Utilization of industrial wastes in the production of sulfate-resistant cement

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Abstract. In connection with the possibility of creating, on the basis of secondary raw materials and wastes of industrial enterprises, the production of new building materials of increased resistance in aggressive environments, there is a further need for systematic research and their use in the production of Portland cement. In this regard, the tailings of concentration of ferrous and non-ferrous metals are promising in terms of the content and reserves of useful components in comparison with the dump deposits of mining enterprises. At the concentration plants of Almalyk Mining And Metallurgical Complex, tens of millions of tons of “tailings”, formed during the enrichment of lead and copper-bearing ores and rich in Al₂O₃, Fe₂O₃, etc. are thrown into dumps annually, which are valuable components for the production of cement. The article presents the results of research on topical problems of the use of tailings from the lead concentration and copper smelting factories of the AMMC in the production of sulfate-resistant Portland cement as an active mineral additive. The influence of mineralogical compositions of clinkers of cement plants in Uzbekistan on the phase composition and properties of the obtained sulfate-resistant cement in the presence of lead-copper active mineral additives is analyzed. It is shown that additives play an important role in forming the structure of a cement stone and increasing its strength. Acceleration of the process of hydration and hardening of sulfate-resistant cement is observed from a change in the mineralogical composition towards a decrease in the content of tricalcium aluminate and a decrease in the basicity of clinker due to high-silica waste, which meets the requirements for sulfate-resistant cements.

1. Introduction

Currently, at the world level, scientific research is being carried out to develop ingredients and compositions that improve the construction and technical properties of cement, create highly efficient energy and resource-saving technologies, and improve their performance indicators. The existing scientific foundations for the production of highly efficient sulfate-resistant cements using secondary resources of various industries have been developed. The influence of the mineralogical composition of clinker on the phase composition and properties of products in the presence of technogenic additives is analyzed.

The question of the influence of the mineralogical composition of Portland cement clinker on the corrosion resistance of cement stone in an aggressive environment was studied by many scientists.
from abroad and the CIS: Isakhodzhaev B.A. [1], Kansepolskiy I. S. [2], Moskvin V.M. [3], Kuznetsova T.V. and Atakuziev T A [4], Davila J. [5], Lokher F.B. [6], Akula P. [7], Reddy B. [8], Sycheva L. [9], Paschenko A. [10], Klassen V.K. [11], Taylor H. [12], Ezziane K. [13], Choriva I.A. and Mukhamedbaeva Z.A. [14].

The high mineralization of surface and subsoil waters in a number of regions of Uzbekistan require corrosion-resistant Portland cement for the construction of hydro technical and irrigation facilities [1-4]. Using local raw materials many types of sulfate-resistant Portland cements for the needs of Uzbekistan industry was developed by Kansepolskiy I.S. [2]. The sulfate-containing cement from low-aluminate and technogenic raw materials was obtained by Sycheva L.I. and Bakeev D.V. [9].

Recently mechanism of formation of cement and effect of concentrated solutions of salts (brines) on blended cement hydration using calorimetry methods was studied by Nocun-Wczełik W. and Meedala M. [15]. Connection between processes of deterioration of concrete structures and formation of thaumasite in concretes and mortars containing fly ash was investigated by Mulenga D.M. and others [16].

For chemical and mineralogical composition of sulfate-resistant cement, special attention is paid to study of the corrosion-resistance of cements during hardening in aggressive environments. To increase the resistance of cement under sulfate solutions attack, the mineralogical composition of the initial clinker is very important. Studies show that the sulfate resistance of Portland cement is achieved with a reduced content of tricalcium aluminite and a moderate amount of alite [17-18]. Especially high salinity of groundwater takes place in the Aral Sea region of Uzbekistan, where construction structures are subjected to complex sulfate-magnesia-chloride aggression [19-21].

In this regard, the purpose of this study was the scientific justification and development of technology for the production of sulfate-resistant cements using flotation waste from metallurgical industries.

2. Research methods
As the objects of research the wastes from the enrichment of lead and copper-containing ores of the Almalyk Mining And Metallurgical Complex (AMMC) and clinker from cement plants of Uzbekistan was chosen.

For the research, modern methods of analyzing raw mixtures and reaction products were used. Chemical analysis of raw materials was determined according to GOST 5382-91. The dependence of the properties of cements on individual factors was studied in accordance with GOST 310-89. The most common and aggressive in practice 3% MgSO₄ solution and 5% Na₂SO₄ solution, corresponding to subsoil and ground waters, were used as aggressive media. The samples were tested after 3, 7, 14, 28, 90, 180, 360 days of hardening. The assessment of the sulfate resistance of cements was carried out according to the resistance coefficient, which after 6 months is at least 0.8. The test for the hydraulic activity of lead production waste (SOF) and flotation waste from copper production (MOF) wastes was determined according to the standard method of absorbing the amount of lime from a saturated solution by grams of additive. XRD-method and Bruker AXS D8 Advance diffractometer, Bruker, Germany was used (Cu-Kα - cathode, step - 0.05, shooting speed 2 sec) for identification of crystal phases. The hydrated samples were dehydrated with acetone at t=20°C. The survey parameters are as follows: 20 angle interval from 6 to 65°, CuKα radiation, tube voltage 24 kV, anode tube current 14 mA.

