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METHODS OF UTILISATION OF WASTE CALCIUM FLUORIDE SLURRY

Utilisation methods of waste calcium fluoride slurry into pulver calcium fluoride and synthetic fluorspar are presented. Synthetic fluorspar could change the way the natural raw material are used in metallurgical industry. To obtain grained synthetic fluorspar calcium fluoride, slurry is calcinated in a rotary kiln at temperature 900–1100K. Grain size and compression strength is strongly depended from calcination time and temperature. Another alternative is using of the briquetting in this process. All utilisation methods were compared.

INTRODUCTION

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

$$Ca_5\,(PO_4)_3F + H_3PO_4 + Na_2CO_3 = 2CaNaPO_4 + Ca_3(PO_4)_2 + CO_2 + H_2O + HF \quad (1)$$

The emerging hydrogen fluoride together with other waste gases was absorbed in lime milk and formed a suspension of calcium fluoride, which was dumped into settling ponds (Schroeder et al. 1972).

$$Ca(OH)_2 + 2HF = CaF_2 + 2H_2O \quad (2)$$

The thermal method was replaced in 1993 with low-temperature wasteless process (Kowalski and Wzorek 1995, 1996), but 200 thousand tons of wasted piled near the centre of Cracow poses a serious environmental problem which urgently needs resolving.

Since 1988 the waste calcium fluoride slurry was exploited from the ponds with hydraulic method and sludge after separation on setting ponds was dried to moisture

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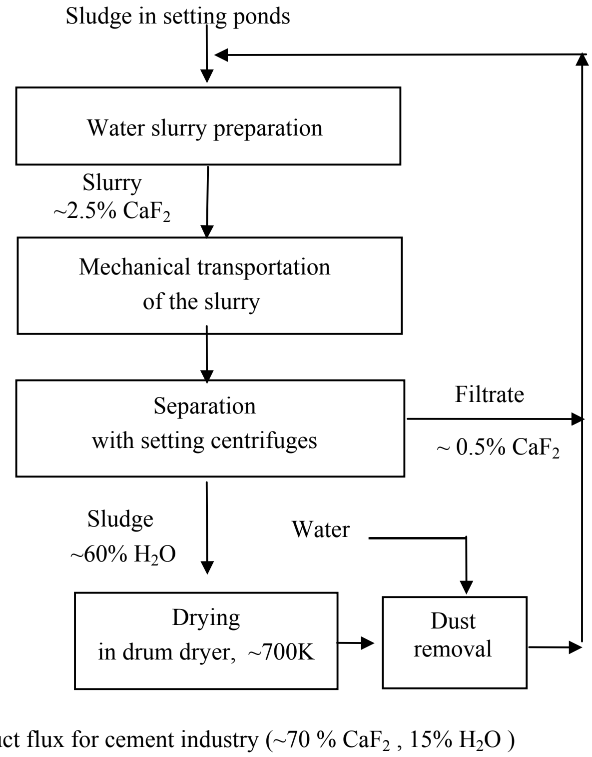

Fig. 1. Flowsheet of calcium fluoride production process

content 13–18%. Produced with this method calcium fluoride is used as an additive in cement production (Fudali and Kurnik 1988). A flowsheet of this method is presented in Fig.1. Calcium fluoride may be used in manufacture of building materials (Gollinger et al. 1993). Utilisation method for building materials with high mechanical strength and freeze resistance (to 40% addition of calcium fluoride) were worked out too (Skrzypek et al. 1994).

MODERNIZATION OF CALCIUM FLUORIDE PRODUCTION PROCESS

Our first efforts were connected with technological and equipment changes in calcium fluoride flux production process (Kowalski et al. 1991). At first centrifugal setting was analysed. This process was not effective (too high content of solid phase in recirculated water) and had rather high electricity consumption figure. Some operating problems with centrifuges and hydraulic exploitation of the sludge were very serious. These resulted in high production costs. In 1991 production unit was modified. A new process is presented in Fig. 2.

