity and their utilization and possibility of re-use are complicated because of high concentrations of sodium and pH level, meaning high alkalinity. That is why their use as a raw material for alkali activated cement based materials, including acid resistant materials, seems to be perspective [4].

Thus, in the paper [5] was highlighted the analysis of the study of production acid resistant materials using red mud. Acid solubility of the specimens was less than 4.5%. Another one example of active use of red mud is the production of glass-ceramic foam materials. Results of the study have showed that with increasing of electric insulators in the wastes different chemical components from the waste promoting appearance of liquid phase, recrystallized from the glass phase in the system from Ca-Al-Si-O to Al-Si-O, and thus a way leading to changes of pore structure of glass ceramic foam. While correspondence of the electric insulators to red mud was 8 parts to 2, glass ceramic foam shows optimal complex properties in the prepared specimens with the density 0.66 g/cm$^3$, porosity 73.6 % and compressive strength 11.3 MPa [6].

At the same time, study [7] expresses influence of red mud on mechanical properties and durability of geopolymer paste in solutions of sulphuric and acetic acid. To formulate geopolymer paste together with alkalis were used red mud and fly ash. Maximal obtained strength was 38 MPa for the paste, containing 30% of red mud and 10M alkaline solution versus 31.69 MPa while using only fly ash. Geopolymer paste, containing 30% and 50% of red mud, have showed better resistance to the acid aggression. Strength loses were minimal for specimens, containing 30% of red mud as for non-organic, so as for organic acids (namely sulphuric and acetic acids).

Thus, preliminary studies to determine mechanical strength, resistance for environmental impact and microstructure of alkali activated cement mortar using red mud confirm their efficiency to produce alkali activated cement [8]. However, possibility to use red mud as a raw component exactly for acid resistant alkali activated cements needs to provide additional studies.

**Aim of the work.** In general, development of materials with increased resistance to aggressive media with low pH contains two main points. Firstly, reducing of basicity of

the cement system itself, which is possible by introduction of $SiO_2$-containing components (for example, aspen), and secondly – direct regulation of structure formation in the direct of formation of stable insoluble phases, which will provide necessary acid resistance properties by using additional source of $Al_2O_3$ oxides (for example, metakaolin).

However, preliminary studies had showed that use of significant amount of metakaolin and aspen leads to appearance of significant problems, connected with increasing of system water demands and reducing of strength properties [9]. To avoid this problems, and also to increase ecological properties of material and to estimate possibility to reduce self-cost of the material, there were investigated possibility to provide partial replacement of alumina silicate components on red mud.

The main goal of the study was to develop acid resistant materials on the basis of hybrid alkali activated cements in the system $R_2O$ – RO – $Al_2O_3$ – $SiO_2$ – $H_2O$ with increased tightness and lowered porosity for application in materials and constructions of common and special use.

***Main objectives:***

– to study physical-chemical conditions of formation of acid resistant phases in hybrid alkali activated cements using red mud;

– to obtain optimal compositions of acid resistant alkaline cements and to determine regularity of regulation of structure formation processes in artificial stone of hybrid alkali activated stone using red mud;

– to analyze influence of technological parameters on peculiarities of hardening of acid resistant alkali activated cements;

– to investigate influence of type of acid media on main physical-mechanical properties of the cements under study;

– to study main physical-mechanical properties of developed compositions of acid resistant alkali activated cements in the direct of storage of the characteristics during exploitation.

**Main part and results of the study.** As a main source of alumina silicates of technogenic origin was used red mud from Mykolaiv alumina plant. Bauxite ore is grinding in the process of alumina production and thus red mud is characterized by specific surface within the ranges 1500 m/kg.

As a main source of alumina silicate component was used ground granulated blast furnace slag from PAT "DMZ" with specific surface 430 $m^2$/kg by Blaine.

To reduce basicity of the system, as an additional source of $SiO_2$ was used aspen. Alkaline component was represented by sodium metasilicate.

According to the test results, introduction of sodium metasilicate within the ranges 10-12% leads to the intensification of initial hardening of the system. Additional introduction of aspen partially slowing down this process and directs setting times to normal meanings (Table 1).

