



Research article

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## Obtaining and using synthetic fluorite for Portland cement clinker production

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**Abstract.** The given paper deals with the issues of natural raw fluorite material replaced by synthetic fluorite. Natural raw fluorite material is used as a mineralizer during clinker production (by means of roasting). The article studies fluorite synthesis from fluorocarbon-containing waste of aluminium production. Moreover, the article focuses on Portland cement clinker application in production. We analysed the studies of the influence of fluorine-containing additives on the efficiency of Portland cement clinker production. The chemical and phase composition of raw material and caustification products were analysed with the help of X-ray fluorescence analysis, X-ray spectroscopy analysis, chemical titration method. Granulometric composition of solid products, obtained by caustification, was studied with the help of laser particle analyser with reverse design of Fourier lenses ANALYSETTE 22 MicroTec. Pills were pressed using raw mixtures and roasted in laboratory furnace: the raw mixture was heated up to 1100–1450° C at the rate 10° C/min. The results of the laboratory research are given. The final product contains from 20.7 % up to 60.5 % of synthetic fluorite. Empirical dependencies of optimal liquid-solid ratio were obtained. Our solution of the task is to enlarge particle size of synthetic fluorite and to reduce alkalescence. A brief characteristic of hardware and technological scheme of waste caustification is given. The paper also gives an assessment of mineralizing effect of synthetic fluorite, obtained by fluorocarbon-containing waste from aluminium production caustification. We proved the mineralizing effect of the additive based on synthetic fluorite and carbon to be correct. Samples containing synthetic fluorite are characterized by higher shrinkage and lower content of CaO<sub>free</sub> at equal temperatures.

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### 1. Introduction

Efficiency of cement industry is specified by the choice and application of fluor-containing additives (mineralizers) during Portland cement clinker production.

The most efficient mineralizers in cement industry are fluorine substances based on natural fluorite, in the form of ore or concentrate. The sources of natural fluorite are located far away from prospective consumers. This is one of the factors, which holds the wide application of natural fluorite back. The main deposits of fluorite ore are located in Siberia, the Far East and Mongolia as well. Significant transport component in natural fluorite (fluorspar) cost decreases the advantages of the mineralizer use for cement plants, located in Ural and the European part of Russia.

Intensification of clinker production increases efficiency of rotary furnaces by 3–5 % due to the use of mineralizers, decreases specific fuel consumption for clinker production up to 3 %, improves operation of furnaces due to stabilization of material coating, improves the quality of clinker and cement [1–3].

The issues, which have to do with theoretical explanation and practice of fluorine-containing mineralizers use, have been studied in our country and abroad [4–6].

It has been established, that addition of small amounts of fluorine salts leads to the increase of reactive capability during all stages of clinker production, though to different extent [7, 8].

Fluorine salts interact with calcium carbonate in the process of heating up to 1100° C, which result in intermediate compounds (such as binary salt). These compounds are distinguished by comparably low melting temperatures. Therefore, materials interact involving liquid phase in the process of clinker production in preparation areas. It makes interaction of lime and silicon oxide easier. Fluorides react on crystalline lattice of calcium carbonate, it may result in the opening of lattice. What is more, there are intermediate compounds within the surface [8–10].

When fluorides interact with SiO<sub>2</sub> we get the compound SiF<sub>4</sub>. It hydrolyzes under the influence of water vapour. As the result we get bulk and very active cristobalite. The most effective use of fluorine salts is marked during the production of hard-sintering clinkers with a high saturation coefficient (SC). Clinkers also contain a small amount of melt and mixtures with a high content of alkaline oxides. Intensive sublimation of alkali involving fluorine accelerates the binding of CaO and increases the activity of a clinker [10].

The production of Portland cement starts with a reaction between thoroughly mixed solid materials. There is synthesis of main cement compounds in the later stages of clinker production, when the liquid phase is formed. The monograph [11] shows that the processes of clinker formation depend on three factors: chemical composition of the mixture, physico-chemical properties of raw materials, temperature and duration of clinker production. The fourth condition that affects the formation of a clinker is the cooling rate. It has to do with the cases when only a small part of the mixture turns into liquid. According to some scientists [11–13], the reactions, which result in the formation of clinker minerals start at 600 °C. Despite the fact, that the maximum clinker production temperature is 1400–1500 °C, only 20 to 30 % of the roasted material melts.