Implementation of the open-cut mining of the calcium fluoride sludge with an excavator and then its transportation with trucks and screw conveyors allow to eliminate centrifugal unit. These solutions allow to decrease production costs at about

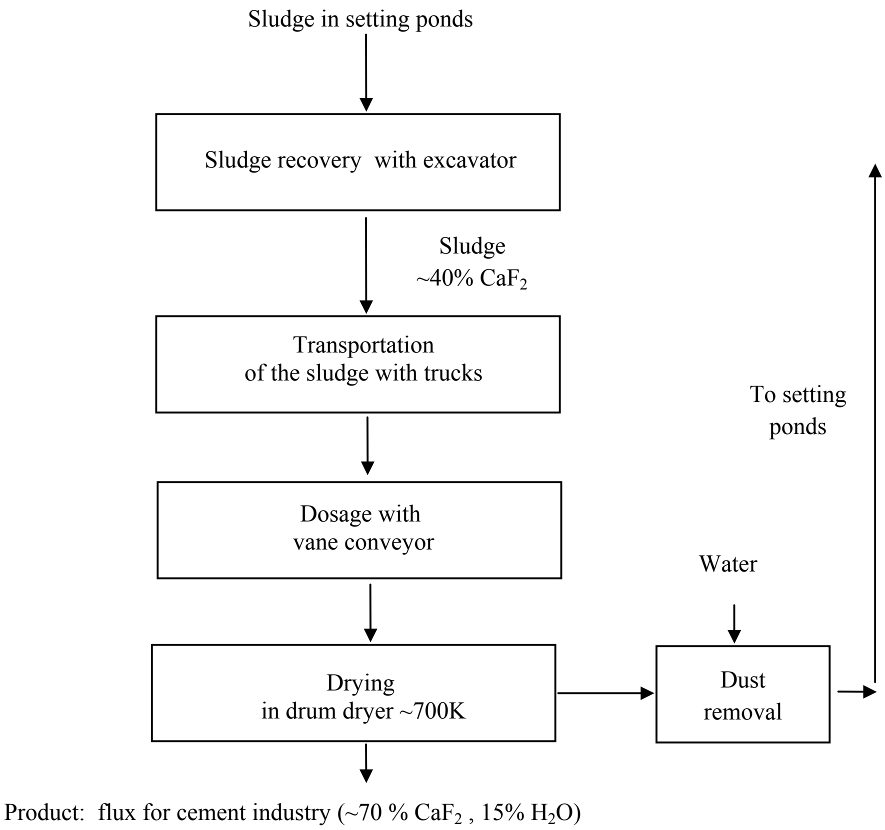

Fig.2. Flowsheet of the modified calcium fluoride production process

45%. The above solutions are not sufficient for the target utilisation of all the waste. Only 1000 t/y of pulver calcium fluoride flux is sold in Polish market. A new utilisation method is needed.

SYNTHETIC FLUORSPAR PRODUCTION FROM CALCIUM FLUORIDE

Slurry

An idea has emerged to use calcium fluoride for the manufacture of synthetic fluorspar as substitute for natural flourspar imported by Polish metallurgy from China. In Poland 4000–5000 tons of fluorspar are consumed each year (Kowalski and Paszek 1995, Kowalski et al. 1995). Literature provides little information on the use of waste calcium fluoride. The paper mentions the possibility of metallurgical use of briquetted CaF_2 derived from waste (Drzyma³a and Hryniewicz 1992). Russian plants producing phosphate fodder additives by thermal defluorination of apatite also use lime milk for absorption of waste gases. Product of absorption, which contains 75% CaF_2, 22%

$CaCO_3$, 1% SiO_2, 1% $Ca_5F(PO_4)_3$ and 1% $Ca(OH)_2$ is used in manufacture of buildings materials (Morgunowa 1978). Fluorine compounds are recovered in the form of CaF_2 from wastewater in the fertiliser plant. The precipitate, washed and briquetted, contains 70–80% CaF_2, 4% P_2O_5 and 6% SO_4^{2-}. It is used as a fluxing agent in a pilot steelmaking plant (Paszek 1995).

Requirements imposed on natural fluorspar used as a slug fluxing agent for steelmaking are specified by Polish standard PN-61/H-11105. The standard specifies mainly the grain size and chemical composition (see Table 1).

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_2 min	SiO_2 max	$BaSO_4$ max
FK 1			85	10	2
FK 2	lumps	30–250	76	15	5
FK 3			66	20	6
FZ 1		3–30	85	10	2
FZ 2	granular	1– 30	76	15	3

Synthetic fluorspar would have to meet the requirements of this standard and some additional requirements. Fluorspar grains must have diameters at least 15 mm, mechanical strength similar to that of natural raw material (over 225 kN) and moisture content under 1%.

The method that proved to be capable of proving a product that would satisfy consumers requirements was the roasting of waste calcium fluoride in a rotary kiln at temperature the above 900 K (Jarosiñski and Natanek 1996).

