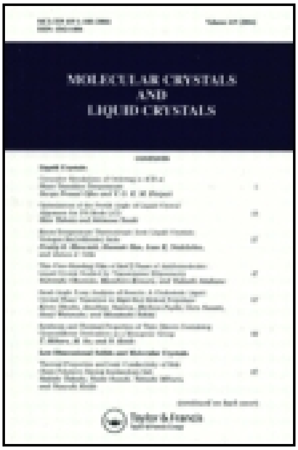

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The Possibilities of Obtaining Hydroxyapatite from Meat Industry

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The goal of this work was investigation of physical and chemical properties of calcining products obtained from bone sludge. The calcining process was carried out at the temperatures of 873–1223 K, in chamber kilns in air atmosphere. X-ray investigations of phase composition confirmed that hydroxyapatite is the main component of calcining products. The phosphorus content in these products was close to the level of concentration of this element in typical phosphoric raw materials which proved right using waste materials from meat industry as a substitute for phosphoric raw materials. Studies of morphology of ashes obtained at different temperatures showed that the calcining temperature did not affect the product properties in essential manner. In all cases fine-crystalline products, with a similar shape and size of grain were obtained. Only ashes calcined at 1223 K were characterized by slightly melted crystallites.

Keywords: bone sludge; hydroxyapatite; phosphoric raw materials; physicochemical properties; thermal utilization

INTRODUCTION

A solution to the problem of depletion of phosphorus raw material deposits [1–3] could be obtaining phosphorus from industrial waste especially from meat industry that generates 18 million tons of phosphorus-containing waste per year. Phosphorus-containing waste from meat industry such as meat-bone pulp and all the elements of animal bodies suspected of having contracted BSE disease belonged to the I high-risk category of waste. Thermal processing was the only

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permissible method of neutralizing this waste at a temperature not lower than 1123 K (within min. 2 s) [4]. Bone sludge, i.e. deproteinized and defatted bones, skins, hooves, horns, bristles, feathers and blood from animals other than ruminants, elements of slaughtered animals considered suitable for consumption and also those which were rejected as not suitable for human consumption and having no symptoms of diseases transmitted onto people, belonged to the III category of waste. This waste should be eliminated through combustion at the temperature of 1123 K. They can also be processed into feed, biogas or compost [4]. The next method of bone-waste utilization was based on the possibility of transforming bones or bone-waste into hydroxyapatite by means of chemical methods. Hydroxyapatite obtained from animal bone waste could become a new, alternative material applied in bone surgery. This theory is based on biocompatibility and structural similarity of hydroxyapatite to mineral parts of human bones. These properties make hydroxyapatite obtained from animal bones osteoinductive, i.e. after its implantation a natural bone can gradually replace an implant [5–7]. The studies also proved that because of its porosity it can be applied in bone surgery and also as a polymer additive increasing their bio- functioning. An organic part of animal bones can be almost completely removed by double extraction of hot sodium hydroxide (4 M) at a temperature not lower than 100°C within 24 h. Thus obtained hydroxyapatite contains 38% P_2O_5 and 52% CaO and also carbonate groups and magnesium, as it happens with hydroxyapatite of human origin. No significant difference in materials from pork and beef bones was recorded, and the crystallites size fell in a range of hundredth parts of micrometer therefore it was classified as a nanomaterial [8,9]. However, the leaching method resulted in a large amount of waste and it was useful only on a small scale.

This article presents the results of research concerning thermal utilization of bone sludge. The goal of the research was investigation of physicochemical properties of bone sludge waste from meat industry and products of its thermal utilization containing hydroxyapatite.

EXPERIMENTAL PART

Research Results

In bone-pulp and bone sludge applied in the research (a mixture of pork legs, pork bones and beef bones at weight ratio 1:1:1) moisture content was determined with the help of a weight-dryer at 387 K, as well as phosphorus content on Marcel Media spectrophotometer with a diffraction-photometric method according to [10], after former sample mineralization with sulphuric and nitric acids. Calcium content was determined with the ASA method, with the apparatus Analyst 300 Perkin Elmer after sample mineralization with nitric acid [11]. Protein content was determined after mineralization with concentrated sulphuric acid at 693 K.

Typical bone sludge varied in size from several to tens of cm and it included [% weight]: ~55.0 H_2O; organic substances, in wet mass ~22.2, in dry mass ~37.0; fat 2.98, protein 14.29; P in wet mass ~6.44, in dry mass ~10.73; Ca in wet mass ~17.55, in dry mass ~29.25. The composition of bone sludge obtained from different animal waste products was also studied and the results are given in Table 1.

The composition of sludge from different kinds of bones is comparable, which made it possible to mix the above-mentioned products in weight ratio 1:1:1 into one product named medium bone sludge. The content of phosphorus ranged from 14 to 16% (at the level of phosphorus content in typical phosphorites used in phosphoric acid production) whereas the content of calcium amounted to 23%. The contents of fat and protein in bone sludge resulted from incomplete deproteinization and deffating of bones in the process described above [16].