Fluorocarbon-containing waste of aluminium production [13–22] are the alternative of natural fluorine mineralizers. Fluorocarbon-containing waste is considered to be cheap technology-related product. Scientists of Siberian federal university (Krasnoyarsk) have carried out the research on obtaining synthetic fluorite made of waste of aluminium production. As a result of fluorocarbon-containing waste of aluminium production treatment with milk of lime in an aqueous solution with stirring and at elevated temperature, sodium aluminium fluoride (cryolite and chiolite) are converted into fluorite [23–25].

Nowadays, obtaining cheap fluorite is an extremely topical issue. Firstly Russia doesn't meet needs for fluorspar at the expense of its own sources of raw materials completely. Secondly, fluorite synthesis with the help of processing of fluorocarbon-containing industrial waste has an obvious environmental and resource-saving orientation.

Modes of synthetic fluorite obtaining at caustification of fluorocarbon-containing waste are developed, mechanism and kinetics of sodium-aluminium fluorides transformation into synthetic fluorite are studied in the article [25]. On the other hand, the research must be continued, as the fundamental hardware and technological scheme of synthetic fluorite obtaining from fluorocarbon-containing waste from aluminium production should be developed and suggested. What is more, it is necessary to try out obtained materials and get the data, which approve the efficient impact of obtained mineralizer on clinker production.

Therefore, further research is aimed at the assessment of mineralizing effect of synthetic fluorite, obtained by fluorocarbon-containing waste from aluminium production caustification.

Main tasks of the current study are as follows:

The research of the impact of synthetic fluorite obtaining conditions on the composition and the product granulometric composition, the development of technological recommendations in order to improve the composition and granulometric composition;

The development of fundamental hardware and technological scheme of synthetic fluorite obtaining from fluorocarbon-containing waste of aluminium production;

The experimental tests of the obtained synthetic fluorite usage in Portland cement clinker production.

## 2. Methods

The current research studies phase composition of coal froth flotation tailings (CFFT), electrostatic precipitation dust (EPD) as well as gas purification sludge (GPS). These wastes are generated due to the Soderberg anode electrolysis technology, which takes place at the public joint-stock company "Rusal Bratsk aluminium smelter" (samples were taken on 06.03.2023). The caustification data are shown by the example of CFFT. Sample collection for the experiment was carried out with averaging by the means of the squaring method. In order to achieve the goals outlined, we used theoretical methods (study and analysis of literature on the research problem), modern physical and chemical methods of analysis, as well as methods established by GOST. We also employed equipment of the Center for collective use "scientifically advanced methods and methods of analysis of new materials, nano materials and mineral raw materials" of Siberian Federal University.

Major types of fluorocarbon-containing waste of aluminium production are used in order to obtain synthetic fluorite. The waste includes electrostatic precipitators dust, gas purification sludge, coal froth flotation tailings. The aluminium production waste includes coal froth (CF) of aluminium electrolyte production. The monograph [23] gives the most complete description of composition and properties of fluorocarbon-containing waste of aluminium production.

Fluorocarbon-containing waste of aluminium production underwent treatment using milk of lime, containing active  $\text{CaO} = 96.0\%$  in aqueous solution at elevated temperature with stirring. Milk of lime is aqueous suspension of solid calcium hydroxide  $\text{Ca}(\text{OH})_2$  containing small amount of dissolved lime.

In experiments with the removal of kinetic dependencies, pulp samples were taken after a certain time period with a 20 ml syringe for the entire duration of the experiment. The caustification was carried out during 60 minutes. At first, samples were taken in 1.0–2.5 minutes within 15 minutes, next samples were taken every 15 minutes. Samples were necessary in order to check the composition.

After caustification, the pulp was filtered through a blue tape filter on the vacuum line for a specified time. The filtrate was analyzed by titrimetric analysis for the content of total, carbonate and caustic alkali (GOST31957), for the content of aluminium (GOST 2542.4-97). The cake was dried to a constant mass at a temperature of  $120^\circ\text{C}$ , the dried product was weighed and given for analysis by XRF.