Introductory studies have been carried out on the thermal processing of waste calcium fluoride in order to confirm the correctness of assumptions made pertaining to the process. Waste calcium fluoride was roasted in various temperatures and under various conditions (stationary conditions – chamber kiln, dynamic conditions – laboratory rotary kiln). The products obtained were analysed with regard to their applicability to steelmaking. The following properties were taken into consideration:

- chemical composition of samples
- mechanical strength of grains and grain size distribution.

Concentration ranges of individual constituents of wastes from the settling ponds are rather wide. 20 samples analysed had the following mean concentration in dry residue: 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_4, < 1.15% CO_2. The residue after drying of the waste at 383 K was 41.0 –45.1%. The mechanical strength of grains has been assumed at this stage of

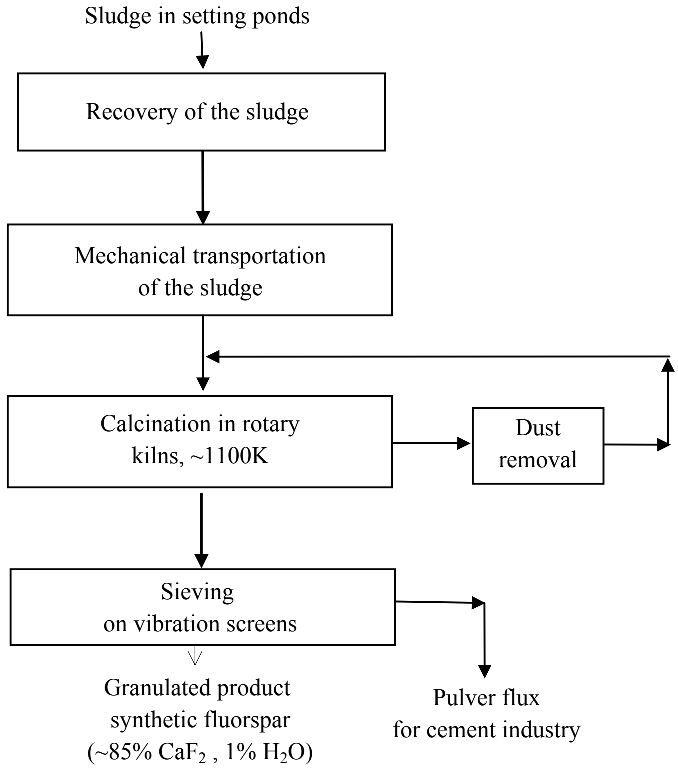

Fig. 3. Flowsheet of the synthetic fluorspar production process

examination to be the basic indicator of physicochemical transformation taking place in the material examined. In order to evaluate this quantity, the so-called means compressive strength of grains was determined. The determination was made according to the method described in the Polish standard BN-80/0604-07. The samples of waste calcium were roasted for 3 hours at temperatures ranging from 293K to t_{max} and then further roasted for 2 hours at t_{max}. 100 non-fractured grains were picked from this material at random (dimensions 4–5 mm), which was then 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 tests confirmed a significant increase of grain durability and enabled the production of synthetic fluorspar with compressive strength comparable to that of natural fluorspar, the mean compressive strength coefficient was 228 kN. Significant grain strength increase (500–700 kN) is obtained for samples roasted in 1000–1150 K (Paszek 1995, Jarosiñski and Natanek 1996). After roasting the product should be sieved on vibrating screens. Oversize (normally > 50% of product) is equivalent, in terms of grain size distribution, to granular steelmaking fluorspar. Undersize could be recirculated or used as a pulver fluxing agent.

