

J. SOKOŁOWSKI\*, P. URBAŃSKA\*\*

## FABRICATION OF CERAMIC AGGREGATE FROM PHOSPHOGYPSUM AND POWER PLANT ASH – PRELIMINARY STUDIES

## OTRZYMYWANIE KRUSZYWA CERAMICZNEGO Z FOSFOGIPSU I POPIOŁÓW ELEKTROWNIANYCH – BADANIA WSTĘPNE

The compositions of phosphogypsum and power plant ash as waste created in the production of an orthophosphoric acid and the coal combustion with the addition of fine coal were prepared. The compositions were then granulated and sintered in a muffle furnace in the atmosphere of air under the conditions previously determined. The compressive strength, open porosity and water absorption were also determined and compared with the results obtained for the commercial aggregate. Chemical and phase compositions of the aggregate were also studied. The results of the research indicate that proposed method of the high temperature utilization of phosphogypsum and power plant ash has a great potential for application and it is worth of further research.

*Keywords:* phosphogypsum, power plant ash, lightweight aggregate

Z odpadów po produkcji kwasu fosforowego i po energetycznym spalaniu węgla spreparowano mieszanki fosfogipsowo-popiołowe z dodatkiem węgla, zgranulowano je oraz wyznaczono parametry spiekania aglomeratów w piecu muflowym, w atmosferze powietrza. Określono wytrzymałość mechaniczną granul kruszywa, ich porowatość i nasiąkliwość oraz porównano je z parametrami kruszywa handlowego. Wyznaczono ich skład chemiczny i fazowy. Wyniki badań wskazują, że zaproponowana metoda wysokotemperaturowej utylizacji fosfogipsu i popiołów elektrownianych ma potencjał aplikacyjny, który uzasadnia prowadzenie dalszych badań.

### 1. Introduction

Processing of phosphorite in a method called “the wet process” creates approximately five tons of strongly acidic, waste gypsum for every ton of the orthophosphoric acid produced. Currently there are about 86 million of tons of the phosphogypsum gathered only by one chemical factory Z. Ch. Police [1]. The national power industry based mainly on hard and brown coal combustion also generates large amount (250 million tons) [2] of waste ash which, particularly in previous years, was simply gathered in the stockpiles.

Nowadays most of the fly ash is utilized. There are also created production technologies to use the ash from stockpiles for the manufacture of lightweight sintered aggregate [3]. The phosphogypsum is utilized only in few percent and that is why every method allowing decrease its amount is desirable. Especially concerning the possible commercial production. One of such methods could be fabrication of the ceramic aggregate from two waste raw materials – phosphogypsum and power plant ash, as long as developed method allows a profitable production and the product can be used in construction and road building. At this point it is necessary to take into consideration the ways of utilization the phosphogypsum created so far, as well as about the limitations of its application [4]. Therefore

the aim of the research within the preliminary laboratory tests was to examine if the fabrication of such ceramic aggregate is even possible and if the further production will not be too energy-consuming.

### 2. Research

The compositions made of the phosphogypsum and ash with the addition of fine coal were granulated and sintered in a muffle furnace, in the atmosphere of air. The mechanical parameters as well as the chemical and phase composition of the obtained aggregate were determined. The compositions for the research on a larger scale were chosen.

As raw materials were used:

- phosphogypsum created during current production of orthophosphoric acid from Syrian phosphorite delivered by Z. Ch. Police,
- dry fly ash gathered on electro-filters in a power plant belonging to Z. Ch. Police, the content of coal was 6.5 wt. %,
- hard coal – milled in a ball mill to obtain a grain fraction under 0.3 mm,
- water – as an agglomeration factor.

\* WARSAW UNIVERSITY OF TECHNOLOGY, FACULTY OF CHEMISTRY, DEPARTMENT OF INORGANIC TECHNOLOGY AND CERAMICS, 3 NOAKOWSKIEGO STR., 00-664 WARSAW, POLAND

\*\* LSA SP. Z O.O., 3 GEN. WŁ. ANDERSA STR., 15-124 BIAŁYSTOK, POLAND

The sintering process during the fabrication of the ash aggregate can be conducted autothermally in a shaft furnace [5] or in a specifically constructed rotary furnace [6], as long as the content of coal in ash exceeds 5-5.5 wt. %. While preparing the compositions from the phosphogypsum and ash, 8 wt. % content of coal was accepted as such that provides the autothermal sintering process [7].

Examined compositions included 95-5 (95 wt. % of phosphogypsum and 5 wt. % of ash) and 50-50 (50 wt. % of phosphogypsum and 50 wt. % of ash), both with 8 wt. % content of fine coal. The composition made only of the phosphogypsum and fine coal was not tested, because of the difficulties occurred during the granulation process.