In order to identify phases of X-ray pattern, we registered using X-ray diffraction analysis and X-ray spectroscopic analysis with the help of X-ray diffractometer XRD-6000 Shimadzu, featuring  $\text{CuK}$  radiation. In order to get the most careful phase identification we used information data system (RetrieveQQPA) and data bank PDFICDD [26, 27]. Photography of sample spectrum for X-ray spectroscopic analysis was carried out using X-ray automated fluorescence spectrometer Shimadzu XRF-1800 (equipped with Rh-anode).

Granulometric composition of solid products, obtained by caustification, was studied with the help of laser particle analyzer with reverse design of Fourier lenses ANALYSETTE 22 MicroTec.

The mineralizing effect was assessed using the product, obtained by coal froth flotation tailings caustification during the laboratory research.

Pills of the following specifications ( $d = 40\text{ mm}$ ,  $h = 7,0\text{ mm}$ ) were pressed using raw mixtures. The pills were roasted in laboratory furnace, raw mixture was heated up to 1100, 1200, 1300, 1400,  $1450^\circ\text{C}$  at the rate  $10^\circ\text{C}/\text{min}$ .

## 3. Results and Discussion

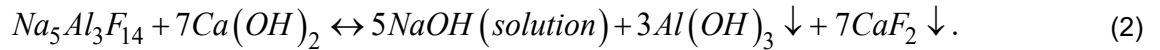
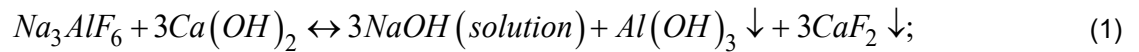
Phase composition of fluorocarbon-containing waste from aluminium production (Table 1).

**Table 1. Phase composition of waste and aluminium industrial waste**

Waste types	$\text{Na}_3\text{AlF}_6$	$\text{Na}_5\text{Al}_3\text{F}_{14}$	$\text{K}_2\text{NaAlF}_6$	$\text{Al}_2\text{O}_3$	$\text{Na}_2\text{SO}_4$	C	$\text{CaF}_2$	$\text{AlF}_3 \cdot 0,5\text{H}_2\text{O}$	The rest
EPD	58.3	0.67	3.80	3.48	4.06	25.7	0.29	–	3.70
GPS	17.1	14.77	–	7.79	–	50.8	0.85	7.46	1.23
SCFFT	15.87	3.47	0.60	1.25	–	74.2	0.21	–	4.40
CF	47.4	12.7	3.73	9.54	–	24.3	2.18	–	0.15

Note. The rest means the following compounds:  $\text{NaAl}_{11}\text{O}_{17}$ ,  $\text{Al}_{\text{met}}$ ,  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$ .

As the authors have already mentioned in the early works [24], cryolite and chiolite interfere with lime, which is a part of the solution:



As dissolved  $Ca(OH)_2$  is used, the solution is fed with new servings of lime. They interact with sodium aluminium fluoride. Therefore, caustification of fluoride contains gradual dissolution of solid  $Ca(OH)_2$ . As the result it breaks into resultants of reaction:  $CaF_2$ ,  $Al(OH)_3$ , and  $NaOH$ .

The carbon contained in waste and industrial products does not undergo changes during lime treatment and transits into a solid product. Thus, the resulting solid product contains synthetic fluorite and carbon. Aluminium oxide and hydroxide are present as impurities in the product. Also, an excess of lime-containing reagent may be present in the product. Sodium from cryolite and chiolite passes into a solution in the form of caustic soda  $NaOH$ , in which aluminium hydroxide is partially dissolved to form sodium aluminate.

Treatment conditions and a brief characteristics of obtained solid and liquid caustification products are given in the Table 2.

**Table 2. Characteristics of original reagents, conditions and caustification products**

Waste and AIW	Waste and APP weight	CaO, g	Weight $H_2O$ , g	Temperature, °C	Mixing time, min.	Solid product		Filtrate		
						Cake weight, g	Solid product weight, g	pH	$Na_2O$ general, $g/dm^3$	$Na_2O$ caust., $g/dm^3$
GPS	50.00	24.43	600	40	60	168.64	55.69	13.15	18.6	12.09
EPD	50.00	20.69	501	50	30	139.0	72.6	12.10	4.75	1.27
CFFT	50.00	9.04	247	50	15	98.2	55.49	13.05	15.4	10.39
CF	50.00	26.06	600	80	30	110.61	61.98	13.23	20.15	14.16

Note. Rotation frequency of the tempering mill in all the experiments is 270 rotations per minute.

