Study of service properties of alkali-activated cement using wastewater treatment residues

Oleksandr Kovalchuk¹,2, Genadiy Kochetov¹ and Dmytro Samchenko¹

¹ Kyiv National University of Construction and Architecture, Povitroflotskyi Avenue 31, 03037 Kyiv, Ukraine

² Email: kovalchuk.oyu@gmail.com

Abstract. The paper discloses the results of the study of treatment of galvanic wastewater residues by incorporation into the alkali-activated cement matrix. Leaching of heavy metals from the artificial stone was studied. It is set that immobilization level of the matrix is 99.96% by mass of heavy metal (97.83 using traditional methods). Application of alkali-activated cement makes it possible to obtain compressive strength of compound up to 40 MPa even when 30% of wastewater residues are involved. Immobilization level of alkali-activated cement matrix met requirements of the standard.

1. Introduction

The greatest ecological problem of galvanic production is utilization of sediments, produced as a result of waste water treatment [1, 2]. Leaching of hazardous compounds of heavy metals from sludge leads to their distribution in the environment [2-5]. That is why it is necessary to develop new methods of sludge treatment for their utilization.

One of the galvanic sludge treatments direct is leaching of heavy metals compounds by treating of sulphuric acid [5]. However, the use of this acid needs high safety conditions on the plant [6]. It is known method of galvanic sludge [7], where sludge is mixed with admixtures containing Cl ions with ratio 1:1.1. Obtained mix is burning at 450 – 500°C. Then the material is ground and treated by sulphuric acid. Disadvantage is high temperature and complicate technological process, so as use large volumes of acid.

The well-known now methods of extraction from galvanic sludge valuable components are economically and ecologically not effective. That is why the main directs of solving galvanic sludge treatment problems are combined with their use as admixtures to produce different materials: concrete [8], aggregates [9], asphalt [10], OPC [11], bricks, ceramic materials [12], pigments, catalysts [13], i.t.c. But there is still not total certainty in safety of such solutions because it is still possible to have leaching of heavy metals ions into the ambient environment [14].

The new direct of galvanic sludge neutralization is ferritization method [15]. Ferritization process includes transformation of ions of Fe²⁺ and Fe³⁺ and others heavy metals or their hydroxides in alkaline environment for future aeration by oxygen. Also this method provides high level of heavy metal incorporation from reactive mix [16].

Analysis of literature sources showed that treatment of galvanic residues by ferritization as a rule is provided at 60°C during over 1 hour. So, traditional thermal method of activation is a little bit energy- and materials consuming. Alternative of thermal method could be activation by electromagnetic...
impulses (EMI). Authors [17] investigate process of treatment of galvanic residues with electromagnetic impulse activation of ferritization process. However, in this work influence of different technological parameters on heavy metals leaching process was not studied.

As a rule, after treatment of galvanic sludge by traditional reagent method residues contained mix of heavy metals, so the ways of their utilizations are very limited. The ways of utilization of such methods after ferritization are significant wider. They could be used for production of soft magnetic high-frequency materials [19], so as for radar absorbing coatings [20]. That is why the question of their utilization is complicated because phase composition of residues depends from qualitative and quantitative composition of wastewater.

From this point of view, we suggest to provide more efficient way to solve this problem, which offers direct use of ferrite sediments with different composition in alkali-activated cement production [21]. Our preliminary studies, provided together with SRIBM KNUCA specialists, showed that such cements are stable to the influence of aggressive environment; acts well with sulfates and have a wide spectrum of unique exploitation properties [22]. They make it possible to safe incorporate elements of radioactive and hazardous materials not only on physical, but also on chemical level [23].

In the paper [24] were shown possibility to introduce into the alkali-activated cement matrix ferrite residue as a filler in the quantity 5.5 to 7.5 % by mass (ferrite metals phase content ≥ 90 %), providing stable strength properties corresponding to the control composition (without sediments). However, such investigations do not cover possibility to utilize residues over 10 % by cement mass.

Thus, analysis of literature sources showed possibility of safe utilization of galvanic wastewater treatment residues in the matrix of alkali-activated cements. Use of such cements make it possible to incorporate heavy metals not only on physical, but also on chemical level, providing reduce of ecological impact on environment.

Aim of the study is to investigate immobilization properties of alkali-activated cement artificial stone using ferrite sediments.

