

# Production of Synthetic Fluorspar from Waste Calcium Fluoride Slurry

Z. Kowalski, A. Paszek\*

Cracow University of Technology, Institute of Chemistry and Inorganic Technology, Warszawska St 24, 31-155 Cracow, Poland

\* Institute of Inorganic Chemistry, Sowinski St 11, 44 -101 Gliwice, Poland

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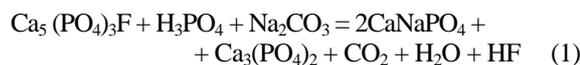
## Abstract

Synthetic fluorspar can be produced from waste calcium fluoride slurry settled on dumpsites located near Cracow centre. Synthetic fluorspar exchanges natural raw material used in the metallurgical industry. To obtain grained synthetic fluorspar, calcium fluoride slurry should be calcinated in rotary kilns at temperatures of 900-1100K. Grain size and compression strength strongly depends on calcination time and temperature. X-ray and thermal analysis indicate that calcium fluoride, apatite and sodium fluoride are basic phases of the synthetic fluorspar.

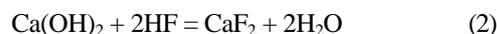
**Keywords:** calcium fluoride, dumpsites, utilization, synthetic fluorspar.

## Introduction

Wasted calcium fluoride slurry was produced during 20 years of manufacturing calcium feed phosphate using the thermal method in the "Bonarka" Inorganic Works in Cracow. The applied technology consisted of the decomposition of apatite and expulsion of fluorine compounds by heating apatite with the addition of phosphoric acid and sodium carbonate at a temperature of about 1723 K. The final reaction follows the equation:



Hydrogen fluoride thus generated, together with other waste gases, was absorbed by lime milk and formed a suspension of calcium fluoride, which was dumped into settling ponds [4].



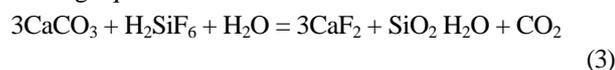
The thermal method was replaced in 1993 with the low-temperature wasteless process [3]. But 200,000 t what of the waste piled near the centre of Cracow still poses a serious environmental problem which urgently needs to be resolved.

At present waste calcium fluoride, after drying to moisture content about 13-18%, is used as an additive in cement production. It may be used in the manufacture of building materials [2, 7]. However, the above solutions, only partially implemented, are not sufficient for the target utilization of the waste.

An idea to use calcium fluoride for the manufacture of synthetic fluorspar as a substitute for natural fluorspar imported by Polish metallurgy from China has emerged [5]. In Poland, 4,000-5,000 tons of fluorspar are consumed each year.

Literature provides little information on the use of waste calcium fluoride. A paper [6] mentions the possibility of metallurgical use of briquetted  $\text{CaF}_2$  derived from waste. Russian plants producing phosphate fodder additives by thermal defluorination of apatite also use lime milk for absorption of waste gases. The product of absorption, which contains 75%  $\text{CaF}_2$ , 22%  $\text{CaCO}_3$ , 1%  $\text{SiO}_2$ , 1%  $\text{Ca}_5\text{F}(\text{PO}_4)_3$  and 1%  $\text{Ca}(\text{OH})_2$  is used in the manufacture of building materials [6].

Fluorine compounds are recovered in the form of  $\text{CaF}_2$  from wastewater in the fertilizer plant according to the following equation:



The precipitate is washed and briquetted and contains

70-80% CaF<sub>2</sub>, 4% P<sub>2</sub>O<sub>5</sub> and 6% SO<sub>4</sub><sup>2-</sup> It is used as a fluxing agent in a pilot steel plant. It was observed that fluorspar fluxes the slag and that phosphorus and sulphur compounds contained in it have no detrimental influence on the quality of the steel [1].

