

PHYSICOCHEMICAL PROPERTIES OF MEAT-BONE MEAL AND ASHES AFTER ITS THERMAL TREATMENT

Kinga KRUPA-ŻUCZEK ^{a*}, Małgorzata I. SZYNKOWSKA ^b, Zbigniew WZOREK ^c,
Agnieszka SOBCZAK-KUPIEC ^a

^a Dr.; Institute of Inorganic Chemistry and Technology, Cracow University of Technology, 24 Warszawska St., 31-155 Cracow, Poland

* E-mail address: kingak@chemia.pk.edu.pl

^b Associate Prof.; Institute of General and Ecological Chemistry, Technical University of Lodz, 116 Zeromskiego St., 90-924 Lodz, Poland

^c Associate Prof.; Institute of Inorganic Chemistry and Technology, Cracow University of Technology, 24 Warszawska St., 31-155 Cracow, Poland

Received: 26.03.2012; Revised: 5.04.2012; Accepted: 13.09.2012

Abstract

A solution to the problem of depletion of phosphorus raw material deposits could be recovering of phosphorus from industrial waste especially from meat industry. Thermal processing at a temperature not lower than 850°C for minimum 2s is the only acceptable method enabling to neutralize this waste. The paper presents production technology of meat-bone meal (MBM) and its physicochemical properties. MBM samples were calcined in a stationary chamber kiln in air atmosphere at temperatures of 600-950°C ($\Delta=50^\circ\text{C}$) for 3 hours. The results obtained indicated that the phosphorus content in ashes after MBM calcining was close to or higher than the concentration of that element in a typical phosphoric raw material. It confirmed the possibility of utilization of meat waste as a substitute for phosphoric raw materials.

Streszczenie

Rozwiązaniem braku surowców fosforonośnych okazało się pozyskiwanie fosforu z odpadów kostnych z przemysłu mięsnego. Proces termicznej utylizacji tych odpadów w temperaturze wyższej niż 850°C przez minimum 2s pozwoli nie tylko na utylizację materiału a także pozyska nowy surowiec fosforonośny. W pracy przedstawiono proces produkcyjny maczki mięsno-kostnej (MMK) oraz jej własności fizykochemiczne. Próbki maczki mięsno-kostnej kalcynowano w piecu stacjonarnym atmosferze powietrza w przedziale temperatur 600-950°C ($\Delta=50^\circ\text{C}$) przez 3 godziny. Badania pokazały, że zawartość fosforu w popiołach z kalcynacji MMK jest na takim samym lub nieznacznie wyższym poziomie jak zawartość tego pierwiastka w typowych surowcach fosforowych. Możliwa jest zatem termiczna utylizacja odpadów z przemysłu mięsnego w celu pozyskania substytutu surowców fosforonośnych.

Keywords: Meat-bone meal; Physicochemical properties; Calcining; Phosphoric raw materials.

1. INTRODUCTION

Meat industry generates large quantities of waste products. 18 million tones of waste per year are produced in EU countries [1-2]. Due to bacteriological hazard and difficulties with storage, utilization process of meat waste has become troublesome.

The meat industry produces large quantities of MBM [3]. As a result of increase amount of BSE European

Parliament and Council of Europe introduce Decree No. 1774/2002 of 3 October 2002. On the basis of this decree the methods of dealing with certain waste depending on its category have been worked out. The classification of the material into a suitable category depends on defining its origin by this product and the only method of their utilization is calcining process at higher temperature [4-5].

Due to changing regulations for the use of meat (and bone) meal, its application as a fuel for energy generation has gained enormous interest [6]. As MBM combustion residues mainly arise from bone combustion, they contain a high amount of phosphate and calcium, two major constituents of bone [3].

In view of rock phosphates gradual depletion, and in an increased phosphorus demand, new alternate sources have to be considered [1]. One of the possible phosphorus sources are wastes derived from meat industry and chicken-farming. Investigations on phosphorus recovery from municipal sludge have been also carried out for many years [6-8]. That sort of activity, consisting in wider application of waste recycling as a substitute for natural sources, and also for energy recovery, is associated with an introduction of cleaner technologies into practice as a basic element for the sustainable development strategy [8-11]. The cost of this recycled material is lower than that of a conventional rock phosphate, and the application of meat-bone meal is economically well-founded [12-13].