2. Raw materials and test methods

The basic components of alkaline cement that were used included granulated blast-furnace slag with a specific surface of 450 m²/kg (by Blaine) and a content of the glass phase of about 80 % and low calcium (Class F, classification ASTM C 618) and fly ash (FA) with a specific surface of 800 m²/kg. Chemical composition of the examined materials is given in Table 1.

| Material | SiO₂ | TiO₂ | Al₂O₃ | Fe₂O₃ | FeO | MnO | MgO | CaO | Na₂O | K₂O | P₂O₅ | SO₃ | Weight loss, % |
|----------|------|------|-------|-------|-----|-----|-----|-----|------|------|------|-----|---------------|
| Slag     | 37.9 | 0.35 | 6.85  | –     | –   | 0.106 | 5.21 | 44.6 | –    | –    | –    | –   |               |
| Ash      | 50.94| 0.94 | 24.56 | 13.25 | –   | 0.03 | 1.98 | 2.86 | 0.69 | 2.69 | 0.02 | –   | 1.36          |

The basic alkaline components used were calcined soda (Na₂CO₃) and sodium metasilicate pentahydrate. To adjust the rheological properties of the material, we used sodium lignosulfonate in the amount of 0.5 % by weight in a powdered state.

The products from industrial wastewater treatment are represented in the form of filtrates (electrolyte) and ferritic residues. On the one hand, the electrolyte is a liquid with a low content of ions of heavy metals, which is in compliance with regulations on water, but, on the other hand, their subsequent discharge to rivers or other bodies of water is problematic due to a high pH value (pH=10.21). At the same time, the alkaline environment of the electrolyte contributes to the structure formation of alkali-activated cements, because it was established [28] that mixing such cements with sulphate or chloride solutions improves operational properties [29]. Results from the chemical analysis of residues are given in Table 2.

Ferritic sediments, obtained by different methods of activation and technological parameters of ferritization process have high grade of crystallinity. Analysis of phase composition shows presence of...
ferrites Fe₂(Fe,Ni,Cu,Zn)O₄, (FeNi)O(OH) and sodium sulfate Na₂SO₄. Determined phases have ferromagnetic properties and spinel-like crystalline lattices.

Table 2. Content of chemical elements in the ferritic residues (% by mass).

| No | Z (Fe/Me) | pH | Electro magnetic impuls (EMI) | Thermal(TERM) |
|----|----------|----|------------------------------|---------------|
|    |          |    | Fe  | Ni  | Cu  | Zn  | Na  | SO₄ | Fe  | Ni  | Cu  | Zn  | Na  | SO₄ |
| S1 | 2/1      | 10.5 | 55.1 | 14.9 | 8.2 | 4.4 | 5.6 | 11.8 | 56.4 | 15.3 | 8.5 | 4.6 | 4.8 | 10.4 |
| S2 | 8.5      | 63.9 | 8.6  | 4.7  | 2.6 | 6.4 | 13.8| 66.7 | 8.9  | 4.9  | 2.7 | 5.4 | 11.4|
| S3 | 9.5      | 67.3 | 9.1  | 5.0  | 2.7 | 5.1 | 10.8| 68.4 | 9.3  | 5.2  | 2.8 | 4.5 | 9.8 |
| S4 | 10.5     | 71.4 | 9.7  | 5.4  | 2.9 | 3.4 | 7.2 | 70.7 | 9.6  | 5.3  | 2.9 | 3.7 | 7.8 |
| S5 | 6/1      | 70.3 | 6.5  | 3.5  | 1.9 | 5.7 | 12.2| 74.9 | 6.8  | 3.7  | 2.0 | 4.0 | 8.6 |

3. Results and discussion

3.1. Examination of mineralogical composition of neo-formations in the alkaline cements that contain products from water treatment by the ferritization method

To investigate a possibility of safe immobilization of heavy metals, the waste from industrial water treatment was used as a component of hybrid alkaline cements. Ferritic sediments were introduced in the amount of 2.5–7.5 % by weight of cement and mixed with the electrolyte. Compositions of the examined cement pastes and their mechanical properties are given in Table 3.