Requirements imposed on natural fluorspar used as a slug-fluxing agent for steel making are specified by the Polish standard PN-61/H-11105. The standard specifies mainly the grain size and chemical composition (Table 1). Synthetic fluorspar has to meet the requirements of this standard and some additional requirements. Fluorspar grains must have at least 15 mm in diameter, mechanical strength similar to that of natural raw material and moisture content below 1%.

This method has proven to be capable of providing a product that would satisfy consumer requirements. It consists of roasting waste calcium fluoride in rotary kilns at temperatures above 900K [3, 5].

### Experimental Procedure

Waste calcium fluoride was roasted in various temperatures and under various conditions (stationary conditions - chamber kiln, dynamic conditions - laboratory rotary kiln). The obtained products were analyzed with regard to their applicability to steel making. The following properties were taken into consideration:

- chemical composition of the raw material samples and their water extracts;
- physicochemical properties of the product samples
- mechanical strength of grains and grain size distribution of the product samples.

Thermogravimetric analysis and drying tests of the waste were carried out with a Derivatograph-c apparatus manufactured by MOM and WPE30S dryer/balance manufactured by Radwag.

In order to elucidate the process of the waste phase composition, samples were X-rayed with a Philips X-Pert apparatus. On the basis of obtained RTG spectra the average size of calcium fluoride and fluorapatite crystals were determined by analyzing the broadening diffraction line.

The mechanical strength of grains was assumed to be the basic indicator of physicochemical transformation taking place in the examined material. In order to evaluate this quantity, the so-called mean compressive strength of grains was determined according to the method described in the Polish standard BN-80/0604-07.

Samples of waste calcium were roasted for 3 hours at temperatures ranging from 293K to  $t_{max}$  and further roasted 2 hours at  $t_{max}$ . 100 non-fractured grains were picked at random from this material (dimensions 4-5 mm); they were subjected to compression tests on a testing machine until they were completely crushed. The value of the mean compressive strength was calculated for the whole sample lot.

The apparent density of synthetic fluorspar grains obtained at selected temperatures was determined according to the Polish standard PN-82/G-04537. Kerosene was used as the pycnometric liquid.

Size analysis of synthetic fluorspar obtained by roasting waste calcium fluoride in a chamber kiln and in a laboratory rotary kiln (internal diameter  $d = 0.1$  m) was made, too. The kiln equipment allowed retaining the samples at a temperature of 1123 K for 3 hours.

Changes in moisture content (determined at 378 K) in synthetic fluorspar samples obtained by roasting the waste in a chamber kiln for 60 minutes were recorded on a monthly basis. During the time of tests the samples were stored in open air under a roof protecting the material against atmospheric precipitation

### Results

Introductory studies were carried out in the thermal processing of waste calcium fluoride in order to confirm the correctness of assumptions related to the process.

Concentration range of individual constituents of waste from the settling ponds was rather wide. In over 20 samples analyzed, average concentration in dry residue was as follows: 37-52% Ca, 29-42% F, 1.3-3.1% P, 1.5-1.8% Na, < 0.5% Fe, < 0.5% Si, < 0.5% SO<sub>4</sub>, < 1.15% CO<sub>2</sub>. Residue after drying of the waste at 383K was 41.0-45.1%.

Average sample of waste drawn from a settling pond underwent subsequent analyses described below contained, in dry residue, 39.3% Ca, 32.5% F, 2.6% P, 1.6% Na, 0.14% Fe, 0.15% SiO<sub>2</sub>, 0.15% CO<sub>2</sub>. Residue after drying of the sample at 383K was 44.8%. These samples were used for our research.

Calcium fluoride, carbonates, orthophosphates, water of crystallization, and adsorbed water were detected in the waste dried at 383K infrared spectrophotometric analysis of the average sample. The amount of orthophosphates in the sample was determined as being twice that of carbonates.

Water extract of the sample contained carbonates, sulphates, water of crystallization, and adsorbed water.

Table 1. Grain size and chemical composition of natural fluorspar according to PN-61/H-11105.

