Synthesis of a mineralizing agent for Portland cement from aluminum production waste

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Abstract. Priority directions in innovative technologies of the construction materials industry are the expansion of the use of mineral and chemical additives in the production of cements, as well as alternative raw materials and fuels in production processes. During the production of aluminum at the enterprise JSC RUSAL Krasnoyarsk, the method of electrolytic reduction of aluminum oxide or alumina dissolved in a cryolite-based melt generates fluorocarbon-containing (FCC) waste, which currently accumulates more than 16,000 tons per year. Due to the increased year-round generation of waste with a high content of carbon, fluorine and aluminum, it is urgent to develop technologies that will effectively use them as a new mineralizer product for the production of Portland cement clinker - calcium fluoride. This paper describes the thermal method of waste processing FCC for receipt of the mineralizing agent (fluorite). The disadvantage of FCC as a raw material is an increased concentration of alkali metals, whose oxides negatively affect the process of hydration of clinker minerals, and lead to the formation of efflorescence on products. To reduce their content, the finished fluorite was washed with water. Calcium fluoride as a mineralizing agent in the production of Portland cement, reduces the clinkerization temperature, increases the content of alite, changes the stability, polymorphism and reactivity of phases. The resulting fluorite with a high mass concentration of 73.9% CaF₂ makes it possible to reduce the clinker formation temperature, which increases the energy efficiency of obtaining Portland cement. The technological process for removing alkaline components from the product will reduce the likelihood of destructive processes in concrete caused by the aggressive action of reactive silica aggregates and freezing and thawing processes.

1. Introduction

In the development strategy of building materials industry for the period until 2020 and further until 2030, approved by Decree of the Government of the Russian Federation from May 10, 2016 No. 868-r, it is stated that “the priority directions of innovative production technologies of building materials industry and new building materials are: the increased use of mineral and chemical admixtures in the production of cement, the use in the technological processes of production of building materials, alternative fuels and raw materials”.

As the Siberian Federal district is redundant in the production of cement, the introduction of energy-efficient technologies for its production is very relevant.
The production of Portland cement is a very energy-intensive process [1]. Producing each ton releases a large amount of CO₂ into the atmosphere and requires 20 to 30% of thermal [2] and 12 to 15% of electrical energy [3] from total industrial consumption. Therefore, new solutions and approaches are required to implement energy-saving policies in the basic industry of building materials – the manufacture of cement binders. There is an urgent need to develop methods for producing Portland cement with reduced CO₂ emissions [4], and there is a need for energy savings, which can be achieved by reducing the firing temperature when using fluxes/mineralizers and other compounds. This solution has economic and environmental advantages [5, 6, 7].

Due to the complex mechanism of changing the crystallographic and other physical and chemical properties of the components of the oxide phases, mineralizers can significantly reduce the temperature of clinker formation. Such compounds as AlF₃, CaF₂, ZnO, MnO₂, SnO₂, CuO are considered to be effective mineralizers [7-10].

Calcium fluoride as a mineralizer reduces the clinkerization temperature, increases the content of alite in the clinker [8], and changes the stability, polymorphism, and reactivity of the phases [10, 12, 13]. However, it is mainly an imported product. The use of CaF₂ in multiphase systems can have both beneficial and adverse effects. As a rule, they were identified during the study of individual compositions and were not systematized to such an extent that it was possible to draw general conclusions and avoid or mitigate negative effects [6, 7, 8, 14-20].

The use of various types of alternative fuels, waste or secondary raw materials in the production of Portland cement allows saving energy and reducing greenhouse gas emissions (especially CO₂) [20]. Papers [8, 22] show that some industrial by-products contain a large amount of fluorine. During the production of aluminum at the enterprise JSC RUSAL Krasnoyarsk, waste with a high content of carbon, fluorine and aluminum is generated by the method of electrolytic reduction of aluminum oxide or alumina dissolved in a cryolite-based melt. By-products of the aluminum industry can be used as a mineralizer in the production of cement clinker [23]. Unlike traditionally used calcium fluoride-based mineralizers, these products have a high content of fluoride and aluminum [8]. Due to the increased circular generation of waste, it is urgent to develop technologies that will allow them to be used as new products [9].