Average molecular composition of waste caustification products and aluminium industrial waste is given in the Table 3.

**Table 3. Content of caustification solid products [25]**

Waste and AIW	$CaF_2$	C	$Ca(OH)_2$	$Al_2O_3$	$Al(OH)_3$	$3Ca(OH)_2 \cdot 2Al(OH)_3$	The rest
GPS	47.9±2.6	32.2±3.6	2.06±0.5	10.3±1.2	-	2.58±0.4	4.96
EPD	33.4±2.1	44.4±3.1	1.24±0.4	10.7±1.5	7.13±1.4	1.3±0.35	1.83
CFFT	20.7±1.6	70.1±4.2	1.20±0.4	3.43±0.6	0.98±0.3	2.51±0.5	1.08
CF	60.5±3.4	22.3±2.3	1.22±0.3	9.3±1.8	2.75±0.6	3.27±1.1	0.66

The maximum composition of synthetic fluorite contains product of coal froth (CF) caustification 60.5 %, the minimum composition contains product of flotation tailings caustification 20.7 %. All solid products are practically free from sodium. It can be found in the solution in the form of caustic soda. The minimum sodium content in solid caustic products removes restrictions on the use of synthetic fluorite during clinker production as an additional source of alkali.

In order to carry out industrial caustification of fluorocarbon-containing waste of aluminium production, you need a simple process flow diagram. Moreover, the diagram can be implemented in continuous or periodic mode of operation. The approximate composition of the main equipment of the diagram includes the following items:

- agitator machine, which is used in order to make milk of lime;
- buffer mixer tank, which is used in order to store and dose suspension of fluorocarbon-containing waste of aluminium production;
- pumps and mud channel, which are used in order to feed milk of lime and waste suspension in chemical reactor;
- continuous or batch reactor, which is heated by indirect or direct steam;
- round basin-thickener, which is used in order to separate the main part of the caustic soda solution from the condensed solid caustic product;

- rotary-drum vacuum filter or band vacuum filter;
- tumble dry;
- bucket elevator;
- storage bunker for finished products.

Hardware configuration is tied round with pipes and pumps, which are used in order to pump over suspensions.

You need to take into consideration the following process-related moments before you start implementing industrial caustification of fluorocarbon-containing waste of aluminium production.

*The choice of liquid to solid (L:S) optimal ratio*

The increase of alkaline intensity of solution due to NaOH recovery reduces solubility of  $\text{Ca}(\text{OH})_2$  during the process of waste treatment by milk of lime. Therefore, the rate of chemical reactions slows down (1, 2). If the concentration of NaOH in the solution is high enough, the dissolution of  $\text{Ca}(\text{OH})_2$  may stop completely. Therefore reactions will stop (1, 2). In such a way, concentration of NaOH in products of interaction is a factor, which influences the rate and the totality of the interaction of sodium aluminium fluoride and calcium hydroxide. It has been established experimentally, that caustification of sodium aluminium fluoride slows down when the concentration of NaOH in the solution is more than  $25 \text{ g/dm}^3$ . Therefore, the concentration of NaOH in the solution depends on the content of sodium and fluorine in waste and industrial products, as well as on the weight ratio of liquid to solid (L:S) in the reaction mixture. The higher the fluorine content in waste and industrial products is, the greater the ratio of L:S in the reaction mixture should be. The reason is to prevent excessive increase of the concentration of NaOH in solution and slow down the rate of interaction of reagents. Dependency of the optimal ratio of L:S in reaction mixture has been established experimentally [28]:

$$L : S = \left[ 1 + (M.R. - 2.4) : 4.8 \right] \times \left[ -0.0028 \times F^2 + 0.3074 \times F + 0.2229 \right], \quad (3)$$

where  $L : S$  is weight ratio of liquid to solid,  $S = 1$ ;  $M.R.$  is molar ratio of  $\text{NaF} : \text{AlF}_3$  in waste;  $F$  is fluoride concentration in waste, % mass.

