Synthesis of high alumina cement based on metallurgy wastes

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Abstract. In this paper efficient types of binders – high alumina cements are considered. The shortage of industrial alumina and its high cost constrain the development of high-aluminate cements production. Waste from a number of metallurgical industries can be used as raw materials for their production. The aim of the investigation was to study the influence of metallurgical waste on the mineral formation of aluminate clinker and the properties of cement based on it. As a replacement of industrial alumina, dust of gas cleaning plants of aluminum electrolysis and slag of ferroalloys production were used. Aluminate clinkers were obtained in a laboratory furnace at a temperature of 1200-14000 ºC. Mineral composition of clinkers was studied using chemical analysis, XRD and optical microscopy. The cements were obtained by grinding clinkers in a laboratory mill, then they tested for strength at the age of 28 days. It was established that the chemical and phase composition of dust allows to use it as a raw component in the production of high alumina cement. The investigations showed that the properties of alumina cement based on slag ferrovanadium production improved. Hydration activity of cement increases especially in the early period of its hydration.

1. Introduction

Alumina cements are one of the highly effective types of binders. These cements are widely known for their remarkable properties and, above all, high initial strength, heat resistance and resistance to sulfate medium [1,2]. The strength of alumina cement at the age of 3 days corresponds to the 28-day strength of Portland cement. Rapid hardening with the release of a large amount of heat allows it to be used for winter concrete industry. In comparison with Portland cement aluminate cement has greater resistance to sulfate and carbonate corrosion. It is the basis for the production of expansive and selfstressing cements, as well as many special cements.

Alumina cements are used in the construction of waterproof structures, drilling of oil and gas wells, elimination of accidents, repairs after fires, urgent construction of foundations for cars, restoration of destroyed structures, construction of objects exposed to mineralized water and sulfur dioxide [1,2].

Another important area of application of aluminate cements is the production of refractory concretes. In this case, cement with a high content of aluminum oxide – high aluminate cement (HAC) [2-7] is used.
However, the shortage of technical alumina and its high cost constrain the development of HAC production [8]. At present, industrial waste containing alumina oxide is showing an increased interest, since their use makes it possible to produce aluminate cements [9-14].

At the number of metallurgical plants there are waste that can be used as a raw material for the production of high alumina cement. These wastes contain, in addition to calcium and aluminum oxides, impurity oxides of other elements, which increase the reactivity of the raw material thanks the formation solid solutions with calcium aluminates. Depending on the CaO/Al₂O₃ ratio in the CaO - Al₂O₃ system, the following minerals are formed: Ca₃Al₂O₆, Ca₁₂Al₁₄O₃₃, CaAl₂O₆, CaAl₄O₇ and CaAl₁₂O₁₉. High technical properties of aluminate cements are provided by the minerals of calcium monoaluminate (CaAl₂O₄) and calcium dialuminate (CaAl₄O₇) [1,2,15-18]. To obtain of these minerals in clinker composition using industrial wastes is an urgent and economically attractive task.

The aim of this research was to study the effect of metallurgical production wastes on the mineral formation of alumina clinker and cement properties based on it.

2. Experimental procedure

2.1. Materials and sample preparation
The experiments were carried out in laboratory conditions. For laboratory studies, mixtures were prepared for the synthesis of alumina clinkers using chalk, dust from gas cleaning plants for the electrolysis of aluminum, industrial alumina and slag from the production of ferrovanadium as the raw materials. The chemical composition of the raw materials are presented in Table 1.

|                | Natural chalk | Alumina | Gas cleaning dust | Vanadium Slag |
|----------------|---------------|---------|-------------------|---------------|
| Loss of ignition, % | 42.65         | –       | 20.85             | –             |
| SiO₂, %         | 1.23          | 0.2     | 1.0               | 1.3           |
| Al₂O₃, %        | 0.6           | 99.48   | 75.05             | 67.4          |
| CaO, %          | 54.5          | 0.32    | –                 | 16.3          |
| MgO, %          | 0.4           | –       | –                 | 10.5          |
| SO₃, %          | 0.2           | –       | –                 | 2.0           |
| Na₂O, %         | 0.20          | –       | 2.1               | 0.9           |
| K₂O, %          | 0.18          | –       | 0.13              | 0.9           |
| Fe₂O₃, %        | 0.4           | 0.1     | 0.95              | 0.45          |
| V₂O₅            | –             | –       | –                 | 2.6           |

The mixture was prepared by joint grinding of raw materials in a laboratory ball mill for 60 minutes. Then prepared cylinder samples measuring 20 mm in diameter and 20 mm in height by pressing under a pressure of 20 MPa. The prepared samples were burned at 1100–1400 °C in a laboratory furnace for 1 hour. The burned samples were ground in a laboratory mill to get a Blaine specific surface area of 3800 cm²/g.