The new valorisation routs of MBM ash are developed and they include such as: phosphoric acid production, phosphate source for industry, agricultural soil enrichment, heavy metals immobilization in soil or water, etc. as developed for other phosphate rich materials (rocks, hydroxyapatites, bone char, etc.) [14-15]. We report here a study on the physical and chemical characterization of meat and bone meal combustion residues. In this work we investigate the possibilities of MBM combustion residues application as a substitute of natural raw material, such as apatites and phosphate rock.

2. EXPERIMENTAL PART

Meat-bone meal production: meat bone meal is obtained from non-edible animal by-products of low biological risk (the 3rd category of waste according to [10]), such as skins, hairs, feathers, horns, hooves, blood and returned from market (not sold) meat products. Proportions of the individual components are variable. Mixtures prepared contain around 40% of moisture. One ton of the manufactured by-product yields about 400 kg of MBM and 200 kg of fat [16]. At the beginning of the process metallic impurities are removed from the raw material, and its size reduction by means of crushing and mixing is carried out. Next, the material is sterilized for 30 minutes, at a temperature of 133°C under the pressure of 0.3MPa. The sterilized material is put into a drier where moisture

is vaporized and a part of fat is separated. After preliminary filtering, the fat is placed in a buffer container. Next, the rest of fat is eliminated from the dried and partially defatted material using a filter-press (pressure 1MPa, temperature 90-100°C). During this process, a solid fraction meat-bone meal is obtained. The product is milled and screened. The above process conditions fulfilled the requirements set by the European Union. The meat bone meal was received from "Farmutil HS" which is one of the largest utilization plant in Poland.

The calcination was realized in chamber kiln with electric heating in air atmosphere at the range of temperature 600-950°C ($\Delta = 50^\circ\text{C}$) in 3 hours.

3. METHODS

The content of moisture was determined at a temperature of 105°C with the use of WPS210S weight-dryer.

The phosphorus content was determined by the spectrophotometric method with a Marcel Media UV-VIS spectrophotometer after former mineralization in a mixture of concentrated hydrochloric and nitric acids. The marking method consists in forming a yellow-tainted phosphorus-vanadium-molybdenum complex and absorbance photometric measurement at a wavelength of 430 nm.

Calcium was determined with the titration method (sodium versenate) taking into account the mixed indicator – calcein and thymolphthalein after dissolving the sample in nitric [12].

The heat of combustion of MBM was measured in oxygen atmosphere with KL-12 Mn Precyzja-Bit calorimeter.

Phase composition was analysed by the X-Ray diffraction method carried out with the use of Philips X'Pert diffractometer (Cu $K\alpha$ 1.54 nm, Ni filter, 40 kV, 30 mA) with graphite monochromator.

Thermal analysis of MBM was carried out at temperatures of 20-1000°C with 2960 Simultaneous DTA-DTG TA Instruments.

Effect of calcining temperature on the microstructure of samples was examined using an S-4700 Hitachi scanning electron microscope.

4. RESULTS AND DISCUSSION

The content of moisture, phosphorus and calcium, heat of combustion and phase composition of MBM were determined. The resulting average numbers,

presented below, are the mean of the three measurements. The samples contained [%w/w]: moisture – 2.43, phosphorus – 5.8, calcium – 7.7.

The heat of combustion of meat bone meal amounted to 18.500 kJ/kg.