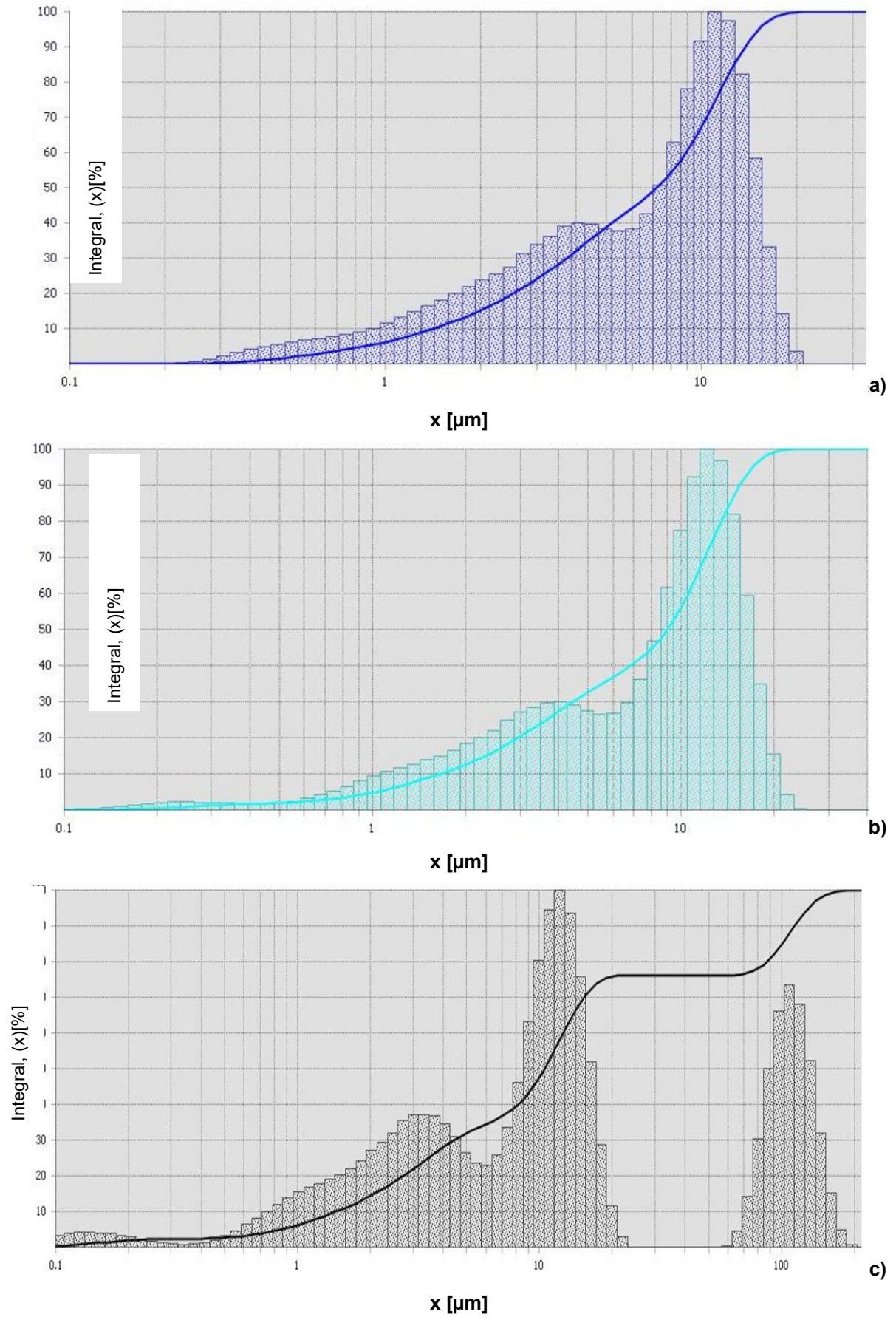
Dependency (3) establishes the initial ratio of  $L : S$  in the reaction mixture. Solid in the reaction mixture is taken as the total and stoichiometric weight of waste, for the formation of  $\text{CaF}_2$ , the weight of  $\text{Ca}(\text{OH})_2$ , excluding excess of  $\text{Ca}(\text{OH})_2$  and the weight of lime impurities.

*High content of caustic solution in filter cake*

It is the result of fine granulometric composition of initial waste and obtained synthetic fluorite. Fig. 1 and table 4 show granulometric composition of solid products, obtained by GPS, EPD and CFFT caustification. These data demonstrate, that the average size of the product, obtained by GPS caustification is 7.19 micron, EPD caustification is 8.96 micron. Granulometric composition of solid products made of CFFT is represented by two distribution curves. Fine fraction of the product, which includes synthetic fluorite, has an average particle size of 10.48 microns. Coarse fraction is mainly carbon and aluminum oxide particles obtained by grinding coal foam.

