


ОППЕРЕДЖЕННЯ СТАБІЛЬНОСТІ ЕЛЕКТРОЛІТУ I УСЛОВИЙ ДЛЯ ОСАЖЕННЯ ЕЛЕКТРОХРОМНИХ ПЛЕНК WO3

Для осаждения электрохромных пленок WO3 предложен гальваностатический режим: \( i= -0.2 \text{ мА/см}^2 \), 30 мин. Пленки, полученные в таких условиях, прозрачные, качественные и имеют хорошую адгезию к основе. Показано, что используемый электролит нестабильный и со временем меняет свои свойства. Для восстановления электролита предложено добавлять перекись водорода согласно рецептуре.

Ключевые слова: оксид вольфрама, осаждение электрохромных пленок, нержавеющая фольга, кислота, окис погружной.


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DEVELOPMENT OF A MINERAL BINDING MATERIAL WITH ELEVATED CONTENT OF RED MUD

Розглянуто можливість збільшення обсягів утилізації відходів виробництва глинозему – червоного шламу шляхом використання як технології сировини для виготовлення в’яжучого матеріалу низько температурного випалу типу романцемент. Показано особливості фазового складу та властивостей в’яжучих на основі систем карбонатного компоненту з полімерізованою глиною, пильковаром і червоним шламом.

Ключеви слова: червоний шлам, техногенна сировина для виготовлення в’яжучого матеріалу, фазовий склад.

1. Introduction

An increase in the volumes of practical utilization of industrial waste on a multi tonne scale is in line with the comprehensive solution to ecological problems, resource saving and development of silicate production. Solving this actual problem requires appropriate development of scientific and technical principles for the chemical technology of silicates with determining the laws relative to the influence of the concentration of varieties of technogenic
raw materials on the structure formation and properties of materials. The multi-tonnage waste of alumina production includes red mud, which, according to known research results, can be used as a technological raw material for silicate production. In particular, as an iron-containing correction component of original blends in the technology of Portland cement; however, the volumes of practical utilization of alumina production waste does not correspond to the volumes of their formation and accumulation. This predetermines the relevance of technical developments in order to solve the task of increasing the volumes of effective disposal of red mud as a technogenic raw material during large-scale production of silicate materials. Present work explores this direction in terms of binding substances.

2. The object of research and its technological audit

In the present study we examined technology of production of mineral binding materials.

Production technology of mineral binding materials is connected with the use of significant amounts of carbonate and clay raw materials of natural and technogenic origin [1, 2].

Production of the most common mineral binder, Portland cement, is characterized by considerable energy consumption at high-temperature roasting (over 1400 °C) of clinker and during its grinding with additives to the highly dispersed state. Modern requirements to resource saving underline the relevance of producing hydraulic mineral binders of low-temperature roasting (900–1200 °C) of the romancement type. These binders could become a substitution for more energy-consuming and costly Portland cement in a number of construction operations [3, 4].

Technology of manufacturing a mineral binder of the romancement type for a long time has been based, mainly, on the application of one kind of a raw material – marl, whose distribution is limited [5, 6]. Extending the varieties of potential raw materials of natural and technogenic origin necessitates improvement of the procedure for determining and optimization of the composition of multicomponent blends for making a hydraulic mineral binder of low-temperature roasting. This contributes to the comprehensive solution of problems on resource saving and chemical technology of silicates.

3. The aim and objectives of research

The aim of present research is to develop mineral binding materials of low-temperature roasting from raw material blends with an elevated content of red mud. This corresponds to the comprehensive solution to the tasks on expanding raw material base of production and on disposing the industrial waste.

To accomplish the set aim, the following tasks had to be solved:

1. To determine dependence of the possible content of red mud in a raw material blend on the qualitative composition and quantitative ratio of the components.

2. To establish the features of formation of phase composition of the binder from the blends with a maximum content of red mud at roasting with the minimization of maximum temperature to 1100 °C.

3. To perform technological testing of the created binding substances with an elevated content of waste from alumina production as a technogenic raw material.

4. Research of existing solutions of the problem

Expanding raw material base for the production of silicate materials is the subject of numerous studies by scientists. The emphasis in this case is on using in technological processes wastes from other industries as a technogenic raw material [7, 8]. The biggest practical achievement in this direction has been the use of waste products of ferrous metallurgy – granulated blast furnace mud and waste from thermal generation – ash from TES as the components of slag-Portland cement and composite cements [9, 10].