3. Results and its discussion
Non-additive Portland cement grade 400 of “Akhangarantsement” JSC, “Bekabadcement” JSC and “Kuvasaycement” JSC (Uzbekistan), tailings of lead-production and flotation waste from copper-enrichment plants was chosen as initial components, the chemical composition is given in table 1.

Phase compositions of matrix material for the production of cement mortars based on clinkers of Akhangaran, Bekabad and Quvasay cement plant, sand and additives SOF and MOF were revealed using X-ray phase analysis. Clinkers of cement plants are mainly represented: C₃S - d = 0.303; 0.296;
0.260; 0.218; 0.192; 0.176 nm, \( C_2S - d = 0.385; 0.277; 0.272; 0.260; 0.208 \text{ nm}, C_3A - d = 0.273; 0.269; 0.216; 0.202; 0.192; 0.154 \text{ nm}, \) \( C_4AF - d = 0.269; 0.264; 0.218; 0.204; 0.192; 0.182 \text{ nm}.\)

**Table 1.** Chemical composition of initial materials, mass.%

| Initial materials          | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO  | MgO  | SO₃  | CaO₆ | R₂O | P.p.p. | Other | Σ    |
|---------------------------|------|-------|-------|------|------|------|------|-----|-------|-------|------|
| Akhangaranportland-cement | 22.68| 4.55  | 3.65  | 65.48| 2.45 | 0.30 | 0.12 | -   | -     | 0.87  | 100  |
| Bekabadportland-cement    | 20.63| 4.52  | 4.05  | 65.92| 1.73 | 2.15 | 0.43 | -   | -     | 0.70  | 100  |
| Quvasayportland-cement    | 21.78| 4.81  | 4.08  | 64.14| 1.89 | 0.64 | 0.37 | -   | -     | 0.60  | 98.31|
| Tails, SOF                | 45.75| 8.72  | 7.19  | 14.59| 7.10 | 2.98 | -    | 2.98| 8.83  | -     | 98.14|
| Flotation waste, MOF      | 60.68| 14.02 | 9.54  | 1.37 | 0.11 | 5.69 | -    | 4.13| 4.11  | -     | 99.65|

The chemical compositions of Portland cements grade 400 of AOO “Akhargantsement”, AOO “Bekadscement” and “Kuvasaycement” (Uzbekistan) are given in table 2.

**Table 2.** Calculated mineral composition of clinkers (production of Uzbekistan cement industry)

| Cement production plant | KN  | n   | c   | Minerals content, mass. % |
|-------------------------|-----|-----|-----|---------------------------|
| Akhangaran              | 0.91| 2.29| 1.33| \( C_3S \) = 64.0; \( C_3A \) = 18.0; \( C_4AF \) = 7.2; \( C_4AF \) = 11.3 |
| Bekabad                 | 0.91| 2.33| 1.19| \( C_3S \) = 65.3; \( C_3A \) = 10.8; \( C_4AF \) = 7.5; \( C_4AF \) = 12.1 |
| Quvasay                 | 0.95| 2.45| 1.18| \( C_3S \) = 57.5; \( C_3A \) = 19.1; \( C_4AF \) = 5.8; \( C_4AF \) = 12.4 |

Table 3 shows the results of changes in the salt resistance of the Akhangaran, Kuvasay, Bekabad no-additive Portland cements, depending on the action of the additives MOF and SOF.

Phase compositions were revealed using X-ray phase analysis of matrix material for the production of cement mortars based on clinkers of Akhangaran, Bekabad and Kuvasay cement plant sand additives SOF and MOF. Clinkers of cement plants are mainly represented: \( C_3S - d = 0.303; 0.296; 0.260; 0.218; 0.192; 0.176 \text{ nm}, C_2S - d = 0.385; 0.277; 0.272; 0.260; 0.208 \text{ nm}, C_3A - d = 0.273; 0.269; 0.216; 0.202; 0.192; 0.154 \text{ nm}, \) \( C_4AF - d = 0.269; 0.264; 0.218; 0.204; 0.192; 0.182 \text{ nm}.\)

Table 3 shows the results of changes in the salt resistance of the Akhangaran, Kuvasay, Bekabad no-additive Portland cements, depending on the action of the additives MOF and SOF.