Fine granulometric composition of solid products of caustification makes filtration more difficult and increases energy consumption while drying. What is more, it contaminates synthetic fluorite with sodium compounds. Therefore, it is necessary to search for solutions in order to enlarge the granulometric composition of caustification products. For example, the introduction of a catalyst into the reaction mixture, which is going to be the source of  $\text{CaF}_2$  crystallization. In order to reduce the sodium concentration in synthetic fluorite, it is possible to use cake washing with water from a caustic soda solution.





**Figure1. Diagram of particles size distribution of solid products, obtained with the help of:**  
**a) GPS; b) EPD; c) CFFT caustification [25]**

**Table 4. Granulometric composition of solid products, obtained by GPS, EPD and CFFT caustification [25]**

x [μm]	GPS	EPD	CFFT
0.10	0.00	0.01	0.32
0.20	0.00	0.49	1.84
0.30	0.26	1.20	2.27
0.50	1.92	1.97	2.66
0.70	3.70	2.82	3.78
1.00	6.23	4.85	6.30
1.50	10.79	8.82	10.49
2.00	15.34	12.66	14.36
3.00	24.02	20.28	21.90
5.00	38.89	32.73	32.02
7.00	49.03	40.59	36.80
10.00	67.55	56.46	47.71
20.00	99.88	99.04	75.73
30.00	100.00	100.00	76.20
40.00	100.00	100.00	76.20
50.00	100.00	100.00	76.20
60.00	100.00	100.00	76.21
70.00	100.00	100.00	76.61
80.00	100.00	100.00	78.17
90.00	100.00	100.00	81.02
100.00	100.00	100.00	84.78
150.00	100.00	100.00	100.00

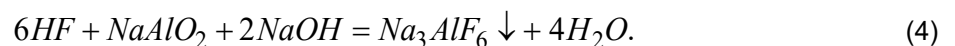
*Preparation of synthetic fluorite in the form of pellets and grains*

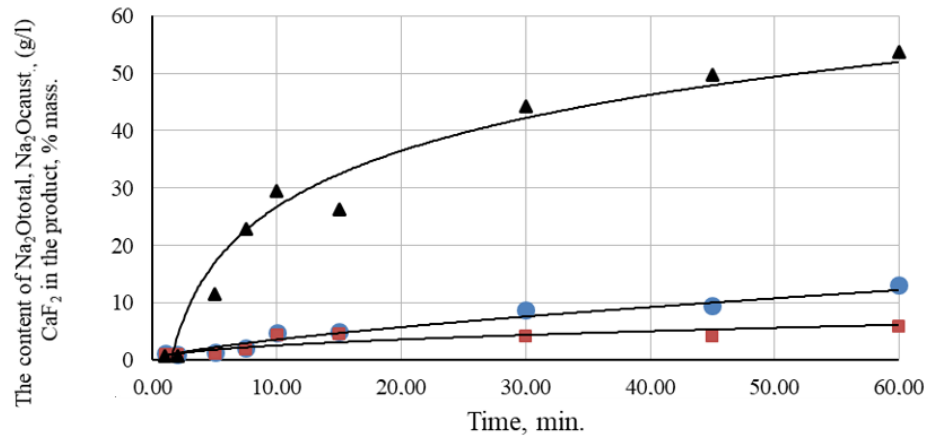
There are many dusty materials in cement production. Therefore, synthetic fluorite, obtained from fluorocarbon-containing waste from aluminium production, should be shaped as granules or pellets. Synthetic fluorite, which looks like powder shouldn't be used. A drum rotary dryer should be used in order to dry the cake of synthetic fluorite. The product should be dried to a residual humidity of 8–10 % mass, which will ensure the production of pellets and granules of 5–50 mm [28].