Designation of grade	Fluoride form	Grain size [mm]	Content of constituents [wt. %]		
			CaF <sub>2</sub> min.	SiO <sub>2</sub> max.	BaSO <sub>4</sub> max.
FK 1	lumps	30-250	85	10 15	2
FK 2			76	20	5
FK 3			66		6
FZ 1	granular	3-30	85	10 15	2
FZ 2		1-30	76		3

Table 2. Mean compressive strength and apparent density of synthetic fluorspar samples.

Maximum roasting temperature [K]	Mean compressive strength [N]	Apparent density [g/cm <sup>3</sup> ]
773	1.96	–
823	–	2.07
873	47.09	3.07
973	272.72	–
1023	711.22	3.06
1073	622.93	–
1123	711.22	3.12
1173	640.59	–
1223	622.93	3.16

Table 3. Moisture content in synthetic fluorspar samples.

Sample	Moisture content in sample roasted at [%]			Mean air humidity during 3 days before measurement [%]
	873K	1023K	1223K	
initial	0.09	0.07	0.07	60
after 1 month	0.21	0.52	0.39	55
after 2 month	4.73	0.69	1.03	63
after 3 month	1.34	0.80	0.52	75
after 4 month	2.7	1.15	0.90	80

Derivatogram of a waste sample made at temperature range 293-1223K revealed an endothermic peak at temperature 433 K, which was identified as the effect of loss of water not chemically bound and crystallization water; total loss of mass amounted to 43.3%.

The total loss of mass determined from the TG curve (43.3%) was close to the loss of mass of the sample dried to constant weight at 353 K (42.3%) and 413 K (44.3%). This may indicate that the total water content in the sample was close to that value and rate of water loss depended on drying conditions.

In the first place were analyzed waste samples dried at 293 K and 393 K, followed by samples roasted for 3 hours in a muffle kiln where temperature increased within the range 823 K to 1223 K. On the X-ray diagrams of the dried waste samples only a slight indication of crystalline calcium fluoride could be distinguished, while the RTG spectra of roasted samples showed evidence of crystalline phases of calcium fluoride and fluorapatite and indicated the presence of small quantities of calcium carbonate and sodium fluoride. Calcium fluoride peaks became more distinct with the

Table 4. Size analysis of calcium fluoride after roasting in a chamber and rotary kiln.

Grain diameter [mm]	Mass fraction [wt. %]	
	Sample roasted in chamber kiln at 1123K	Sample roasted in laboratory rotary kiln at 1123K
> 15	92	56.1
15-5	7.2	37.3
5-3	0.5	6.0
< 3	0.3	0.6

increase of roasting temperature and with a growing number of counts for individual peaks (Figure 1).

Sizes of calcium fluoride and fluorapatite crystals were determined by analyzing the broadening diffraction line on the basis of RTG spectra. The average size of calcium fluoride crystals in raw waste was  $100 \cdot 10^{-10}$  m, whereas their size in a sample roasted for 3 hours in 1123K increased to  $400 \cdot 10^{-10}$  m, and the average size of fluorapatite crystals in this sample was  $5000 \cdot 10^{-10}$  m.

Results of the investigation led to a conclusion that the waste in question contains ca. 37% calcium fluoride with a low degree of crystallinity. The presence of phosphates in the form of  $\text{Ca}_3(\text{PO}_4)_2$  (5.6%) and  $\text{CaNaPO}_4$  (6.5%) and  $\text{Ca}(\text{OH})_2$  (8%) was highly probable. The content of highly crystalline calcium fluoride in the roasted samples was estimated to be 70% and the content of fluorapatite to be ca. 6%.