The efficiency of using partially calcined or amorphous alternative raw materials in the production of Portland cement due to lower energy consumption has been studied and implemented well [24]. In the literature, there are examples of the use of fluorine-containing waste as a mineralizer, which differ in different fluorine content and different phase composition [5, 8, 9, 23], and are also used without first improving the purity and quality of the used mineralizer. These studies show the suitability of using such products, when they act, the firing temperature is reduced by 100-150°C, and the use of waste raw materials reduces production costs. Waste adsorbents after water treatment are also used as waste, for example, fluorine-containing sludge obtained during defluorination using Aluminum-PHA, which is obtained by applying hydroxyl aluminum oxide to the surface of PHA. Here it was found that fluoride works as a good mineralizer and is able to reduce the firing temperature for clinker preparation by 100°C [22]. It is worth noting that there is no data in the literature on the production of high-purity CaF₂ from aluminum production waste, pre-purified from the amorphous component (most often C) and alkaline components. As a rule, manufacturers do not want to use direct waste in the production process, which does not have stability. This makes it difficult to select the weight ratio of raw materials and reduces the quality of the finished product.

We used a by-product of aluminum production of JSC RUSAL Krasnoyarsk, which currently accumulates more than 16,000 tons of FCC waste per year on its territory and landfills, to obtain a mineralizer for the production of Portland cement clinker - calcium fluoride. The disadvantage of this raw material is the increased concentration of alkali metals, whose oxides negatively affect the process of hydration of clinker minerals and lead to the formation of efflorescence on products. In addition, alkalis can interact with reactive SiO₂ included in the aggregate (opal, chalcedony), causing excessive expansion and even destruction of concrete, as well as reducing its frost resistance. Therefore, in some cements, for example for hydraulic engineering, the alkali content should not exceed 0.6%.
This study describes the optimal conditions for the synthesis of a high-purity fluorite mineralizer from FCC waste, with the preservation of useful components in the waste, such as aluminum and iron, and getting rid of impurities - alkali metal compounds. The composition, physical-mechanical and thermal properties of the product and raw materials were studied.

2. Materials and methods

2.1. Materials
The fluorocarbon-containing waste was provided by JSC RUSAL Krasnoyarsk. Grade 2 quicklime is a national commercial product that contains 87% of active CaO+MgO according to chemical analysis results.

2.2. Methods
Chemical and x-ray phase analysis methods were used to determine the chemical composition of the FCC waste. The composition of the obtained fluorite was determined by x-ray phase analysis. The thermal stability, rolling boundary, lower yield boundary are considered, the number of plasticity, ash content, and bulk density of the mixture of FCC and quicklime waste are determined.

Powder radiographs of the FCC waste and the resulting fluorite were taken at room temperature using an x-ray diffractometer “X’pertpro” (PANanalytical). The wavelength of the radiation (CuKα) is 1.54 Å. The materials were identified using information and search engines (ISE FI).

The thermogram of the compound was obtained using a synchronous thermal analysis device SDT-Q600 TA Instruments Thermal Analyzer with an IR prefix Nikolet 380 in an argon atmosphere. Heating was performed in the temperature range from 273K to 1273K at a speed of 10K/min. The weight of the hitch was 55mg.

3. Results

3.1. Study of FCC waste
The FCC waste was studied to determine the composition and its stability. The radiograph of the FCC waste is shown in figure 1.

![Figure 1. Radiograph of FCC waste.](image)

Samples for analysis were taken in five parallels for several batches of waste, which were averaged by quartering. The results of x-ray phase and elemental analyses of FCC waste are presented in tables 1 and 2.
Table 1. Results of x-ray phase analysis of FCC waste.

| Formula     | Name of mineral | % wt. |
|-------------|-----------------|-------|
| Al₂O₃       | Corundum        | 2.4   |
| Na₃AlF₆     | Cryolite        | 15.3  |
| Na₅Al₃F₁₄   | Chiolite        | 9     |
| Na₃Ca₃Al₂F₁₄| Verneite        | 3.0   |
| NaCa(AlF₆)  | Thomsenolite    | 2.2   |
| K₂NaAlF₆    | Elpasolite      | 0.9   |
| C           | Graphite        | 67.1  |