Based on the above data, we can conclude that the addition of SOF and MOF additives to the compositions of Portland cements of different mineralogical composition sharply increases its sulfate resistance. Increasing the sulfate resistance of cements due to the introduction of SOF and MOF additives can be explained by a change in the structure of the cement stone. The introduction of SOF and MOF additives leads to a decrease in the proportion of \( C_3A \) in cement and to the binding of calcium hydroxide released during hydration, which leads to a significant increase in the resistance of cements against sulfate corrosion. An increase in salt resistance is associated with a change in the mineralogical composition of cements towards a decrease in the content of \( C_3A \) and a decrease in the basicity of cement. The introduction of additives MOF and SOF reduces the \( C_3A \) content from 9-10% to 2-3%, the basicity of cement to 0.84-0.86, which meets the requirements for sulfate-resistant cements.
Table 3. Strength for sulfate resistance of cements with the addition of metallurgical waste MOF and SOF

| №  | Introduced additive | Aggressive environment | Compressive strength of the sample, MPa, days |
|----|---------------------|------------------------|---------------------------------------------|
|    |                     |                        | 3   | 7   | 14  | 28  | 90  | 180 | 360 |
| 1. | MOF                 | 3% MgSO₄               | 30  | 38  | 40  | 46  | 66  | 80  | 94  |
| 2. | SOF                 | 3% MgSO₄               | 38  | 42  | 48  | 59  | 71  | 87  | 103 |
| 3. | No additives        | 3% MgSO₄               | 14  | 19  | 20  | 29  | 33  | 36  | 50  |
| 4. | MOF                 | 5% Na₂SO₄              | 32  | 38  | 41  | 50  | 73  | 75  | 80  |
| 5. | SOF                 | 5% Na₂SO₄              | 38  | 41  | 47  | 58  | 64  | 77  | 89  |
| 6. | No additives        | 5% Na₂SO₄              | 15  | 19  | 25  | 33  | 39  | 38  | 38  |

Akhangaran Portland cement

Quvasay Portland cement

Bekabad Portland cement

The data obtained are consistent with the results of determining the coefficient of resistance of samples in aggressive media, depending on the time of their hardening. The dependence of the coefficient of resistance of the samples and aggressive media on the hardening period are shown in figure 1.

It is generally known that the interaction of cement with water begins almost instantly, while hydration particles are gradually deposited on the cement grains, water flows inside, new surfaces of non-hydrated cement particles are exposed, which leads to accelerated dissolution of minerals and crystallization of new formations. While exposure of unhydrated surfaces prevail over the process crystallization of neoplasms, a decrease in the strength of the cement stone is not observed. Over time, within the setting time, the number of neoplasms increases, few new non-hydrated surfaces are found, and the strength increases and does not decrease.

As a result of our research, physicochemical basis for a new progressive energy-saving technology for the production of highly efficient sulfate-resistant cements using waste from metallurgical industries developed, considered the issues of the formation of hydrate phases in silicate material, such as low-basic calcium hydrosilicates, tobermorite, hydrocarbosilicates, as well as gel-like CSH.
structures, the regularities of the reaction were established when mineral additives MOF and SOF are introduced into the composition of Portland cements, amorphous silica sorts out Ca(OH)$_2$ and other impurities contained in additives, fixing them on the surface of silica particles.

**Figure 1.** Coefficients of resistance of samples of Akhangaran, Kuvasay and Bekabad Portland cements in a solution of 3 % MgSO$_4$ (A) and 5 % MgSO$_4$ (B):

1-Akhangaran Portland cement with the addition of MOF;
2-Akhangaran Portland cement with SOF additive;
3-Akhangaran Portland cement without additive;
4-Kuvasay Portland cement with the addition of MOF;
5-Kuvasay Portland cement with SOF additive;
6-Kuvasay Portland cement without additive;
7-Bekabad Portland cement with addition of MOF;
8-Bekabad Portland cement with SOF additive;
9-Bekabad Portland cement without additive.
As a result, the activating ability of the additives increases and, consequently, due to the acceleration of the removal of Ca\(^{2+}\) ions from the liquid phase, the formation of hydrated minerals and the formation of cement stone are intensified.

4. Conclusion

A complex of studies of lead and copper production wastes was carried out, the results of which indicate the constancy of the content of the main components in them and the possibility of using the production wastes as a mineral additive in the production of cements. The physical and mechanical properties of the studied cements fully meet the requirements for sulfate-resistant cement, the most optimal amount of additive is 5-10 %. Based on the experiments carried out, the large role of the mineralogical composition and activity of the matrix Portland cement clinker in the production of cements with SOF and MOF additives is confirmed. The results obtained state that for the manufacture of cements with SOF and MOP additives, it is advisable to use alumina clinker as a matrix clinker. A comparative assessment of the Ca(OH)\(_2\) content in the composition of the cement stone containing SOF and MOF allows us to conclude that the introduction of 5% SOF and 3% MOF favorably affects the process of Ca(OH)\(_2\) binding into hydro silicates and calcium hydroaluminates, and also in carbonate containing hydrated products.

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