The mechanical strength of grains was assumed at this stage of examination to be the basic indicator of physico-chemical transformation taking place in the examined material. Samples of the raw material were roasted for 3 hours

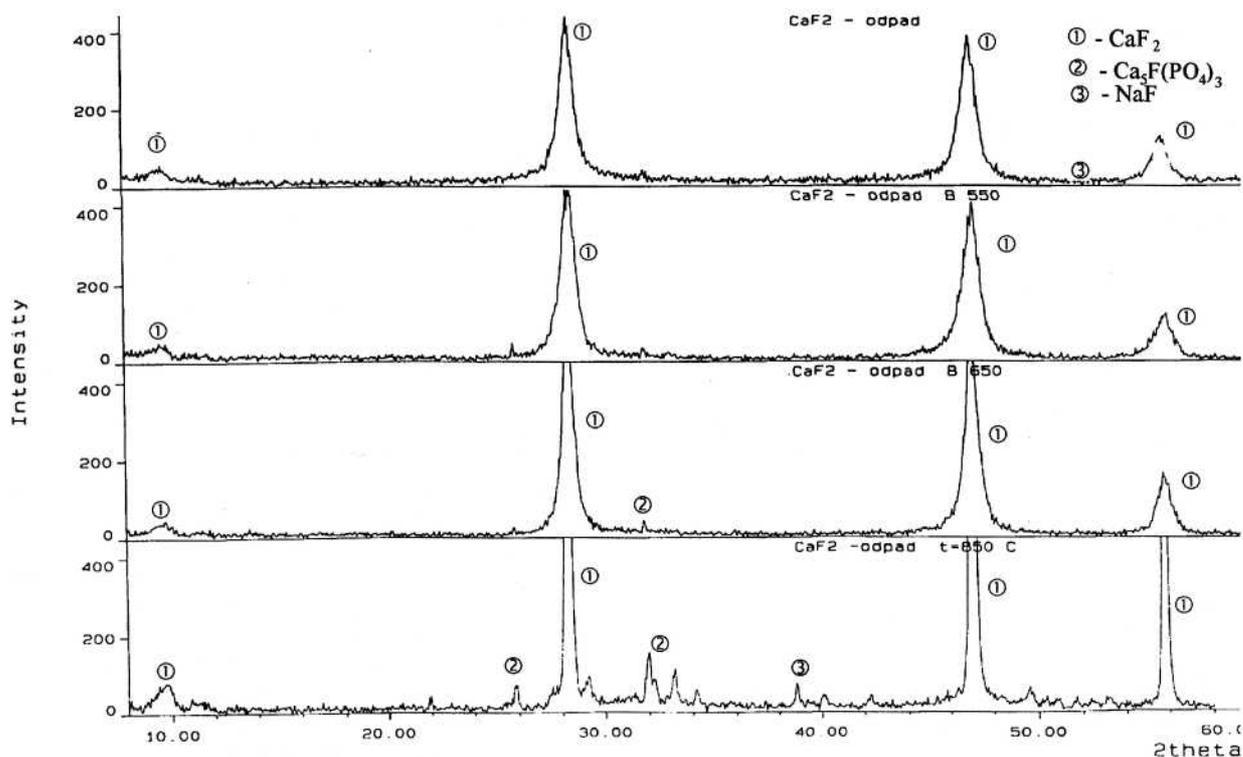


Fig. 1. X - ray diagrams of waste calcium fluoride slurry and sludge samples after roasting.

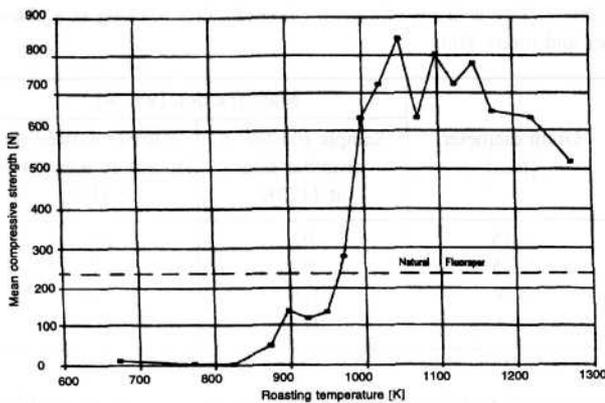


Fig. 2. Dependence of compressive strength on the temperature of roasting fluorspar samples.