The compositions were granulated on a granulation plate with water as an agglomeration factor. Granules, after the drying process at below 100°C, were then sintered in a muffle furnace in the atmosphere of air at the rates 7°C/min or 8°C/min, at 1050, 1100 or 1130°C, during one or two hours. These parameters were chosen on the basis of the process efficiency, possible emission of SO<sub>2</sub> and need to obtain aggregate of sufficient mechanical strength, required for the planned applications.

**3. Results**

Phosphogypsum, fly ash and both compositions were subjected to the Thermogravimetric – Mass Spectrometry Analysis.

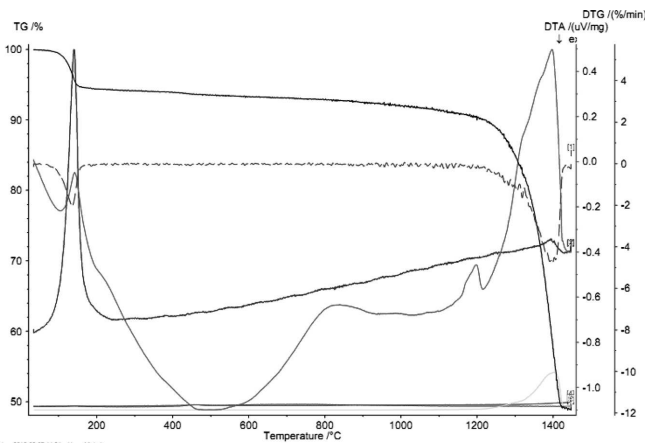


Fig. 1. TG-MS Analysis of phosphogypsum obtained from Syrian phosphorite

In Fig. 1 (blue curve) there is a distinct, sharp peak for water around 100-200°C, which is associated with the decomposition of gypsum to anhydrite through hemihydrate. The same peak also appeared for both of the compositions. Disintegration of anhydrite starts at above 1000°C, but according to the mass spectrometry analysis (yellow curve) SO<sub>2</sub> begins to emit at about 1300°C.

The analysis of dry fly ash indicated only the emission of CO<sub>2</sub> at around 400-800°C, what is mainly associated with the combustion of coal. In the case of the composition 95-5 the emission of CO<sub>2</sub> occurred below 600°C and the release of SO<sub>2</sub> occurred at above 1300°C, just like for the phosphogypsum.

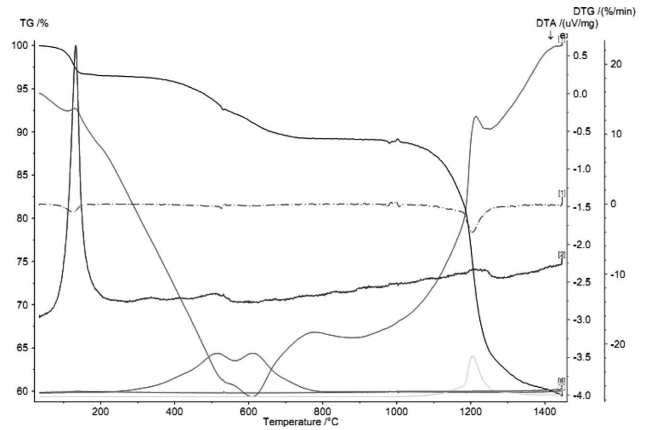


Fig. 2. TG-MS Analysis of composition 50-50

The analysis of the composition 50-50, presented in Fig. 2, showed the emission of CO<sub>2</sub> at around 300-800°C, similarly as in the case of fly ash, whereas the SO<sub>2</sub> peak appeared already at 1150°C. The emission of fluorine (green curve) has not been observed for any of the conducted analyses.

In Fig. 3 there are presented values of the compressive strength for the aggregate 95-5 depending on adopted sintering parameters.

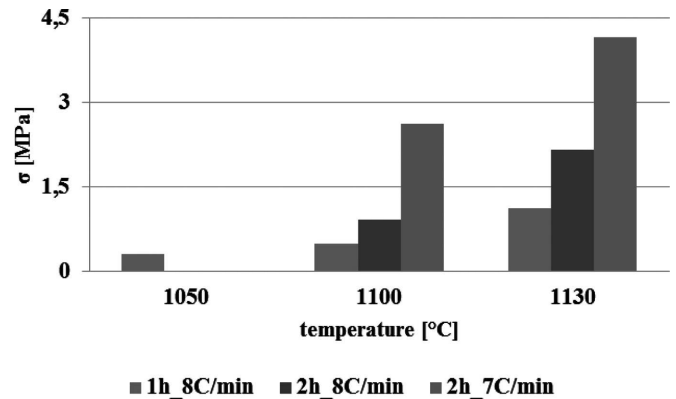


Fig. 3. Compressive strength depending on the temperature, the time and the rate of sintering for 95-5 aggregate

The longer the time of sintering, the smaller the rate of sintering and the higher the temperature of sintering was used, the higher compressive strength was found. Exactly the same dependence was observed for the aggregate 50-50.