Table 3. Composition and properties of alkaline cements that include wastewater treatment products.

| No | Cement composition, % |
|----|------------------------|
|    | Slag | Ash | Soda | Water (W)/Electrolyte (E) | Ferritic sediments | Paste of normal consistancy, % | Compressive strength, MPa, 28 days |
|----|------|-----|------|--------------------------|-------------------|-----------------------------|-----------------------------------|
| 1  | 66.7 | 28.6| 4.7  | W                        | –                 | 26                          | 60.2                              |
| 2  | 66.7 | 28.6| 4.7  | E                        | –                 | 25                          | 40.5                              |
| 3  | 65.0 | 27.8| 4.7  | E                        | 2.5               | 27                          | 56.2                              |
| 4  | 63.3 | 27.0| 4.7  | E                        | 5.0               | 28                          | 51.2                              |
| 5  | 61.5 | 26.3| 4.7  | E                        | 7.5               | 26                          | 58.7                              |
| 6  | 65.0 | 27.8| 4.7  | E                        | 2.5               | 26                          | 54.5                              |
| 7  | 63.3 | 27.0| 4.7  | E                        | 5.0               | 26                          | 62.0                              |
| 8  | 61.5 | 26.3| 4.7  | E                        | 7.5               | 26                          | 50.2                              |
| 9  | 65.0 | 27.8| 4.7  | E                        | 2.5               | 26                          | 55.0                              |
| 10 | 63.3 | 27.0| 4.7  | E                        | 5.0               | 26                          | 62.2                              |
| 11 | 61.5 | 26.3| 4.7  | E                        | 7.5               | 26                          | 52.7                              |

Based on the obtained results, it can be noted that the replacement of water with electrolyte and the introduction of sediments do not affect the consistency of cement pastes and changes their strength indicators in a limited range. However, provided investigations do not incorporate more than 7.5 % of residues. The next step was to study possibility to use 10-30 % of residues by mass.

Analysis of the obtain results (Table 4) showed that introduction of 10 % of residues by mass of alkali-activated cement significantly reduces material exploitation properties. Moreover, increasing ferritic residues content the compressive strength properties of material reduces up to 50 %. As it
shows analysis of the preliminary studies [24], in case of introducing of ferritic sediment as a filler within the range 5.5 to 7.5 % by mass (ferritic metals phases content ≥ 90 %) it is observed stabilization of strength at 43 MPa, corresponding to composition without residues incorporated. Generally the strength varies within the 5 % ranges.

Table 4. Composition and exploitation properties of alkali-activated cements using ferritic sediments.

| No | Slag | Sodium metasilicate | Soda ash | Ferritic sediments | Compressive strength, Rc, MPa, after, days |
|----|------|---------------------|----------|--------------------|------------------------------------------|
| 1  | 95   | 3                   | 2        | -                  | 13.4, 31.1, 41.3                        |
| 2  | 85.5 | 2.7                 | 1.8      | 10                 | 0.7, 5.0, 35.0                         |
| 3  | 76   | 2.4                 | 1.6      | 20                 | 0.5, 4.1, 25.0                         |
| 4  | 66.5 | 2.1                 | 1.4      | 30                 | - , 2.0, 12.5                          |

Thus, from the mechanical properties point of view, ferritic residues content in the studied alkali-activated cements is appropriate to limit not higher than 10 % by mass.

3.2. Studying the immobilizing capacity of the matrix of alkaline-activated materials relative to the heavy metal ions

The reliability of immobilization of water treatment waste can be confirmed by examining the leaching of heavy metals from the body of the cement and concrete. The study was carried out using a statistical method on samples-cylinders of height 5.0 cm and a diameter of 2.8 cm. The ratio of volume of the dispersed medium to the disperse phase volume was 10:1. We evaluated results by determining the content of Fe and Ni ions in the environment of leaching using a method of atomic adsorption spectrometry at the age of 7, 14, and 28 days. The results obtained are shown in Figure 1.

According to the obtained results, it can be stated that the primary intensity in leaching of heavy metals occurs on day 7, after which the process stabilizes. The total concentration of heavy metals is negligible, 0.32 mg/dm$^3$ for Fe and 0.28 mg/dm$^3$ for Ni.

For determination of possibility of safe immobilization of heavy metals using high incorporation of water treatment residues the composition S4 (Table 2) was used. Ferritic sediments were introduced in the quantity 10–30 % by mass of alkali-activated cement. Experimental results of leaching are shown in Table 5.