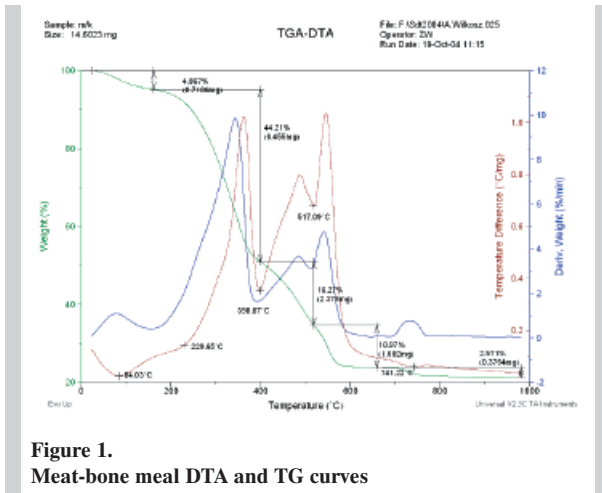


Figure 1.
Meat-bone meal DTA and TG curves

Thermal analysis of MBM (Figure 1.) proved that meat-bone meal was decomposing in three stages. Up to 550°C the whole organic substance was removed. The loss of weight at 750°C resulted from the decomposition of carbonate groups present in natural bone. Meat-bone meal was calcined in a chamber kiln for 3 hours within the temperature range of 600°C to 950°C ($\Delta=50^\circ\text{C}$). The loss of weight in the material calcined at 600°C amounted to 70%. The samples after calcination at 750°C contained [%]: phosphorus – 17.9, calcium – 33.3.

For the ashes obtained at 950°C the loss of weight amounted to 77%. The samples contained [%]: phosphorus – 17.0, calcium – 36.1. The content of phosphorus in ashes was at a concentration level comparable to that element in typical phosphoric raw materials (13.2-17.2%) [2].

The X-Ray analysis showed that the main crystalline phase in ashes obtained from MBM was hydroxyapatite (Figure 2). In contrast to MBM, in ashes obtained from bone sludge (deproteinized and defatted pork bones) hydroxyapatite is only crystalline phase indicated by XRD [17].

Figures 3 and 4 show surface of hydroxyapatite observed under a scanning electron microscope. Pictures obtained with different enlargement had similar properties. Particles with a diameter of approximately 60-90 μm were observed in a few cases.