*There is sodium aluminate in the caustic soda solution*

It has been established, that a solution, which is separated from solid caustification products, the concentration of  $\text{Na}_2\text{O}_{\text{total}}$  is generally greater than  $\text{Na}_2\text{O}_{\text{caust.}}$ , while treating fluorine-containing waste and industrial products with a lime-containing reagent. The graph (Fig. 2) shows the dynamics of the concentration change of  $\text{CaF}_2$  in the solid product,  $\text{Na}_2\text{O}_{\text{total}}$  and  $\text{Na}_2\text{O}_{\text{caust.}}$  in solution during the treatment of cryolite ( $\text{Na}_3\text{AlF}_6$ ) with lime milk. The experimental data obtained indicate that part of the  $\text{Na}_2\text{O}$  in solution is associated with  $\text{Al}_2\text{O}_3$  in sodium aluminate  $\text{NaAlO}_2$ .

If the solution is rich in  $\text{NaAlO}_2$ , it means, that it can be used in a limited way at wet gas purification system of aluminium smelters. Absorption of electrolysis gases by a mixture of caustic and aluminate solutions will lead to crystallization of cryolite in wet gas purification system of aluminium smelters (reaction 4). Electrolysis gases contain hydrogen fluoride.

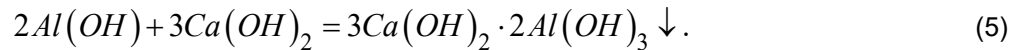




**Figure 2 Change of CaF<sub>2</sub> ( ■ ), Na<sub>2</sub>O<sub>total</sub> (▲) and Na<sub>2</sub>O<sub>caust.</sub> ( ● ) concentration at cryolite caustification [25]**

The loss of fluorides and GPS will follow as well as mud channel will be filled with cryolite precipitation.

It is proposed to introduce an additional amount of lime into the reaction mixture in order to exclude the formation of an aluminate solution. Excess of lime binds forming aluminum hydroxide into the insoluble compound named katoite  $3Ca(OH)_2 \cdot 2Al(OH)_3$ :



As the result we get the solution of caustic alkali free of sodium aluminate. Moreover solid products of caustification are enriched with calcium hydroxide and aluminium hydroxide.

Empirical dependency of recommended dosage of active lime  $Ca(OH)_2$  was obtained during the experiments.  $Ca(OH)_2$  is used in order to treat sodium-fluorine-carbon-containing waste and semiproducts of aluminium electrolytic production:

$$Ca(OH)_2 = (1 \pm 0.02) \times [1.95 \times F + 4.11 \times Al], \quad (6)$$

where  $Ca(OH)_2$  is the amount of active lime (% mass.), which is added to 100 % of waste and aluminium industrial waste;  $F$  is fluor concentration in fluorocarbon-containing waste from aluminium production, which is a part of NaF and  $AlF_3$ , % mass.;  $Al$  is aluminium concentration in fluorocarbon-containing waste from aluminium production, which is a part of  $AlF_3$ , % mass.;  $(1 \pm 0.02)$  is confidence interval, which 95 % safe fits experiment results.

Next step of the research is focused on the assessment of mineralizing effect of synthetic fluorite. The experimental research on clinker production was carried out using the product, obtained by coal froth flotation tailings caustification (the mineralizer). CFFT are characterized by the minimum fluorine concentration. It is represented mostly by cryolite  $Na_3AlF_6$  and chiolite  $Na_5Al_3F_{14}$  as well as maximum content of graphitized carbon. CFFT were used at the experiments on clinker production. CFFT are considered to be the best product, which fit for industrial implementation of the developed technology. Upgrading is being carried out, it will cause the reduction of EPD and GPS formation until they totally vanish. Upgrading implies the substitution of wet gas purification equipment by dry gas purification equipment. Dry gas purification equipment includes metallurgical alumina as an adsorbing material. Coal froth is an aluminium production waste, which is processed nowadays at aluminium smelters by reverse flotation technology. The given technology results in flotation cryolite obtaining (which can be recycled) and CFFT. CFFT is the only waste which is difficult to be recycled. The mineralizer contained 20.7 % of synthetic fluorite and 70.1 % of carbon (Table 3). A comparative assessment was made, based on the results of clinker production of a specific raw material mixture and a mixture with the addition of a mineralizer based on synthetic fluorite and carbon. The composition of basic oxides in the raw mixture is given in Table 5. The mineralizer was added to the composition of the raw mixture more than 100 %. The concentration of  $CaF_2$  in the raw mixture with the mineralizer is 0.28 % mass.