Among other multi-tonnage wastes, red mud attracts attention as a byproduct of processing bauxites into alumina by the Bayer's method in nonferrous metallurgy [7, 11–21]. Employing the indicated industrial method, during treatment of bauxites with caustic soda, approximately 35–40 % of the original ore are wasted, forming alkaline red mud with a concentration of solid phase at 15–40 %. As a result, during production of 1 tonne of alumina, 0.8–1.5 tonne of red mud is created [11, 12]. There are data on that at annual world production of 101 million tonnes of alumina, there are 120 million tonnes of red mud created [13], and including about 1 million tonne in Ukraine during work of the Mykolayiv Alumina Plant and Zaporizhia Aluminum Plant.

Large amounts of red mud accumulation pose an environmental hazard that emphasizes the relevance of developing its disposal [11, 14] taking into account the physical-chemical properties and effects on the rheological characteristics of aqueous systems and the properties of finished product [15, 16]. In this case, from a point of view on the resulting effectiveness of solving this problem, it is promising to utilize red mud in large-scale silicate production. This is shown by relevant development in the production of ceramics with plastic formation, including chemically resistant, ceramic tiles and finishing materials [17, 18]. Regarding the development on the use of red mud in cement technology, it is mainly related to the introduction of a small amount of 3–5 % by weight of this waste into raw material blends as a correcting iron-containing additive in accordance with the regulated standards for existing production [19–21].

Thus, results of an analysis lead to the conclusion that most techniques concerning the disposal of red mud are aimed at its use in the known existing technological processes, as is the case in the production of Portland cement. In the given production, the amount of waste that is introduced into original blend is limited by the accepted composition of carbonate and clay components. It is obvious that the choice of the most suitable technical solution to significantly increase the amount of waste as a technogenic raw material should be based on the development and implementation of new compositions of raw material blends with appropriate changes in the technological rules of manufacturing.

5. Methods of research

In order to accomplish the set aim, we used in present study a combination of computer calculations with
the new software, modern physical-chemical methods of analysis and standardized testing of the properties of raw materials and binding materials.

Expansion of varieties of potential raw materials of natural and technogenic origin necessitates improvement of the procedure for determining and optimization of the composition of multicomponent blends for manufacturing a hydraulic mineral binder with the use of computer calculations [22, 23].

In the present work, in order to develop binders of low-temperature roasting, we applied the new computer software «RomanCem» [24]. In this case, in line with the established technique for romacement, composition of mineral binder is calculated using the assigned value of hydraulic module $HM = 1.1–1.7$ that characterizes ratio between the most important oxides by formula:

$$HM = \frac{CaO}{SiO_2 + Al_2O_3 + Fe_2O_3}.$$

The principle of operational optimization of a problem solution based on software comes down to the following:

1. Tabular data are entered with a number of chemical compositions of probable raw material components.
2. The value of hydraulic module $HM$ is assigned.
3. By using established formula of calculation, all the combinations of two or three components are determined, which ensure the assigned values of $HM$. Thus, at any sufficiently large raw material base, it is possible to quickly determine rational ratios of the components in the original raw material blend.

Solving the problem is carried out by the software «RomanCem», which is written in the programming language C#. It can be deployed on any PC running Windows operating system, starting from version NT.

Chemical composition of any amount of potential raw materials is recorded as source data in the file Components.txt, in the format CSV. It can be compiled and corrected in any text editor or with the use of Excel spreadsheet.

The software performs calculation for variants with a 2- or 3-component blend. The variant is selected by the user after launching the program under interactive mode through the window on the display (Fig. 1).

After selecting the option for calculation, the user is given a choice to enter the assigned parameter of computations – number $HM$, then it is required to press <Enter>. If the number is entered correctly, button Calculate is enabled; pushing it initiates calculation of the variant. The software informs the user about the end of the computation by displaying a window with the message Done. If the variant is selected in the list, the software generates source text file that contains a composition of possible raw material blends (% by weight of components), chemical composition of the blend and the binder made of it (% by weight of oxides), corresponding number $HM$. File name denotes results of particular calculation.

Accuracy of the obtained results depends only on the magnitude of error in the source data that are entered to PC, that is, on the accuracy of determining a chemical composition of possible raw materials.

The developed software «RomanCem» is employed in the present study for quantitative determining of the composition of raw material blends of a mineral binder of low-temperature roasting at varied content of red mud. In this case, operating speed of calculations allowed us to obtain considerable amount of analytical information.