Table 1. – Paste of normal consistency and setting time test results of acid resistant alkali activated cements using red mud

| No | Components content, % | | | | PNC, % | Setting time, min | |
|---|---|---|---|---|---|---|---|
| | MS | Red mud | aspen | slag | | initial | Final |
| 1 | 10 | 20 | 0 | 70 | 23 | 50 | 130 |
| 2 | 8 | 30 | 0 | 62 | 25 | 75 | 125 |
| 3 | 12 | 15 | 0 | 73 | 21 | 35 | 65 |
| 4 | 10 | 30 | 10 | 50 | 26 | 80 | 120 |
| 5 | 10 | 15 | 5 | 70 | 24 | 75 | 105 |
| 6 | 12 | 15 | 5 | 68 | 23 | 55 | 85 |

Direct determination of acid resistance was done by the following methods:

- by express method via boiling of cement paste specimens during 1 hour in the 35% solution of sulphuric acid ($H_2SO_4$). Test results are given in Table 2.

- by storying of mortar specimens in 5% solution of sulphuric acid ($H_2SO_4$) during 30 days, after preliminary hardening during 28 days in normal conditions. Physical-mechanical properties of the materials under study are given in Table 3 and on Figure 1.

Table 2. – Test results after the boiling of specimens of cement paste using red mud

| No | Component content, % | | | | Mass, g | | Compressive strength at the age of 28 days, MPa | | $K_c$ | Δm, % |
|---|---|---|---|---|---|---|---|---|---|---|
| | MS | red mud | aspen | slag | before test | after test | before test | after test | | |
| 1 | 10 | 20 | 0 | 70 | 17.1 | 17.0 | 54.0 | 50.0 | 0.92 | 0.58 |
| 2 | 8 | 30 | 0 | 62 | 17.9 | 17.6 | 50.0 | 40.0 | 0.80 | 1.68 |
| 3 | 12 | 15 | 0 | 73 | 17.2 | 16.8 | 60.0 | 55.0 | 0.92 | 2.33 |
| 4 | 10 | 30 | 10 | 50 | 17.1 | 16.9 | 52.0 | 45.5 | 0.88 | 1.20 |
| 5 | 10 | 15 | 5 | 70 | 17.1 | 17.0 | 55.0 | 52.5 | 0.95 | 0.58 |
| 6 | 12 | 15 | 5 | 68 | 17.2 | 17.1 | 65.0 | 55.0 | 0.85 | 0.58 |

According to acid resistance coefficient meaning ($Kc \geq 0.8$), cements under study are acid resistant. This I also proved by mass loses results after test (less than 2.5% by mass).

Analysis of the obtained results shows that use of red mud replacing part of the alumina silicate component do not leads to the strength drop under influence of acid environment by boiling. The lowest destructions after boiling have the material with higher content of alumina silicate content together with increased content of silicate component in the system.

Table 3. – Compressive strength of acid resistant alkali activated cements using red mud

| No | Component content, % | | | | W/C ratio | Compressive strength, MPa | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | MS | red mud | aspen | slag | | 28 days | 60 days | 30 days, 5% $H_2SO_4$ solution | 90 days | 90 days, 5% $H_2SO_4$ solution |
| 1 | 8 | 30 | 0 | 62 | 0.41 | 30.2 | 31.4 | 23.7 | 41.0 | 30.7 |
| 2 | 10 | 20 | 0 | 70 | 0.38 | 36.3 | 37.8 | 29.0 | 44.7 | 36.9 |
| 3 | 12 | 15 | 0 | 73 | 0.36 | 40.2 | 42.5 | 38.1 | 56.8 | 43.4 |
| 4 | 10 | 15 | 5 | 70 | 0.40 | 37.9 | 41.0 | 30.4 | 62.1 | 43.5 |
| 5 | 12 | 15 | 5 | 68 | 0.37 | 48.5 | 51.0 | 38.7 | 58.7 | 40.6 |
| 6 | 10 | 30 | 10 | 50 | 0.42 | 38.5 | 37.7 | 30.7 | 44.5 | 29.7 |

Graphical interpretation of destructive influence of $H_2SO_4$ solution on the strength properties of the cements under study are given on Figure 1.

