Hydrocarboaliminate calcium application in aluminum processing for production of special cement brands

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Abstract. The possibility of applying hydrocarboaliminate calcium, synthesized in aluminum processing for production of special cement brands as by-products in a complex processing of nepheline raw material, is justified in this article. Basic technical characteristics of new products are provided.

1. Introduction
The principles of applying industrial hydrocarboaliminate calcium (HCAC – 4CaO·Al₂O₃·mCO₂·11H₂O) and theoretical possibility of new product development in a complex processing of nepheline raw material were first justified in works [1-3].

The analysis of the above mentioned works suggests that new processing ways of by-products in a complex processing of nepheline raw material are:

1. interaction between Ca(OH)₂ and sodium-aluminate solution (NaAlO₂) after the manner suggested by Mining University [4];
2. interaction between calcium with gypsum and Al(OH)₃;
3. possible substitution of hydrocarboaliminate calcium for product of interaction between HCAC and SiO₂ - under saturated hydrogarnet Ca.
4. thermal dissociation of hydrogarnet and hydroaliminate calcium.

2. Interaction in the system «4CaO·Al₂O₃·mCO₂·11H₂O – CaSO₄·2H₂O – H₂O»
Synthesized hydrocarboaliminate calcium irrespective of CO₂ content interacts with gypsum according to the formula almost equally:

\[
4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot0,5\text{CO}_2\cdot11\text{H}_2\text{O} + 3(\text{CaSO}_4\cdot2\text{H}_2\text{O}) + \text{aq} \rightarrow \\
3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot3\text{CaSO}_4\cdot31\text{H}_2\text{O} + \text{CaCO}_3 + \text{aq.}
\]  

(1)

Up to 100% of gypsum hardens in the hydrated prows within 6 hours at 60°C. Initial materials are not found neither at indoor temperature nor at elevated temperature while hydrated within more than 24 hours. Increasing of temperature influences the speed of gypsum hardening only within the first 2 hours of the interaction.

Solid body volume is increased by about 10% within the first 6 hours as a result of ingredient interaction; then it remains practically unchanged.
Compositions of self-stressing cement, oilwell cement, rapid hardening cement and hermetic were suggested as the results of theoretical researches and experiments [3, 5]. However, direct using of the above mentioned results for producing of sulfonic carboaluminate mineralizer in a processing of cement clinker by means of burning of nepheline sludge and limestone with corrective additives failed.

The technology of the new mineralizer bases on the reaction (1), that contains phosphogypsum as sulfated ingredient and HCAC as a part of nepheline sludge (ca. 2%).

Attempts of using proper phosphogypsum as a mineralizer were initiated in the middle of the twentieth century in the workshops of the cement production at Volhov aluminum plant (Russia), but all of them were unsuccessful. The reason was lack of theoretical grounds about the mineralizer with HCAC. However, later theoretical knowledge was received, but it did not solve practical problems. It has been found that if we add phosphogypsum at the stage of preliminary nepheline crushing, it does not give any positive effect. The effect increases that if we transfer phosphogypsum to sludge-limestone stock two or three times.

The research suggests that interaction between HCAC and phosphogypsum at the preliminary nepheline crushing goes according to the topochemical reaction on the surface producing low-basic sulfoaluminate:

\[
4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 0.5\text{CO}_2\cdot 11\text{H}_2\text{O} + 0.5\text{CaSO}_4 + \text{aq} \rightarrow 4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 0.5\text{SO}_2\cdot 12\text{H}_2\text{O} + 0.5\text{CaCO}_3 + \text{aq.} \tag{2}
\]

The stabilizer of low-basic phase is a base adsorbed on the hydrocarboaluminate surface. Bases transform into a liquid phase at the stage of preliminary nepheline crushing, and further it does not affect the reaction (1) producing ettringite; then phosphogypsum is added in sludge-limestone stock.