Table 2. Elemental analysis of FCC waste.

| Element concentration, % wt. | O   | C   | Al  | Na  | Ca  | F   | K   |
|------------------------------|-----|-----|-----|-----|-----|-----|-----|
|                              | 1.1 | 67.1| 5.5 | 7.9 | 1.2 | 16.8| 0.3 |

The thermal behavior of the FCC waste was investigated. The thermogravimetric analysis curve (figure 2) shows that the substance is stable up to 550°C. At the stage of thermolysis in the temperature range 550-1000°C oxidative decomposition of the substance occurs with the release of CO₂, which is confirmed by the results of IR spectroscopic analysis of the exhaust gases. The mass loss at 725 and 948°C corresponds to exoeffects, and at 929°C - endoeffect.

Figure 2. FCC waste thermogram.

3.2. Synthesis of CaF₂
Fluorite synthesis was carried out by mixing the components to a homogeneous mass, then the mixture was fired in a muffle furnace for 2 hours at t=1000°C, and then cooled in air to room temperature.

A series of experiments were conducted with the excesses and drawbacks of FCC waste, as well as an experiment in accordance with the calculation of the stoichiometric ratio. Table 3 below shows the results of a chemical analysis of one of the experiments with a lack of FCC waste, at a ratio of 60/40 (FCC waste/quicklime).

Experiments with an excess, as well as with a lack, did not show a high content of fluorite. At these ratios, the mass fraction of fluorite is less than 35%, which is insufficient for an effective mineralization process in the production of Portland cement.

Table 3. Results of chemical analysis with a lack of FCC waste.

| Concentration of the component, % | poi | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO  | MgO  | SO₃ | TiO₂ | CaF₂ | Na₂O | K₂O | F    |
|----------------------------------|-----|------|-------|-------|------|------|-----|------|------|------|-----|------|
|                                  | 2.23| 4.41 | 18.34 | 4.77  | 26.73| 0.73 | 10.08| 0.83 | 33.58| 15.00| 1.09| 20.87|
The optimal ratio of the components of the FCC waste with quicklime 79/21 by weight was selected in accordance with the stoichiometric ratio. For example, the reactions of the interaction of CaO and cryolite/chiolite components (the main components of the waste mass, excluding carbon) are shown below:

- for the cryolite component:
  
  \[
  \begin{align*}
  2\text{Na}_3\text{AlF}_6 &= 6\text{NaF} + 2\text{AlF}_3; \\
  2\text{AlF}_3 + 3\text{CaO} &= 3\text{CaF}_2 + \text{Al}_2\text{O}_3; \\
  6\text{NaF} + 3\text{CaO} &= 3\text{CaF}_2 + 3\text{Na}_2\text{O}; \\
  2\text{Na}_3\text{AlF}_6 + 6\text{CaO} &= 6\text{CaF}_2 + 3\text{Na}_2\text{O} + \text{Al}_2\text{O}_3.
  \end{align*}
  \]

- for the chiolite component:
  
  \[
  \begin{align*}
  3\text{Na}_5\text{Al}_3\text{F}_{14} &= 5\text{Na}_3\text{AlF}_6 + 4\text{AlF}_3; \\
  5\text{Na}_3\text{AlF}_6 &= 15\text{NaF} + 5\text{AlF}_3; \\
  9\text{AlF}_3 + 13.5\text{CaO} &= 13.5\text{CaF}_2 + 4.5\text{Al}_2\text{O}_3; \\
  15\text{NaF} + 7.5\text{CaO} &= 7.5\text{CaF}_2 + 7.5\text{Na}_2\text{O}; \\
  3\text{Na}_5\text{Al}_3\text{F}_{14} + 21\text{CaO} &= 21\text{CaF}_2 + 4.5\text{Al}_2\text{O}_3 + 7.5\text{Na}_2\text{O}.
  \end{align*}
  \]