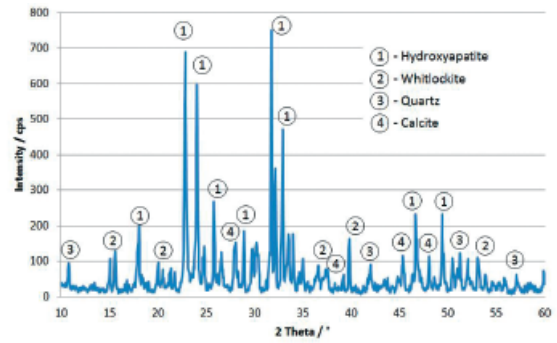


Figure 2.
X-ray diagram of meat-bone meal ash obtained at a temperature of 600°C

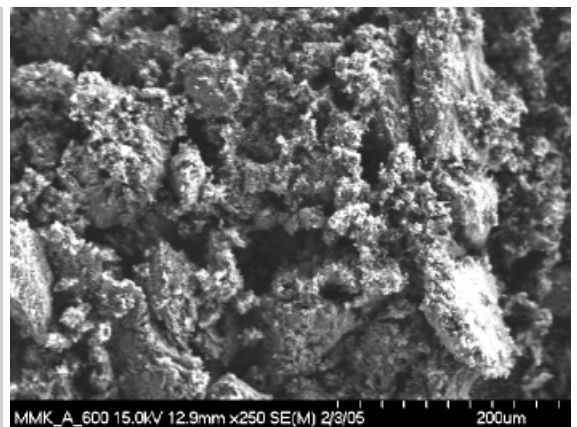


Figure 3.
Image of surface of MBM ash after calcining at 600°C

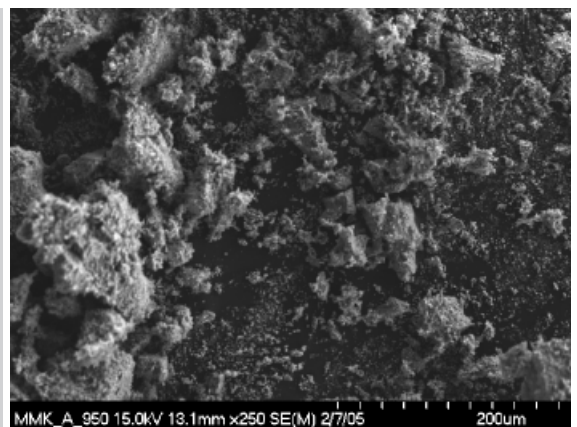


Figure 4.
Image of surface of MBM ash after calcining at 950°C

5. CONCLUSIONS

1. Research results on physicochemical properties showed that meat-bone meal contained on average [%w/w]: H₂O – 2.43; P – 5.8; Ca – 7.7. The heat of combustion was 18.500 kJ/kg. The main crystalline component of MBM was hydroxyapatite. Decomposition of MBM was carried out at temperatures increasing up to 550°C. The loss of weight related to organic compound combustion amounted to ~76%.
2. The analyses of physicochemical properties of meat-bone ashes showed that phosphorus content was in the range of 15-17%; that was comparable with the level of phosphorus content in typical rock-phosphate.
3. The temperature range of 600-950°C ($\Delta=50^\circ\text{C}$) in a chamber furnace is effective for MBM calcining. Investigation showed that temperature had no influence on the morphology of the obtained ashes. In each case a fine-crystalline product was obtained.
4. In conclusion, the results obtained confirmed the possibility of application of meat-bone ashes as an alternative, high quality phosphoric raw material for phosphoric compound production.

ACKNOWLEDGEMENT

This work was supported by the Grant of the Minister of Science and Higher Education-Grant number 1850/B/H03/2009/36.

REFERENCES

- [1] European Chemical Industry Council and C.E.E.P. Phosphates.1997
- [2] Kowalski Z., Wzorek Z., Krupa-Żuczek K., Konopka M., Sobczak A.; The possibilities of obtaining hydroxyapatite from meat industry. *Mol. Cryst. Liq. Cryst.*, Vol.486, 2008; p.282-290
- [3] Deydier E., Guilet R., Sarda S., Sharrock P.; Physical and chemical characterisation of crude meat and bone meal combustion residue: “waste or raw material?” *J. Hazard. Mater.*, Vol.121, No.1-3, 2005; p.141-148
- [4] Coutand M., Cyr M., Deydier E., Guilet R., Clastres P.; Characteristics of industrial and laboratory meat and bone meal ashes and their potential applications. *J. Hazard. Mater.*, Vol.150, No.3, 2008; p.522-532
- [5] Phosphate rock grade and quality – Phosphorus & Potassium. 1992; p.178
- [6] Garcia R. A., Rosentrater K. A.; Concentration of key elements in North American meat & bone meal. *Biomass And Energy*, Vol.32, 2008; p.887-891
- [7] Directive 2000/76/CE of European Parliament on waste incineration
- [8] Directive 96/23/CE of European Parliament
- [9] Regulation (EC) No(WE) Nr 999/2001 of the European Parliament and the Council of 22 May 2002
- [10] Regulation (EC) No 1774/2002 of the European Parliament and the Council of 3 October 2002 laying down health rules concerning animal by-products not intended for human consumption, *Official Journal of the European Communities*, No L 273, 10.10.2002
- [11] Gorazda K., Kowalski Z., Wzorek Z., Jodko M., Rzepecki T., Kulczycka J., Przewrocki P.; Possibilities of phosphorus recovering from municipal sewage and sewage sludge. *Pol. J. App. Chem.*, Vol.47, No.2, 2003; p.51-63
- [12] Wzorek Z.; The phosphorus compounds recovery from thermally treated waste and its use as a substitute of natural phosphorus raw materials. *Wydawnictwo PK, Kraków*, 2008, (in Polish)
- [13] Kowalski Z., Krupa-Żuczek K.; A model of the meat waste management. *Pol. J. Chem. Technol.*, Vol.9. No.4, 2007; p.91-97
- [14] Deydier E., Guilet R., Cren S., Perea V., Mouchet F., Gauthier L.; Evaluation of meat and bone meal combustion residue as lead immobilizing material for in situ remediation of polluted aqueous solutions and soils “Chemical and ecotoxicological studies”. *J. Hazard. Mater.*, Vol.146, No.1-2, 2007; p.227-236
- [15] Staroń P., Kowalski Z., Krupa-Żuczek K., Wzorek Z.; Thermal utilization of mixtures of bone waste. *Pol. J. Chem. Technol.*, Vol.12, No.4, 2010; p.26-30
- [16] Kowalski Z., Krupa-Żuczek K.; Modelowe rozwiązania bezodpadowej gospodarki odpadami mięsnymi (Simulation solution of waste free management of meat waste) *LAB*, Vol.13, No.5, 2007; p.20-27 (in Polish)
- [17] Sobczak A., Kowalski Z., Wzorek Z.; Preparation of hydroxyapatite from animal bones. *Acta of Bioengineering and Biomechanics*, Vol.11, No.6, 2009; p.26-28