at temperatures ranging from 293K to  $t_{\max}$  and then further roasted 2 hours at  $t_{\max}$ . 100 non-fractured grains were picked at random from this material (dimensions 4-5 mm); they were subjected to compression tests on a testing machine until they were completely crushed. The value of the mean compressive strength was calculated for the whole sample lot. These tests confirmed the significant increase of grain durability and enabled the production of synthetic fluorspar with compressive strength comparable to that of natural fluorspar (Figure 2). The mean compressive strength coefficient was 223.69 N.

Significant increase of grain strength was obtained for samples roasted at 1023-1123K.

The results of mean compressive strength and apparent density of synthetic fluorspar samples roasted in selected temperatures are given in Table 2.

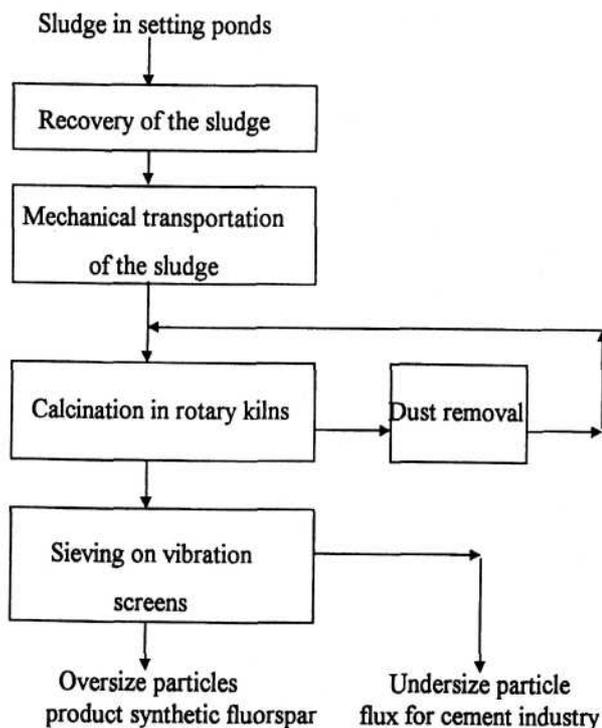


Fig. 3. Flow sheet of the synthetic fluorspar production process

Changes in moisture content (determined at 378K) in synthetic fluorspar samples (which were obtained by roasting the waste in a chamber kiln for 60 minutes) were recorded on a monthly basis (Table 3).

Table 4 lists the results of size analysis of synthetic fluorspar obtained by roasting waste calcium fluoride in a chamber kiln and in a laboratory rotary kiln (internal diameter  $d = 0.1\text{m}$ ). The kiln equipment allowed retaining the samples at 1123K for 3 hours.

The data indicated that the obtained synthetic fluorspar was equivalent, in terms of grain size distribution, to granular fluorspar used for steel making.

## Conclusions

The problem of disposal of wasted calcium fluoride slurry produced during 20 years of calcium feed phosphate manufacture using the thermal method at the "Bonarka" Inorganic Works in Cracow could be solved by using the synthetic fluorspar production method using waste calcium fluoride slurry settled on dumpsites. Synthetic fluorspar would replace natural raw material used in the metallurgical industry.

The results of tests and examinations of waste calcium fluoride roasted at high temperatures (as described above) have enabled the creation of manufacturing technology of synthetic metallurgical grade fluorspar from waste calcium fluoride sludge (Figure 3). Roasting of the waste in a rotary kiln at temperatures of 1023-1123 K was the optimum condition for processing. This technology would provide synthetic fluorspar at costs lower than the price of natural fluorspar imported from abroad.

Research being conducted now on detailed identification of physicochemical transformations and the possibilities of using sintering point lowering additives will further optimize this process.

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