2.2. Methods
Clinker samples were examined by chemical analysis, X-ray diffraction and optical microscopy. The change in the mineralogical composition of clinker, the crystallization of minerals depending on the ratio of the minerals CA and CA₂ are studied. To determine the compressive strength of cements from laboratory clinkers, they were mixed with the necessary amount of water, and then samples with a size of 20x20x20 mm were prepared. Samples hardened in water for 28 days.
3. Experimental results and discussion

3.1. High alumina cement using gas cleaning dust

Optical microscopy analysis showed that the phase composition of alumina present in the gas cleaning dust is represented by the $\gamma$-form and transitional forms from $\gamma$-$\text{Al}_2\text{O}_3$ to $\alpha$-$\text{Al}_2\text{O}_3$ which are closer in optical properties to $\alpha$-$\text{Al}_2\text{O}_3$. XRD analysis also revealed the presence of $\gamma$ and $\alpha$-$\text{Al}_2\text{O}_3$. Infrared spectroscopy showed mainly $\alpha$-form of alumina, which is explained by the predominance and optical properties of transitional form. Dust is a homogeneous and fine material (the residue on a 008 sieve is less than 16%).

To confirm the feasibility of dust use instead of industrial alumina to obtain HAC, their chemical activity was compared. For this aim the assimilation of CaO in mixtures based on alumina and dust was compared. Experiments shows that dust gas treatment plants react with CaO more actively than alumina, which can be explained by the presence of impurity elements in the waste (Figure 1).

![Figure 1](image1.png)  ![Figure 2](image2.png)

**Figure 1.** The dependence of CaO$_{\text{free}}$ in the samples on the isothermal firing at 1400 °C.

**Figure 2.** The change in the intensity of the peaks CA ($d = 2.9773\text{Å}$) and CA$_2$ ($d = 3.5107\text{Å}$) depends on the calculated phase composition of the clinker.

The phase composition of calcination products at 1400° C with an exposure during 1 h corresponds to CA and CA$_2$, which is confirmed by X-ray diffraction. With an increase in the content of $\text{Al}_2\text{O}_3$ in the raw mix, the proportion of lower basic minerals increases, which is accompanied by an increase in the heat resistance of the material. Figure 2 shows of the intensity the dependence of the main diffraction peaks of CA ($d = 2.9773\text{Å}$) and CA$_2$ ($d = 3.5107\text{Å}$) depending on the calculated composition of the clinker.

Clinker compositions that lie in the area of 50% CA and 50% CA$_2$ are the most interesting from a practical point of view. Cements of such composition should provide high strength characteristics and sufficient heat resistance. To determine the optimal cement composition, the main indicator was selected compressive strength of the samples at the age of 28 days. The dependence of strength on the phase composition of clinker is shown in Figure 3.

Thus, the studies allow us to conclude that the chemical and phase composition of dust, its higher chemical activity than industrial alumina, allow it to be used as a raw material for the preparation of HAC.
3.2. High-alumina cement using ferrovanadium slags

Slag from ferrovanadium smelting is a granular material with irregularly shaped pieces. Slag color is gray-green. The mineral composition of the slag according to XRD is (%): CA₆ ~ 15, CA₂ ~ 50, CA ~ 10, spinel ~ 10, vitreous phase ~ 10.

The determination of slag hydration activity showed that the presence of CA₂ in the slag provides it with a slight strength after 3 days of hardening, but at one day age the cement based on it has very low strength. Therefore, slag in its pure form cannot be used for the production of either high alumina or high alumina cement. Based on the obtained results, it was necessary to investigate the possibility of using ferrovanadium slags as a component of the raw mix in the synthesis of alumina and high alumina cements.

To determine the effect on the kinetics of mineral formation, a factory raw mixture composed of chalk and industrial alumina (mixture K) was used, and a mixture in which part of the alumina (up to 30%) was replaced with ferrovanadium slag (mixture F). The mixture was burned at a temperature of 1200-1400° C. Isothermal exposure time was 60-120 minutes. The completeness of the mineral formation reaction was determined by the presence of CaO free and free Al₂O₃. Based on the obtained data, reaction rate constants were calculated using the known formulas [2]. Table 2 presents the results of the experiments.

Analysis of the data in Table 2 shows that the synthesis of high-alumina cement minerals depends on both the duration and the burning temperature, and to a greater extent on the temperature.