The heat of combustion of bone sludge was measured with KL-12 Mn Precyzja-Bit calorimeter according to PN-81/G-04513 and it amounted to 7900 J/g, in comparison to coal heat of combustion which was 20662 J/g [12].

The phase composition was determined with the X-Ray method on Philips X'Pert diffractometer equipped with PW 1752/00 graphite monochromator. The X-Ray analysis showed that the only crystalline phase in bone sludge is hydroxyapatite (Fig. 1).

Bone sludge was calcined at temperatures ranging from 873 K to 1223 K at every $\Delta = 50$ K within 3 hours in a chamber kiln with electric heating, in air atmosphere. In obtained ashes phosphorus and calcium contents as well as phase composition were analysed with the X-Ray method.

TABLE 1 Chemical Composition of Difference Bone Sludge [16]

	Composition [% weight]				
Kind of sludge	Water	Phosphorous	Calcium	Fast	Protein
From beef bones	7.07	14.12	25.8	2.37	20.38
From pork bones	6.53	14.09	22.8	3.13	24.04
From pork legs	7.06	13.98	20.6	2.89	18.69
Medium bone sludge	7.00	14.08	38.39	2.98	14.29

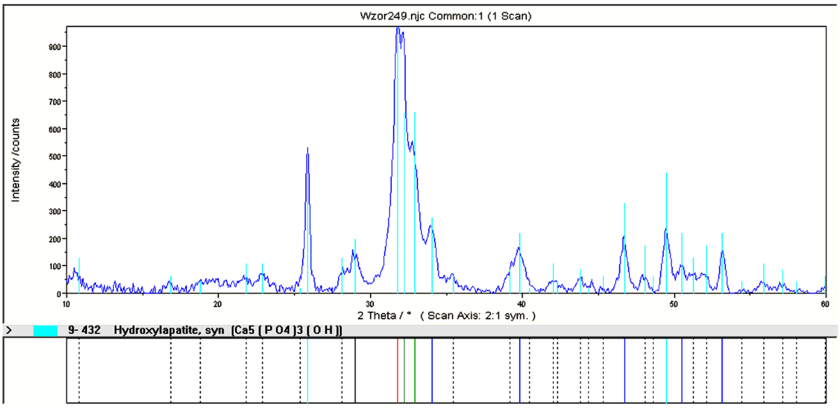

FIGURE 1 X-ray diagrams of bone sludge.

The X-ray diagram of bone ashes from deproteinized bone sludge in the calcining process showed that hydroxyapatite was the main component of the ashes (Fig. 2). The obtained product was a homogeneous raw material as regards its chemical composition and chemical properties, which facilitated its processing.

In bone ashes obtained by combustion of a bone sludge mixture at 1:1:1 ratio at the temperature of 873 K and 1223 K in air atmosphere within 3 hours the following were determined:

- calcining at 873 K resulted in mass loss of 34%; phosphorus content 15.8%, and calcium content 38.9%,

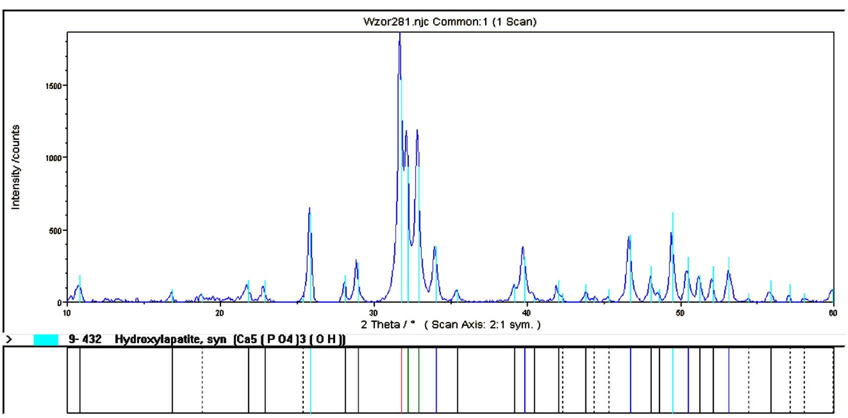

FIGURE 2 X-ray diagrams of bone ash, obtained by combustion of a sample in a chamber kiln in air atmosphere at the temperature of 873 K.

- calcining at 1223 K resulted in mass loss of 34%; phosphorus content 16.5%, and calcium content 39.3%.

Morphology samples of ashes were investigated with the SEM-EDS method. The SEM (scanning electron microscopy) research used S-4700 Hitachi electron microscope equipped with an attachment for the EDS X-Ray microanalysis [13,14]. The goal of these investigations was to define an influence of calcining temperature of deproteinized bone-waste on changes in the properties of ash surfaces. Ashes obtained by combustion of bone sludge mixture (1:1:1) at temperatures ranging from 873 K to 1223 K were compared.

Figures 3 and 4 show the distribution of chemical elements on the ash surfaces. These images show very good homogeneity of the analyzed ash surfaces. The distribution of sodium, magnesium, aluminium, silicon, phosphorus and calcium in each case is almost uniform [15].