During laboratory tests, a number of experiments were conducted to increase the percentage of \(\text{CaF}_2\) in the resulting mineralizer and to reduce the alkaline salts in the composition. Chemical analysis of the product after the firing stage showed an increased content of by-products, about 47%, of which 15% is sodium salt, which is undesirable for the finished fluorite. According to qualitative x-ray phase analysis (XPA) (figure 3), the by-products are CaSO\(_4\)·(H\(_2\)O)\(_2\) (gypsum), Na\(_2\)SO\(_4\), Ca\(_2\)(SO\(_4\))\(_2\)·H\(_2\)O (bassanite), MgAl\(_2\)O\(_4\) (spinel), Ca\(_6\)(Al(OH)\(_6\))\(_2\)(SO\(_4\))\(_3\)(H\(_2\)O)\(_{26}\) (ettringite), (CaO)\(_{11}\)(Al\(_2\)O\(_3\))\(_7\)(CaF\(_2\)) (fluoromayenite), CaSO\(_4\) (anhydrite). To minimize the presence of reaction byproducts in the finished mineralizer, it was washed with water.

According to x-ray phase analysis (XPA) (figure 3, table 4), the resulting fluorite consists mainly of calcium fluoride (73.9%), the rest of it consists of the minerals MgAl\(_2\)O\(_4\) (spinel), Ca\(_6\)(Al(OH)\(_6\))\(_2\)(SO\(_4\))\(_3\)(H\(_2\)O)\(_{26}\) (ettringite), (CaO)\(_{11}\)(Al\(_2\)O\(_3\))\(_7\)(CaF\(_2\)) (fluoromayenite), CaSO\(_4\) (anhydrite).

![Radiograph of the obtained fluorite.](image)

**Figure 3.** Radiograph of the obtained fluorite.

| Formula | % wt. |
|---------|-------|
| CaF\(_2\) | 73.9  |
| MgAl\(_2\)O\(_4\) | 8.50  |
| Ca\(_6\)(Al(OH)\(_6\))\(_2\)(SO\(_4\))\(_3\)(H\(_2\)O)\(_{26}\) | 4.78  |
| (CaO)\(_{11}\)(Al\(_2\)O\(_3\))\(_7\)(CaF\(_2\)) | 4.65  |
| CaSO\(_4\) | 8.11  |
3.3. Analysis of physical and mechanical parameters
To assess the possibility of using a mixture of waste and quicklime in production as a precursor for the synthesis of fluorite, the physical, mechanical and thermal parameters of the mixture were analyzed. An analysis of the assessment of physical, mechanical and thermal parameters of the mixture of FCC waste and quicklime is shown in table 5.

| Indicator                                      | Result |
|------------------------------------------------|--------|
| Humidity corresponding to the lower yield limit, % | 61     |
| Humidity corresponding to the rolling boundary, % | 50     |
| The number of plasticity, %                     | 11     |
| Bulk density, kg/m³                              | 925    |
| Heat of combustion, J/g                          | 31712  |
| Ash content, %                                   | 32     |

4. Discussion
As a result of evaluating the process of obtaining and composition of the fluorite mineralizer, it is recommended to burn a mixture of FCC waste and quicklime in a ratio of 79/21 in the form of granules with a diameter of 10-20 mm, controlling the humidity of the mixture by adding water to 55% humidity. Washing of the firing product should be carried out at a low flow rate, no more than 8 m³/h. The resulting fluorite with a high mass concentration of 73.9% CaF₂ will reduce the clinker formation temperature, which will increase the energy efficiency of obtaining Portland cement. The technological process for removing alkaline components from the product will reduce the likelihood of destructive processes in concrete caused by the aggressive action of reactive silica aggregates and freezing and thawing processes.

5. Summary
Thus, this paper describes a thermal method for processing FCC waste to obtain a mineralizer (fluorite), the mass fraction of CaF₂ in which is 73.9%. The obtained data confirm the possibility of using the product as a mineralizer in the production of Portland cement clinker. The increased content of calcium fluoride in the composition allows reducing its dosage when using. As there are currently no raw materials for the production of mineralizers in Russia, the production of fluorite will ensure that the manufacturer of the cement industry minimizes the risks of logistics costs and saves resources in the technological process.

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