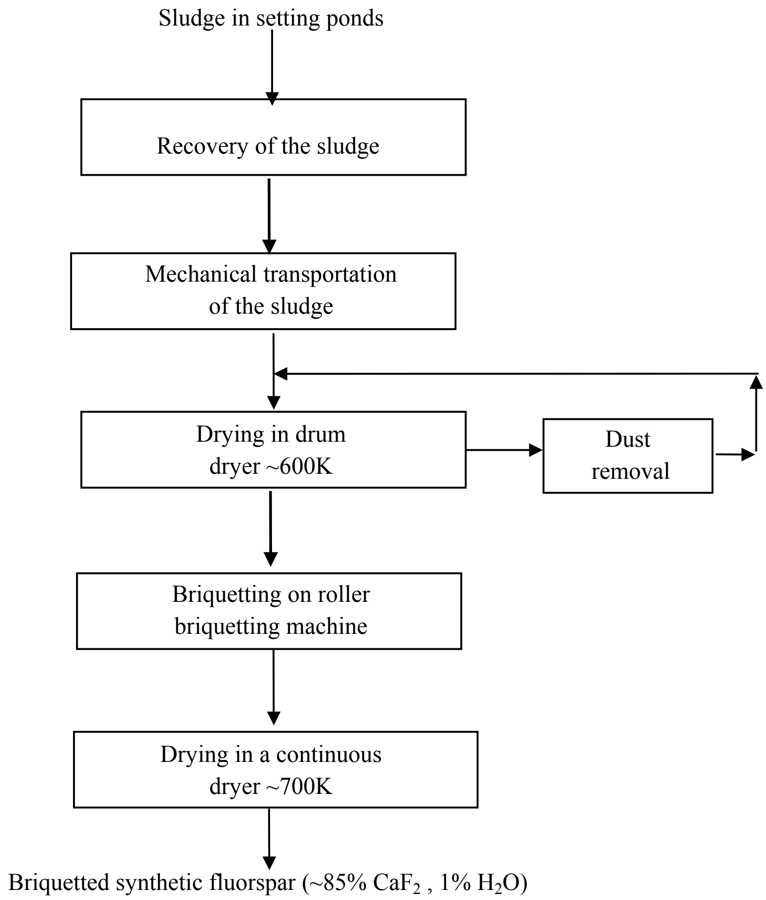

Fig. 4. Flowsheet of the synthetic briquetting fluorspar production process

The results of tests and examinations of waste calcium fluoride roasted at high temperatures enabled one to devise the manufacturing technology of synthetic metallurgical grade fluorspar from waste calcium fluoride sludge. Waste calcium fluoride processing flow-sheet is presented in Fig. 3. The optimum conditions for the processing of the waste is roasting in a rotary kiln at temperatures within range of 1023
–1123 K. This technology would provide synthetic fluorspar at costs lower than the price of natural fluorspar imported from abroad (Kowalski, Paszek 1997).

BRIQUETTED SYNTHETIC FLUORSPAR PRODUCTION METHOD

Our further research on synthetic fluorspar production process concentrated on the application of the briquetting process. This method was first tested on the calcium fluoride powder produced by the method presented in Fig. 2, but mechanical strength of produced briquettes was too low. Research on this technology (Drzyma³a et al. 1997) allow to find detailed briquetting parameters but the briquetted product had too low mechanical strength.

Our final solution was the combination of briquetting an roasting methods. Flowsheet of briquetting fluorspar technology is presented in Fig. 4.

Briquetted synthetic fluorspar produced in this alternative of the process has mechanical strength over 500 kN after drying at 700 K. Quantity of the granulated material in the product increased to 97%. These allow to decrease energy consumption figure and finally synthetic fluorspar production costs at 25% comparing to the method presented in Fig. 3. Research conducted now on detailed identification of physicochemical transformations will further optimise the process.

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Odpadowy flluorek wapniowy powstawał jako produkt uboczny podczas produkcji paszowego fosforanu wapnia metodą termicznego odfluorowania apatytu. Metoda termiczna została w roku 1993 zastąpiona bezodpadową metodą niskotemperaturową, ale pozostało po niej 200 000 ton odpadów na składowiskach położonych w centrum Krakowa. Próby utylizacji rozpoczęto w roku 1988, uruchamiając produkcję pylistego fluorku wapniowego, stosowanego jako topnik w przemyśle cementowym. Proces ten został zmodernizowany technologicznie i aparaturowo w 1992 roku, co pozwoliło na jego uproszczenie i obniżkę kosztów przerobu odpadów. Wspomniana metoda pozwalała na sprzedaż około 1000 Mg/rok pylistego CaF_2.

Dalsze prace badawcze pozwoliły na opracowanie metody otrzymywania ze szlamów fluorkowych fluorytu syntetycznego, zamiennika fluorytu naturalnego stosowanego jako topnik w przemyśle metalurgicznym. Proces polega na spiekaniu odpadu w temperaturze ponad 1023 K i oddzielaniu otrzymanych granulek na sitach wibracyjnych. Kolejna wersja nowej technologii otrzymywania fluorytu syntetycznego polega na brykietowaniu suszonego wstępnie odpadu i następnie suszeniu wyprodukowanych brykietów w znacznie niższej temperaturze, wynoszącej tylko 700 K. Pozwala to obniżyć znacznie koszty procesu. Przewidywana ilość wyprodukowanego fluorytu syntetycznego wyniesie 10 000 Mg/rok.