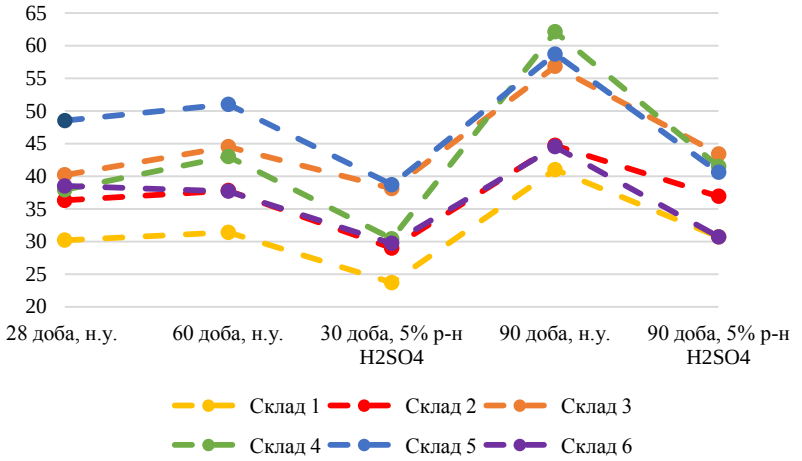


Figure1 –Influence of $H_2SO_4$ solution on the strength properties of the cements under study

According to the analysis of the obtain results use of red mud in the quantity up to 30% makes it possible to obtain material with compressive strength 30.7 MPa after 90 days of storying in 5% solution of $H_2SO_4$. There sodium metasilicate content is 8% by mass and is minimal comparing to other compositions. Increasing of alkaline component content leads to the rising of compressive strength. However, such regularity are present for storying in normal conditions, because increasing of alkalinity in the system leads to

the higher intensity of neutralization reaction, which flows in the process of influence of aggressive environment on the material.

Additional introduction of $SiO_2$ source represented by the ground aspen makes it possible to regulate this process by reducing basicity of the system. Thus, introduction of 5% $SiO_2$ and increasing of sodium metasilicate content to 10% makes it possible to obtain material with compressive strength 43.5 MPa after 90 days of influence of acid environment.

**Conclusion.** Obtained results are proving the possibility of partial replacement of alumina silicate component on red mud to obtain alkali activated cements with increased acid resistant properties. It was determined that introduction up 30% of red mud makes it possible to obtain material with acid resistance coefficient within the ranges 0.8-0.95.

In general, study of the strength properties of the compositions under study shows that the higher residual strength are characterized systems with increased content of alumina silicate component and reduced silicate modulus of the system, proving theoretical backgrounds.

**Aknowledgement.** Authors would like to thank Ministry of Education and Science for financial support of the project (No 0122U001199), which is performed according to Ukrainian budget financing in 2022-2023.

***References:***

1. Krivenko, P., Kovalchuk, O., Pasko, A., Croymans, T., Hult, M., Lutter, G., ... & Schroeyers, W. (2017). Development of alkali activated cements and concrete mixture design with high volumes of red mud. *Construction and Building Materials*, 151, 819-826. https://doi.org/10.1016/j.conbuildmat.2017.06.031

2. Krivenko, P., Drochytka, R., Gelevera, A., & Kavalerova, E. (2014). Mechanism of preventing the alkali–aggregate reaction in alkali activated cement concretes. *Cement and Concrete Composites*, 45, 157-165. https://doi.org/10.1016/j.cemconcomp.2013.10.003

3. Zinoveev, D., Pasechnik, L., Fedotov, M., Dyubanov, V., Grudinsky, P., & Alpatov, A. (2021). Extraction of valuable elements from red mud with a focus on using liquid media – a review. *Recycling*, 6(2), 38. https://doi.org/10.3390/recycling6020038

4. Wang, S., Jin, H., Deng, Y., & Xiao, Y. (2021). Comprehensive utilization status of red mud in China: A critical review. *Journal of Cleaner Production*, 289, 125136. https://doi.org/10.1016/j.jclepro.2020.125136