X-ray phase analysis of the samples of raw materials and the binder (powder preparations) was carried out using the diffractometer DRON-3M manufactured by NNP «Burevestnik», Russian Federation (Cu Kα radiation 1-2, voltage 40 kV, current 20 mA, speed 2 deg/min.).

6. Research results

In order to identify the possibility of increasing the volumes of disposal of red mud in the technology of binding materials, we analyzed compositions of raw material blends for the production of material of the romacement type.

An analysis of the results obtained revealed that in the interval of $HM = 1.1–1.7$ possible concentration of red mud in the composition of raw material blends significantly depends on the types and quantitative ratio of other components. In this case, there is an inversely proportional dependence of the concentration of mud and the number of hydraulic module on the content of other component.

Based on computer calculations, we determined that a three-component blend based on the system chalk – kryvynska clay – red mud might possibly contain the latter in the amount:

- at $HM = 1.7$ from 2.4 to 18.4 % by weight;
- at $HM = 1.1$ from 2.4 to 29.1 % by weight, and increases with a decrease in the hydraulic module and the amount of clay (Fig. 2).

![Fig. 1. Interactive window on the display of a personal computer](image1)

![Fig. 2. Dependence of the concentration of red mud ($C_{\text{mud}}$) on the hydraulic module ($HM$) at the content of kryvynska clay: a – 10 % by weight; b – 25 % by weight](image2)
In a three-component blend based on the system chalk – quartz powder – red mud, possible content of the latter is 15.6 to 27.7 % by weight and increases with a decrease in the hydraulic module and the amount of quartz powder (Fig. 3).

![Fig. 3. Dependence of the concentration of red mud (Crm) on the hydraulic module (HM) at the content of quartz powder 10 %](image)

The blends chosen for the research with maximal possible concentration of red mud at 27.0–27.5 % by weight, based on the systems of chalk – clay and chalk – quartz powder, at the same quantitative ratio of components, are characterized by differences in the chemical composition (Tables 1, 2).

### Table 1

<table>
<thead>
<tr>
<th>Code of blend</th>
<th>Component content, % by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>chalk</td>
</tr>
<tr>
<td>Чг</td>
<td>63.0</td>
</tr>
<tr>
<td>Ч10</td>
<td>62.5</td>
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</tbody>
</table>

At the same content of CaO, Ч10 with quartz powder is different from Чг with a polymineral clay by the larger amount of SiO2 (12.6 versus 9.1 % by weight) and the ratio SiO2:Al2O3 (2.4 versus 1.3) with a somewhat lower content of Fe2O3 and MgO.

After roasting the examined blends, resulting binders differ in chemical composition and, respectively, in the values of silica and alumina modules (Table 3). At generally low numbers of the specified modules, the sample Чг with polymineral clay is characterized by somewhat larger alumina number (0.43 versus 0.34), while the sample Ч10 with quartz powder – by alumina (0.62 versus 0.38).

![Fig. 4. Diffractogram of material from blend Ч10 after roasting at 1100 °C](image)

The obtained results of X-ray phase analysis indicate certain differences in the physical-chemical transformations during roasting of the examined blends, which, at the same content of red mud, is associated with reactive capacity of rock-forming minerals of clays and quartz powder (Fig. 4, 5).
Thus, the sample Чг with polymineral clay, compared to the sample Ч10 after roasting, is characterized by the larger development of crystalline phases of silicates and calcium alumina ferrite. The sample Ч10 with quartz powder differs by the larger development of crystalline phases of quartz and calcium aluminates.

Obtained results of testing the samples of examined materials after roasting at maximal temperature 1100 °C testify to certain differences in their binding properties.

According to the classification of DSTU B V.27-91-99 [25], by the speed of setting, samples of binder belong to the quick-setting group (starting period from 15 to 45 minutes) whose typical representatives include anhydrite and alumina cement and slag-alkaline binders (Table 4).

Table 4

<table>
<thead>
<tr>
<th>Code of blend</th>
<th>Milling fineness (residual in sieve 0.168 mm, %)</th>
<th>Setting periods, min.</th>
<th>Compressive strength, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Start</td>
<td>Finish</td>
</tr>
<tr>
<td>Чг</td>
<td>7</td>
<td>20</td>
<td>190</td>
</tr>
<tr>
<td>Ч10</td>
<td>8</td>
<td>80</td>
<td>50</td>
</tr>
</tbody>
</table>

However, it is obvious that when using polymineral clay in the original blend, there is an increase in the time of finish and in general of the process of setting: at the same time of the start of setting, finish of the setting process of the sample Чг is extended to 190 against 50 min. for Ч10.