The method for producing sulfo-carboaluminate mineralizer was introduced on the cement production plant in Pikalyovo (Russia). This technology provided the following characteristics: stable high quality of producing portland cement; increasing compressive strength by 3-4MPa; jumping of lining performance in a clinker-forming zone from 45 to 180 days; decreasing fuel consumption by 1%; best producing of clinker corns; simplifying of the automation process for technical control of cement kiln.

The technology of rapid hardening cement (type «Rapid-SFS») was developed based on the reaction (1).

The regular clinker from the cement plant, calcium sulfate dehydrate and hydrocarboaliminate calcium of industrial production were used in the experiments. HCAC and gypsum were batched at the rate of 2-2.5%. Rapid hardening cement was received in a laboratory conditions. Strength of this cement was 24MPa within the first 24 hours, on the 3rd day – 38MPa, on the 7th day – 48.5MPa. It is better than characteristics of the rapid hardening cement of type «Rapid-SFS» by ca. 20-25%.

This technology was verified in experimental-industrial conditions; as a result 500t of rapid hardening cement were produced. However, the characteristics of industrial produced cement were lower. Strength of this cement was 18 MPa within first 24 hours, on the 3rd day – 32 MPa, on the 7th day – 42.6 MPa without contraction. It is similar to characteristics of the rapid hardening cement of type «Rapid-SFS».

Comparative analysis of laboratory and experimental-industrial samples showed following results: 2-2.5% HCAC additive to clinker with the matched amount of gypsum leads to producing an additional quantity of HCAC-3 during hydration. More quantity of HCAC-3 causes expansion properties of hardening cement structures.

Analysis of cement expansion properties with HCAC small additives showed that contraction is missing. It has been believed that initiation of negligible strain broadening at early stages in the hardening process of new cements provides an opportunity to fully relax inherent stresses (ca. 0.05%) and to enhancement strength in cements (especially at early stages of hydration). The strength enhancement at early stages of hardening in comparison with straight cement exceeds by 10-12 MPa.
(laboratory results) and by 6 MPa (experimental-industrial results); after 28 days – by 8 MPa and by 4 MPa respectively.

Comparative analysis showed that decreasing of strength characteristics of rapid hardening cements at the experimental-industrial stage associates with rougher clinker grinding, that is organized within an open cycle in industrial conditions. On the basis of the researches practical use of clinker grinding in a close cycle is recommended. It increases the specific surface area of ground products from 3500 cm$^2$/g up to 5000-5500 cm$^2$/g. As the result, hydration conditions of clinker components increase cement strength up to 32MPa within the first 24 hours. This characteristic value corresponds to the standard for extra strong cement type (“Very Rapid”).

3. Interaction in the system “Al(OH)$_3$ – 3CaO·Al$_2$O$_3$·6H$_2$O – SiO$_2$ – 4CaO·Al$_2$O$_3$·mCO$_2$·11H$_2$O – H$_2$O”

The works [1, 3, 7] show, that reaction of interaction between hydroaluminates (HCAC) with aluminum hydrate within clinkering temperature leads to producing of low base aluminates of calcium: CaO·2Al$_2$O$_3$ and CaO·Al$_2$O$_3$(CA$_2$ and CA):

$$1400^\circ\text{C} \quad 3\text{CaO}·\text{Al}_2\text{O}_3·6\text{H}_2\text{O} + 5\text{Al(OH)}_3 \rightarrow 3(\text{CaO}·2\text{Al}_2\text{O}_3) + \text{H}_2\text{O}$$ \hspace{1cm} (3)

$$1400^\circ\text{C} \quad 3\text{CaO}·\text{Al}_2\text{O}_3·6\text{H}_2\text{O} + 4\text{Al(OH)}_3 \rightarrow 3(\text{CaO}·\text{Al}_2\text{O}_3) + \text{H}_2\text{O}$$ \hspace{1cm} (4)

In other words, it leads to producing of main phases as a component of high alumina cement (HAC) [7].

As a result of reaction researches (3) and (4), a new way of producing HAC by manner of minor inters clinkering in a deep desiliconization of hydrogarnet sludge with aluminum hydrate was suggested in the articles [1, 7].