5. Hanahan, C., McConchie, D., Pohl, J., Creelman, R., Clark, M., & Stocksiek, C. (2004). Chemistry of seawater neutralization of bauxite refinery residues (red mud). *Environmental Engineering Science*, 21(2), 125-138. DOI: 10.1089/109287504773087309

6. Tian, X., Wu, B., & Li, J. (2008). The exploration of making acidproof fracturing proppants using red mud. *Journal of Hazardous materials*, 160(2-3), 589-593. https://doi.org/10.1016/j.jhazmat.2008.03.032

7. Liu, T., Zhang, J., Wu, J., Liu, J., Li, C., Ning, T., ... & Lu, A. (2019). The utilization of electrical insulators waste and red mud for fabrication of partially vitrified ceramic materials with high porosity and high strength. *Journal of cleaner production*, 223, 790-800. https://doi.org/10.1016/j.jclepro.2019.03.162

8. Song, S., Zhang, N., Yuan, J., Zhang, Y. (2021). New attempt to produce red mud-iron tailing based alkali-activated mortar: Performance and microstructural characteristics. *Journal of Building Engineering*, 43, 103222. https://doi.org/10.1016/j.jobe.2021.103222

9. Kovalchuk O., Zozulynets V., (2023). Doslidzhennia kyslotostiikosti hibrydnykh luzhnykh tsementiv normalnoho tverdnennia. *Mistobuduvannia ta terytorialne planuvannia*, 81, 189-198. https://doi.org/10.32347/2076-815x.2022.81.189-198

***В.В. Зозулинець, О.Ю. Ковальчук***

***Ефективність використання червоного шламу при розробці кислотостійких гібридних лужних цементів***

*Використання вторинних продуктів промисловості вже давно є невід'ємною складовою будівельної галузі. Найбільш поширеними сировинними матеріалами техногенного походження, які використовуються при виготовленні будівельних матеріалів окрім шлаку є зола-виносу та червоний шлам.*

*Дана робота присвячена дослідженню ефективності використання червоного шламу в якості додаткового джерела алюмосилікатної складової техногенного походження при виготовленні лужноактивованих цементів з підвищеними показниками кислотостійкості.*

*В звичайних цементних системах використання значної кількості червоного шламу не є можливим з огляду на високий вміст сполук лужних металів та важких елементів, проте це не є проблемою для лужноактивованих в'яжучих речовин.*

*Червоні шлами, отримані шляхом переробки бокситової руди за процесом Байєра мають високу лужність, а їх утилізація та можливість повторного використання ускладнюється високими концентраціями натрію та високим показником pH. Саме тому, згідно з аналізом літературних джерел, дослідження комплексного використання червоного шламу в основному знайдено лише в кількох сферах, серед яких будівництво займає передову позицію.*

*В ході досліджень було визначено показники тіста нормальної густини, термінів тужавлення та міцності для розроблених систем. А також проведено безпосереднє визначення показника кислотостійкості за двома методиками: прискореною та шляхом довготривалого витримування зразків. Таким чином було визначено основні фізико-механічні характеристик розроблених складів та проведено аналіз результатів.*

*Отриманими результатами дослідження було підтверджено можливість часткової заміни алюмосилікатних компонентів на червоний шлам для отримання кислотостійких лужних цементів. Виявлено, що введення до 30% червоного шламу дає змогу отримати матеріал з коефіцієнтом кислотостійкості (Кс) в межах 0,8-0,95.*

***Ключові слова: лужноактивовані цементи, кислотостійкість, агресивне середовище, промислові відходи, червоний шлам.***

***Посилання на статтю***

**APA:** Zozulynets, V., & Kovalchuk, O. (2023). Efficiency of the use of red mud in the development of acid-resistant hybrid alkaline cements. *Shliakhy pidvyshchennia efektyvnosti budivnytstva v umovakh formuvannia rynkovykh vidnosyn*, 51, 283-289.

**ДСТУ:** Zozulynets V., Kovalchuk O. Efficiency of the use of red mud in the development of acid-resistant hybrid alkaline cements. *Шляхи підвищення ефективності будівництва в умовах формування ринкових відносин*. 2023. № 51. С. 283-289.