According to the given results (Table 5), leaching of heavy metal ions depends on influence of ambient media and from ferritic sediment content in the cement. It should be mentioned that for all specimen series leaching met the Permissible Limits requirements of Directive 6/278/EU. Also, in acid media it insignificant leaching Fe, Ni and Cu is recorded, but their residual concentration in eluate stays lower than the Limits. In addition, it should be mentioned that concentrations of heavy metals in elute met requirements for drink water. That is the evidence of safe chemical bonding of heavy metals in alkali-activated cement matrix (residue content less than 10 % by mass).

Thus, it was proposed to use alkali-activated cements as a matrices for utilization of galvanic waste water treatment products. It was proved that alkali-activated cements are able to bond chemically heavy metals ions in the matrix of cement. Use of such technology will make it possible to obtain safe materials for common application, meeting the technical and ecological requirements.
Figure 1. The results of leaching Fe (a, c, e) and Ni (b, d, f) from the stone of alkaline cement that included water treatment products depending on the activation method at treatment: a, b – without activation, c, d – with thermal activation, e, f – with electromagnetic activation. Content of ferritic sediments in the composition: – 2.5 % by weight; – 5.0 % by weight; – 7.5 % by weight.

Table 5. Determination of ferritic sediments stability in alkali-activated cement matrix.

| No | pH of initial eluate | Ferric sediment content in the cement composition, % by mass | Leaching of heavy metals | A, mg/kg | C_{res.}, mg/dm³ | A, mg/kg | C_{res.}, mg/dm³ | A, mg/kg | C_{res.}, mg/dm³ | A, mg/kg | C_{res.}, mg/dm³ |
|----|---------------------|----------------------------------------------------------|-------------------------|----------|-----------------|----------|-----------------|----------|-----------------|----------|-----------------|
| 1  |                     |                                                          | Fe_{total}              |          |                 | Ni^{2+}  |          | Cu^{2+}  |          | Zn^{2+}  |          |
|    |                     |                                                          | A, mg/kg               | 0.08     | 0.03            | N/D      | N/D             | N/D      | N/D             | N/D      | N/D             |
| 2  | 3.5                 |                                                          | 10 N/D                 | N/D      | N/D             | N/D      | N/D             | N/D      | N/D             | N/D      | N/D             |
| 3  |                     |                                                          | 20 N/D                 | N/D      | N/D             | 0.34     | 0.16             | 0.18     | 0.08             | N/D      | N/D             |
| 4  |                     |                                                          | 30 N/D                 | 0.18     | 0.08            | 0.44     | 0.21             | 0.30     | 0.14             | N/D      | N/D             |
| 5  | 6.6                 |                                                          | 10 N/D                 | N/D      | N/D             | N/D      | N/D             | N/D      | N/D             | N/D      | N/D             |
| 6  |                     |                                                          | 20 N/D                 | N/D      | N/D             | N/D      | N/D             | N/D      | N/D             | N/D      | N/D             |
| 7  |                     |                                                          | 30 N/D                 | N/D      | N/D             | N/D      | N/D             | N/D      | N/D             | N/D      | N/D             |
| 8  | 11.5                |                                                          | 10 N/D                 | N/D      | N/D             | N/D      | N/D             | N/D      | N/D             | N/D      | N/D             |
| 9  |                     |                                                          | 20 N/D                 | N/D      | N/D             | N/D      | N/D             | N/D      | N/D             | N/D      | N/D             |

Remark: N/D is heavy metals content out of equipment: < 0.1 mg/dm³ - Fe_{total}; < 0.05 mg/dm³ - Ni^{2+}; < 0.01 mg/dm³ - Cu^{2+}; < 0.01 mg/dm³ - Zn^{2+}.
4. Conclusion

1) High immobilizing properties of sediments obtained by different activation technologies and technological parameters of ferritization process were shown (heavy metal immobilization level after leaching is 99.96 % by mass, while for the conventional technology it is < 97.83 %). That is the evidence of safety of following application of obtained materials from the ecological point of view.
2) Alkali-activated cement compositions using galvanic wastewater treatment residues was developed. It is found that using up to 10 % by cement mass of ferritic residues artificial stone compressive strength at the age of 28 days is up to 40 MPa.
3) Environmental safety of alkali-activated cements using galvanic waste water treatment residues was investigated by leaching of heavy metal ions in neutral, acid and alkaline media. It was shown that heavy metal immobilization level in the cement with residue content 30 % by mass is higher than 99.98%, meeting the requirements of standards about limits of concentration in the water and soil.

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