Table 2. Kinetics of the interaction of CaO and Al₂O₃ in an additive-free mixture.

| T, °C | Time, τ, min | The degree of binding, in fractions of a unit | Speed constant Kᵣ·T⁻³ |
|-------|--------------|---------------------------------------------|-----------------------|
|       |              | Mixture K | Mixture F | Mixture K | Mixture F | Mixture K | Mixture F |
| 1200  | 60           | 0.286     | 0.486     | 6.0       | 9.0       |
|       | 90           | 0.319     | 0.519     | 7.5       | 9.5       |
|       | 120          | 0.345     | 0.545     | 8.1       | 10.1      |
| 1300  | 60           | 0.520     | 0.720     | 19.5      | 23.5      |
|       | 90           | 0.585     | 0.750     | 21.6      | 24.6      |
|       | 120          | 0.600     | 0.770     | 22.7      | 25.7      |
| 1400  | 60           | 0.805     | 0.905     | 29.3      | 39.3      |
|       | 90           | 0.832     | 0.921     | 30.7      | 40.7      |
|       | 120          | 0.857     | 0.957     | 31.8      | 41.8      |
This indicates that the process of mineral formation is largely dependent on the rate of diffusion of ions. Consequently, the earlier the melt appears in the system, the faster the mineral formation reactions will proceed. According to DTA, the appearance of micro alloys in the initial mixture is observed at 1270 °C, respectively, at 1300 °C the faster binding of aluminum oxide occurs. The role of the liquid phase in the reaction rate of the interaction between CaO and Al₂O₃ is especially noticeable when V₂O₅ is introduced into the composition of the raw mix. Micro-melt in the mixture by addition of vanadium oxide appears already at 1100 °C, respectively, the degree of binding of aluminum oxide is accelerated 1.7 times, and at a temperature of 1400 °C it is 95.7%, while in a mixture without the addition of vanadium oxide, this value is 85.7%.

The obtained data indicate the acceleration of the reaction of mineral formation in the presence of slag containing V₂O₅, that is, vanadium oxide plays the role of a mineralizer. This is also confirmed by the results of XRD analysis.

Studies have shown that during the calcination of the mixture K, the primary product of the interaction of CaO formed during the decomposition of calcium carbonate with aluminum oxide is C₁₂A₇.

![Figure 4. The change in the phase composition of the cake during firing of the mixture K, depending on the firing temperature.](image)

As the temperature increases, the rate of diffusion of the Ca²⁺ cation and the anionic complex AlO₄⁻ increases, resulting in a certain quantity of CA.

With an increase in the firing temperature, the amount of CA increases, along with which CA₂ is formed. According to XRD data up to 1300 °C, the formation of CA and CA₂ proceeds in parallel, a further increase in temperature accelerates the formation of CA₂, but full absorption of alumina is not achieved even at 1400 °C. The corresponding sintered specimen is a polyphase product (Figure 4).

Introduction to the composition of the slag mixture production of ferrovanadium accelerates the process of interaction of calcium carbonate with alumina.

Even with the introduction of 10% slag into the raw mix at the same temperature and the firing time, the amount of CA₂ increases by 4% by weight in the burned sample. The number of C₁₂A₇ and free alumina is reduced. It was revealed that as the amount of slag increases to 40%, the amount of CA₂ and CA increases in the mixture during burning, while reducing the amount of alumina and C₁₂A₇. The impurities contained in the slag not only reduce the appearance of the eutectic melt, but also modify the clinker phases. This provides an increase the strength of cements (Table 3).

| Cement | Setting time, hour – min | Compressive strength, MPa |
|--------|--------------------------|---------------------------|
|        |                          | 6 h | 1 day | 3 days | 7 days | 28 days |
| K      | 8-15                     | 10-45 | - | 18 | 49 | 64 | 70 |
| F      | 4-00                     | 5-35 | 25 | 41 | 62 | 69 | 74 |
Analysis of the obtained data allows us to conclude that the use of ferrovanadium slag as a substitute for part of industrial alumina in the raw mixture allows improving the properties of the HAC: reduce the setting time and increase the strength, especially in the early period of hardening.

4. Conclusion

The effect of metallurgical production wastes on the mineralization of aluminate clinker and the properties of cement based on it was studied. According to the research, the following conclusions were made.

It has been established that the higher chemical activity of dust from gas cleaning plants for the electrolysis of aluminum than industrial alumina allows it to be used as a raw material in the synthesis of high aluminate cements.

Introduction to the composition of raw mixes for the synthesis of calcium aluminates wastes of metallurgical production contributes to the early appearance of the melt, which is accompanied by accelerated diffusion of ions and accelerated synthesis of calcium aluminates.