As a source of calcium aluminate materials, hydrogarnet sludge from Russian alumina plant processing nepheline was used.

The developed method is more effective than the traditional method that is used for producing HCAC by manner of limestone and alumina colliquation at a high temperature of 1500-1550$^\circ$C [7]. However, this method has serious problems [1]. For example, using of hydrogarnet sludge restricts possibility of cement producing with the highest refractory property, because there is a high concentration of silica (4-6%) and other impurity oxides (Fe$_2$O$_3$, R$_2$O) in sludge. Developing of deep desiliconization technology allows the using of a cleaner input product (HCAC) for producing HAC. Hydrocarboaliminate sludge is characterized by low content of unwanted impurity oxides (0.6-3%) and is a part of rough materials with high capacity of reaction that makes it possible to produce high alumina clinker at a low clinkering temperature up to 1250-1275$^\circ$C.

As the result of researches, it was established that raw charges based on HCAC and aluminum hydrate are specified with a wide clinkering area (100-150$^\circ$C), while high alumina clinkers with 75-80% Al$_2$O$_3$ have good grindable properties and produce cement with high hydraulic activity in grinding.

Trial batch of clinker synthesized on the base of hydrocarboaliminate in industrial conditions had alumina concentration in the range of 60% to 80% and activity level up to 45 MPa on the 3rd day, and 50-60 MPa on the 7th day. Phase composition of the produced high alumina cement is CaO$_2$·Al$_2$O$_3$ – 25-45%; CaO$_2$·2Al$_2$O$_3$ – 50-70%. Refractory property is over than 1670 degrees Celsius.

Expecting elemental composition of HAC produced in experimental-industrial experiences within optimal technological conditions is compared with aluminous cement produced in world leading companies. The result of this comparison is shown in table 1.
Table 1. Elementary composition of HAC

| Name and manufacture place of cement | SiO₂ | Al₂O₃ | CaO | Fe₂O₃ | TiO₂ | MgO | Na₂O | K₂O | SO₃ | Total additives |
|--------------------------------------|------|-------|-----|-------|------|-----|------|-----|-----|-----------------|
| HAC I (Russia)                       | 3.0  | 60    | 32  | 1.0   | 0.05 | 1.5 | *    | *   | 2.0 | 7.55            |
| HAC II (Russia)                      | 1.5  | 79    | 28  | 1.0   | 0.05 | 1.0 | *    | *   | 2.0 | 5.55            |
| HAC III (Russia)                     | 0.5  | 80    | 28  | 0.5   | 0.05 | 0.5 | *    | *   | 0.5 | 2.55            |
| HAC received in industrial conditions (Russia) | 0.5  | 75-80 | 14-20 | 0.03 | 0.03 | 0.26-0.3 | 0.03 | 0.005 | 0.001 | 0.9 |
| HAC (USA)                            | 2-3  | 60-65 | 32-35 | 1    | -    | 0.40 | 0.60 | -   | 0.25 | 5.25            |
| HAC (Hungary)                        | 2-3  | 65-68 | 30-32 | 1    | -    | 0.30 | 0.30 | -   | 0.18 | 4.8             |
| HAC “Electro G. Lafarge” (France)    | 0.05 | 72-75 | 26-27 | 0.2  | -    | 0.1  | 0.40 | -   | 0.25 | 1.0             |
| HAC (Japan)                          | 0.10 | 75-80 | 14-20 | 0.2  | -    | 0.2  | 0.2  | -   | 0.20 | 0.9             |

* – base not rated.

As it follows from table 1, HAC received in industrial conditions (Russia) is the world’s best cement type in terms of total additives (0.9%) determining all the main technical product characteristics.

4. Interaction in the system “3CaO·Al₂O₃·6H₂O – SiO₂ – 3CaO·Al₂O₃·nSiO₂·(6-2n)H₂O – H₂O”

The thermal dissociation process of some continuous solid solutions of hydrogarnet calcium type was researched [1, 3]. Existence of unique partially dried phases 3CaO·Al₂O₃·1.5H₂O – 3CaO·Al₂O₃·nSiO₂·(1.5-2n)H₂O with binding properties was proved. That is why they received a product name - «Hydroalum» cements.