The values of the compressive strength obtained for both of the aggregate were compared and the comparison with the values obtained for the commercial aggregate LSA was presented in Fig. 4.

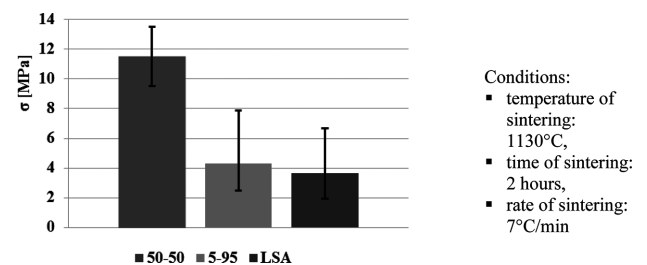


Fig. 4. Compressive strength – comparison of the best results

The compressive strength of the aggregate 50-50 is definitely the highest, while the compressive strength of both, the aggregate 95-5 and the LSA aggregate, is comparable.

The open porosity and water absorption for both compositions were also studied. The values of the porosity of both obtained aggregate are similar, about 22%, and they are by 1/3 lower than the value obtained for the LSA aggregate. It results from a higher content of unporous anhydrite in both examined aggregate.

Both of the aggregate were subjected to the X-ray Powder Diffraction Analysis to determine chemical and phase composition.

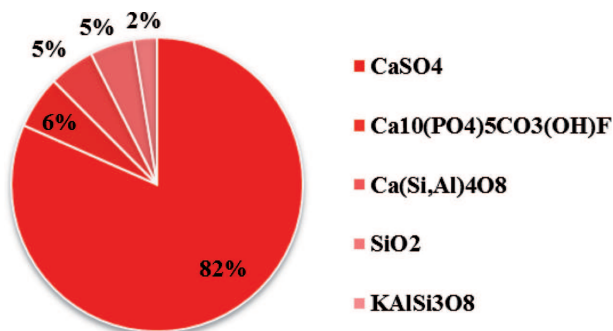


Fig. 5. Quantitative and qualitative composition of aggregate 95-5

The aggregate 95-5, Fig. 5, consisted mainly of anhydrite (82%) and the amorphous phase did not appear. Fluorine appeared in carbonate hydroxyl fluorapatite and if it is washed out, it may cause difficulties during concrete setting, as far as it is used for such application.

The aggregate 50-50 contained 16% of the amorphous phase, which turned out to have a favorable influence on the compressive strength. Moreover, it probably also contained fluorine. However, the PXRD Analysis did not show its presence in the crystalline phase.

The research were granted by Faculty of Chemistry, Warsaw University of Technology.

#### 4. Conclusions

1. The granulation of the compositions proceeds easily and as a result the granules of a good mechanical strength are obtained, what has a favorable influence on the further processes and the need of transportation.
2. The granules sintered for 2 hours in 1130°C have higher mechanical strength, but lower open porosity and water absorption than the LSA aggregate.
3. The aggregate 95-5 contains no amorphous phase and in the crystalline phase dominates anhydrite.
4. The XRPD Analysis showed no fluorine content in the aggregate 50-50. However, possibly it is present in the amorphous phase. In the case of the aggregate 95-5, fluorine appeared in Ca<sub>10</sub>(PO<sub>4</sub>)<sub>5</sub>CO<sub>3</sub>(OH)F.
5. It is necessary to determine a fluorine wash out effect, since it can make it difficult to use the aggregate 95-5 in the production of concrete.
6. The TG-MS Analysis showed the emission of SO<sub>2</sub> appeared so it is necessary to measure the emission stream of SO<sub>2</sub> in flow-meter apparatus.

#### REFERENCES

- [1] Phosphogypsum – unpublished conference materials of Z.Ch. Police received by courtesy of Z.Ch. Police (in Polish).
- [2] Inorganic waste of chemical industry – technological foresight, Project WND-POIG.01.01.01.-00-009/09, Final report, B. Cichy, January 2012 (in Polish).
- [3] J. Sokołowski, K. Łuczaj, P. Urbaniśka, Archives of Metallurgy and Materials **56**, 4, 1185-1192 (2011).
- [4] A. Bójnowicz - Bablok, Chemical Industry **92**, 4, 450 (2013) (in Polish).
- [5] Pat. pol. no 197 301 (2008).
- [6] Pat. pol. no 196 842 (2008).
- [7] Patent application P-398148 (2012).