7. SWOT analysis of research results

Strengths. Among the strengths of the present study, we should note the results obtained in determining new compositions of source raw material blends for making a mineral binder of low-temperature (1100 °C) roasting with an elevated (27–27.5 % by weight) content of waste from alumina production – red mud. This provides a comprehensive solution to the issues of ecology (due to reduced volumes of waste accumulation), resource saving (through a replacement with waste of part of the raw materials of natural origin), and technology of binders (due to obtaining a product of the romancement type with improved indicators of properties).

Weaknesses. Weaknesses of the present study are related to the fact that the technique is based on the application of one of the known carbonate components – chalk. This necessitates additional procedures in the potential use of such common carbonate components as limestone, marl, etc.

Opportunities. Additional possibilities to ensure accomplishment of the goal of the research might include the features of using red mud from other manufacturers of alumina, in addition to the selected samples from the enterprises of Ukraine. In this case, depending on the chemical composition of the original raw material (bauxite) and parameters of processing bauxite into alumina, a variation is possible in the composition of red mud and, accordingly, its influence on the properties of binding material.

Threats. Difficulties in the implementation of prepared techniques are related to the following factors.

The first of them is management risks when investing into a new technological line to manufacture a mineral binder with an elevated content of red mud in the absence of confirmed demand for the new product in the market. A lack of the high result guaranteed in advance is a limiting factor for company top managers. Such risk is certainly justified given the fact that promoting a new product in the construction market requires time and additional marketing budget.

The second factor is the risks associated with the need to guarantee the supply of binders of red mud with regulated technical specifications by chemical composition and moisture content to the would-be production.
Thus, the SWOT-analysis of results of our work allows us to define main directions to successfully accomplish the set goal. They include:

- application of the new software for the calculation and analysis of compositions of the raw material blends with maximal possible content of Red mud;
- taking into account the features of phase composition of the binder, which forms at roasting and determines resulting properties of the product.

8. Conclusions

1. We determined inversely proportional dependence of the concentration of red mud ($C_{rm}$) in 3-component blends on the type and content of other component and the number of hydraulic module of a binder IM. In the blends based on the system chalk-clay, $C_{rm}$ increases from 2.2 to 27.3 % by weight with decreasing content of clay from 35.0 to 10 % by weight, at $NM = 1.1$ from 2.2 to 17.2 % by weight with decreasing content of clay from 25.0 to 10.0 % by weight. In the blends based on the system chalk-quartz powder, $C_{rm}$ increases from 15.6 to 27.7 % by weight with decreasing content of quartz powder from 10.0 to 20.0 % by weight, at $NM = 1.1$, it is 16.7 % by weight at the content of quartz powder 10 % by weight and $NM = 1.7$.

2. We established features in the formation of phase composition of the binder from the blends with a maximal content of red mud at roasting with a maximal temperature of 1100 °C, which is associated with reactive capacity of rock-forming minerals of clay and quartz powder. The material based on the system chalk-clay is characterized by a larger development of crystalline phases of silicates and calcium alumina ferrite, based on the system chalk–quartz powder – differs in a greater development of crystalline phases of quartz and calcium aluminates.

3. Results of technological testing of the created binders with the introduction of 27–27.5 % by weight of red mud in the compositions of raw material blends after roasting at 1100 °C revealed that they belong to the quick-setting group (starting period from 15 to 45 minutes). Typical representatives of this group are anhydrite and alumina cement, and by compressive strength of 18–22 MPa, they exceed indicators of romancement (5–10 MPa).

Increasing the volumes of practical use of multi-tonnage industrial waste – red mud – contributes to the comprehensive solution of the issues on ecology, resource saving and technology of production of silicate building materials.

References


РАЗРАБОТКА МІНЕРАЛЬНОГО ВЯЖУЧЕГО МАТЕРІАЛА С ПОВЫШЕНИМ СОДЕРЖАНИЕМ КРАСНОГО ШЛАМА

Рассмотрена возможность увеличения объемов утилизации отходов производства глинозема – красного шлама путем применения как техногенного сырья для изготовления вяжущего материала низкотемпературного обжига типа романцемента.

Показаны особенности фазового состава и свойств вяжущего на основе систем карбонатного компонента с полиминеральной глиной, пылекварцем и красным шламом.

Ключевые слова: красный шлам, техногенное сырье для изготовления вяжущего материала, фазовый состав.

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