Hydration reaction specifying the setting and hardening of foundry cement components is as follows:

\[
3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 1.5\text{H}_2\text{O} + 4.5\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}.
\]  (5)

Cement types «Hydroalum» can be used in foundry production as a 3-5% additive for foundry and core sands. The effect is as follows: during casting «Hydroalum» cement hydrates and hardens. Then during cooldown period dehydration reaction takes place, foundry sand diffuses itself and hard hand work is not used at the knockout stage. The process is characterized by ecological cleanliness. Trial batches of «Hydroalum» cement were produced at the cement production plant in Pikalyovo (Russia). Hydrogarnet sludges of ultra deep desiliconization were used as raw materials. Sludge calcination was realized in the experimental batch furnace with the external firing system at the temperature of 450°C.

During experimental-industrial testing, the effect of the kinetic threshold appeared [6]; then hydration reaction did not complete; 50% of foundry cement with required quality, ca. 20% of incompletely burned material and 30% of calcium aluminate 12CaO·7Al₂O₃ (instead of sesqui-water phase) were produced. As the result, sand blend becomes hard and the whole technological process of foundry interrupts.

Analysis of irregularities in the «Hydroalum» foundry cement producing allowed one to establish that the main cause of unequal calcination of hydrogarnet sludge was in unequal enrichment of...
Hydrogarnet sludge by silica. If an average value of enrichment equals \( n = 0.15 \), the variation ranges from 0 to 0.4 in an outer zone. It is connected with an existing technology of ultradeep desiliconization at the cement production plant in Pikalyovo. This technology bases on periodical using of 100% white mud recycling that is produced as a result of desiliconization reaction.

We suggested an increase in mud recycling up to 200% for stabilization of silicon-oxygen ions \([SiO_4]^{4-}\) in the crystal latitude and to use hydroseparators with a filter layer (for example, type «Larox») for a continuous discharge of concentrate materials. The research suggests that saturation rate variations of hydrogarnet calcium by alumina is practically nonexistent.

Calcination of equal enriched hydrogarnet calcium provides producing of high quality foundry cements. Produced foundry and core sands are characterized by following parameters: survivability – ca. 30-40 min. full strength (after the 1st hour) – ca. 0.7 MPa. gastightness – 150 points.

5. Conclusions
1. The method for producing of the sulfocarboaluminated mineralizer was introduced at the cement production plant in Pikalyovo (Russia). In this technology, phosphogypsum is proportioned in the slime-limestone sludge in the cement producing. This technology has the following characteristics: stable high quality of produced portland cement; jumping of lining performance in the clinker-forming zone from 45 to 180 days; decreasing of fuel consumption by 1%; simplifying of the automation process for technical control over the cement kiln.
2. The technology of the rapid hardening cement of type «Rapid-SFS» was verified under experimental-industrial conditions. As a result, 500 t of rapid hardening cement was produced at the cement production plant in Pikalyovo (Russia). On the basis of the researches, the practical use of clinker grinding in a closed cycle is recommended. It increases the quality of rapid hardening cement.
3. The developed technology. that is used for effective producing HAC by manner of clinkering HCAC and alumina at the temperature up to 1250-1275°C. This temperature is by 250-300°C lower than a traditional technological temperature of 1500-1550°C

It was demonstrated that HAC received under industrial conditions (Russia) is the world’s best cement type in terms of total additives (0.9%) determining all the main technical product characteristics. This technology was verified under experimental-industrial conditions, as a result 2000 t of rapid hardening cement (type HAC I and HAC II) was produced.
4. It was shown that quality improvement of «Hydroalum» foundry cements and reliability growth of the technology are based on the synthesis of equal enriched (by alumina) hydrogarnet calcium - sludge of ultradeep desiliconization. This effect is archived by means of using of the hydrocarboaliminate method of ion Al(III) and Si(IV) separation as a result of equal mud recycling up to 200%.

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