The data given below in tables 5–8 shows the work of mineralizer and confirms the data by authors [4–8] on the impact of fluorite on reactive capability of raw materials.



**Table 5. Composition of initial raw cement mixtures containing synthetic fluorite and free of it**

Composition of compounds, % mass.													
Ignition loss	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	Σ	CaF <sub>2</sub>	C
33.42	13.86	3.61	2.65	42.9	2.40	0.26	0.28	0.30	0.20	0.12	100.0	–	–
33.42	13.86	3.61	2.65	42.9	2.40	0.26	0.28	0.30	0.20	0.12	100.0	0.28	1.0

Note. Modular characteristics of raw mixture:  $SC = 0.93$ ;  $n = 2.21$ ;  $p = 1.36$ .

Shrinkage level and free calcium oxide  $CaO_{free}$  content were assessed in sintered samples. The results are presented in Tables 6, 7 down below.

**Table 6. Shrinkage of samples, mm at temperatures of clinker production**

№	Sample	1100°C	1200°C	1300°C	1400°C	1450°C
1	free of fluorite	39×6.8	37.5×6.4	35.3×5.9	33.6×5.6	31.7×5.5
2	containing fluorite	39×6.5	37.5×6.2	34.8×5.8	32.8×5.4	31.2×5.2

**Table 7. Content in samples of  $CaO_{free}$ . (% mass.) at temperatures of clinker production**

№	Sample	1100°C	1200°C	1300°C	1400°C	1450°C
1	free of fluorite	35.5	34.1	17.8	4.2	0.20
2	containing fluorite	31.0	26.3	12.1	1.9	0.0

Table 8 shows the results of the study of obtained clinkers composition.

**Table 8. Mineralogical composition of burnt mixtures, % mass**

№	Clinker	1400°C					1450°C				
		C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF	CaO <sub>free</sub>	C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF	CaO <sub>free</sub>
1	free of fluorite	46.1	27.0	14.0	8.6	4.2	63.8	15.4	11.1	9.5	0.2
2	containing fluorite	52.1	22.8	13.0	10.2	1.9	64.7	14.4	10.4	10.5	0

Note. C<sub>3</sub>S – 3CaO·SiO<sub>2</sub>, C<sub>2</sub>S – 2CaO·SiO<sub>2</sub>, C<sub>3</sub>A – 3CaO·Al<sub>2</sub>O<sub>3</sub>, C<sub>4</sub>AF – 4CaO·Al<sub>2</sub>O<sub>3</sub>·Fe<sub>2</sub>O<sub>3</sub>.

The given research confirms the study [17]. Synthetic fluorite additive leads to the full binding of calcium oxide compared to other samples. Samples containing synthetic fluorite are characterized by higher shrinkage and lower content of  $CaO_{free}$ . at equal temperatures. Therefore, if we add synthetic fluorite, it will stimulate clinker sintering.

#### 4. Conclusion

As the result of research, we obtained a mineralizer for Portland cement clinker production by means fluorocarbon-containing waste caustification. Because of the mineralizer content (20.7–60.5 % of synthetic fluorite, the minimum sodium content) it may be used as a mineralizer for Portland cement clinker production.

It was determined that the average size of the mineralizer containing synthetic fluorite after caustification of GPS, EPD and CFFT makes up 7.19; 8.96; 10.48 microns. It has been established that the fine granulometric composition causes increased alkalinity. In order to reduce the sodium concentration in synthetic fluorite, it is proposed to introduce an inoculation into the reaction mixture for crystallization of CaF<sub>2</sub> and rinsing the cake with water to get rid from caustic soda. It is recommended to dry the cake of synthetic fluorite to a residual humidity of 8–10 % by weight in a drum rotary dryer in order to obtain pellets and granules of 5–50 mm in size.

The fundamental hardware and technological scheme of aluminium production waste caustification was developed. The final result is synthetic fluorite. The scheme may be implemented in continuous and periodic mode. There is an exemplary list of basic equipment.

We assessed the mineralizing effect of CFFT caustification product. The mineralizing effect of the additive based on synthetic fluorite and carbon was proved correct experimentally. The additive was obtained with the help of coal froth flotation tailings treatment. Samples containing synthetic fluorite are characterized by higher shrinkage and lower content of  $\text{CaO}_{\text{free}}$  at equal temperatures. Therefore, the additive causes clinker production.

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