It was established that vanadium oxide V\textsubscript{2}O\textsubscript{5}, contained in slags from the production of ferrovanadium, in small quantities during the synthesis of the minerals CA and CA\textsubscript{2} forms solid solutions with them. As a result of flowing ion exchange at high temperatures of synthesis, solid solutions of substitution are formed, which is accompanied by a change in the parameters of the crystal lattice of calcium aluminates and an increase in their hydration activity.

An increase in the hydration activity of the CA and CA\textsubscript{2} minerals in the composition of aluminate clinker increases the properties of high aluminate cement. The hydration activity of high aluminate cement increases, especially in the early period of its hydration.

Replacing industrial alumina with dust from gas cleaning plants for the electrolysis of aluminum and slag from the production of ferroalloys reduces the shortage of raw materials for the production of high-alumina cement and solves the problem of recycling solid waste.

References

[1] Kouznetsova T V 1986 *Alumina and sulphoaluminate cements* (Moscow: Strojizdat) p 209
[2] Kouznetsova T V and Talaber J 1988 *Aluminate cement* (Moscow: Strojizdat) p 272
[3] Alonso M C, Vera-Agullo J, Guerreiro L, Flor-Laguna V, Sanchez M and Collares-Pereira M 2016 Calcium aluminate based cement for concrete to be used as thermal energy storage in solar thermal electricity plants *Cement and Concrete Research* 82 74–86
[4] Yulong Wang, Boquan Zhu, Xiangcheng Li, Pingan Chen 2016 Effect of dispersants on the hydrate morphologies of spinel-containing calcium aluminate cement and on the properties of refractory castables *Ceramics International* 42(1) part A pp 711–720
[5] Wasim Khaliq and Hammad Anis Khan 2015 High temperature material properties of calcium aluminite cement concrete *Construction and Building Materials* 94 475–487
[6] Heikal M, Radwan M M and Al-Duaij O K 2015 Physico-mechanical characteristics and durability of calcium aluminite blended cement subject to different aggressive media *Construction and Building Materials* 78 379–385
[7] Krivoborodov Y R, Samchenko S V and Kuznetsova T V 2018 Structural Changes in Refractory Calcium Aluminate Cement Concrete *Refractories and Industrial Ceramics* 59(2) 151–155
[8] Krivoborodov Y R and Boyko A A 2011 Influence of mineral additions on hydration of alumina cement *Technique and technology of silicates* 18(4) 12–15
[9] Arbi K, Palomo A and Fernández-Jiménez A 2013 Alkali-activated blends of calcium aluminite cement and slag/diatomite *Ceramics International* 39(8) 9237–45
[10] Mladenović A, Mirtić B, Meden A and Serjun V Z 2016 Calcium aluminite rich secondary stainless steel slag as a supplementary cementitious material *Construction and Building Materials* 116 216–225
[11] Ewais E M M, Khalil N M, Amin M S, Ahmed Y M Z and Barakat M A 2009 Utilization of aluminum sludge and aluminum slag (dross) for the manufacture of calcium aluminate cement *Ceramics International* **35**(8) 3381–88

[12] Heikal M, Morsy M S and Radwan M M 2005 Electrical conductivity and phase composition of calcium aluminate cement containing air-cooled and water-cooled slag at 20, 40 and 60 °C *Cement and Concrete Research* **35**(7) 1438–46

[13] Samchenko S V, Krivoborodov Y R and Burlov I Y 2017 Usage aluminiferous waste in the production of aluminates cements *Proc. 17th Int. multidisciplinary scientific geoconference – SGEM 2017* (Bulgaria) **17**(62) 465–472

[14] Samchenko S V, Krivoborodov Y R, Burlov I Y and Krivoborodova S Yu 2018 Sulfoaluminate cements based on technogenic waste *Proc. 18th Int. multidisciplinary scientific geoconference – SGEM 2018* (Bulgaria) **18** 355–362

[15] Midgley H G and Ryder J F 1977 The relationship between mineral composition and strength development of high alumina cement *Cem. Concr. Res.* **7** 669–672

[16] Klaus S R, Neubauer J and Goetz-Neunhoeffer F 2013 Hydration kinetics of CA₂ and CA – Investigations performed on a synthetic calcium aluminate cement *Cement and Concrete Research* **43** 62–69

[17] Yongpan Tian, Xiaolin Pan, Haiyan Yu and Ganfeng Tu 2016 Formation mechanism of calcium aluminate compounds based on high-temperature solid-state reaction *Journal of Alloys and Compounds* **670** 96–104

[18] Di Zhang, Xiaolin Pan, Haiyan Yu and Yuchun Zhai 2015 Mineral Transition of Calcium Aluminate Clinker during High-Temperature Sintering with Low-lime Dosage *Journal of Materials Science & Technology* **31**(1) 2 1244–50