Morphology of the analyzed ashes was investigated with the help of a SEM S-4700 Hitachi scanning electron microscope. Figures 5 and 6

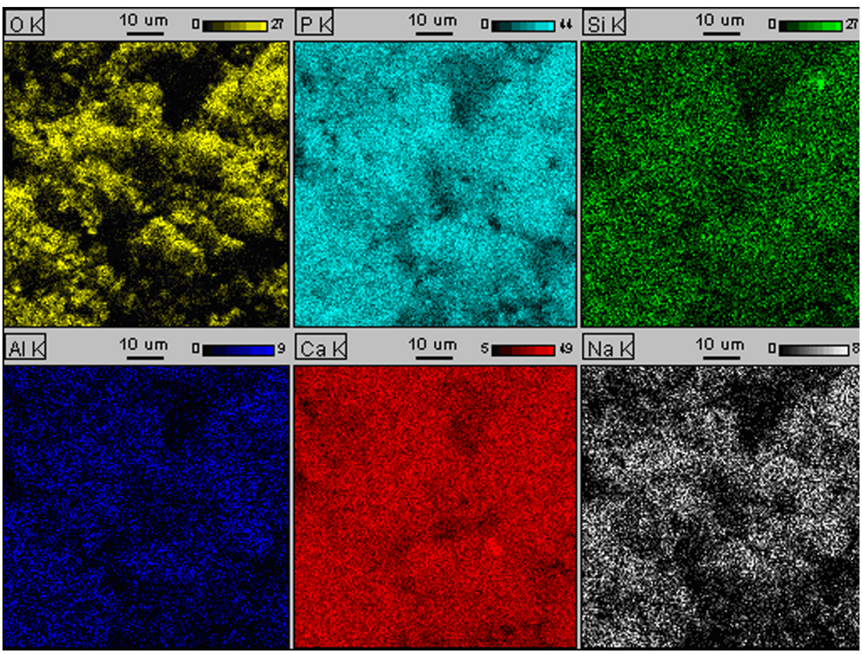

FIGURE 3 Ion images on ash surface obtained by combustion of bone sludge within 3 h in air atmosphere at 873 K.

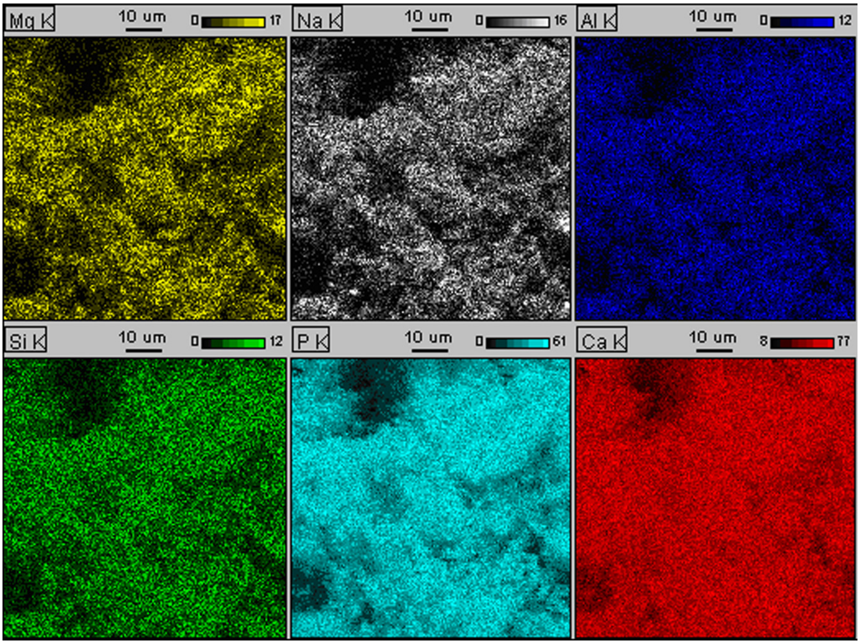

FIGURE 4 Ion images on ash surface obtained by combustion of bone sludge within 3 h in air atmosphere at 1173 K.

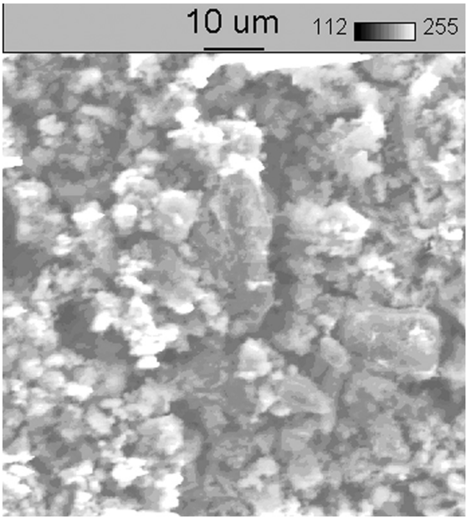

FIGURE 5 Images of ash surface obtained by combustion at the temperature of 873 K.

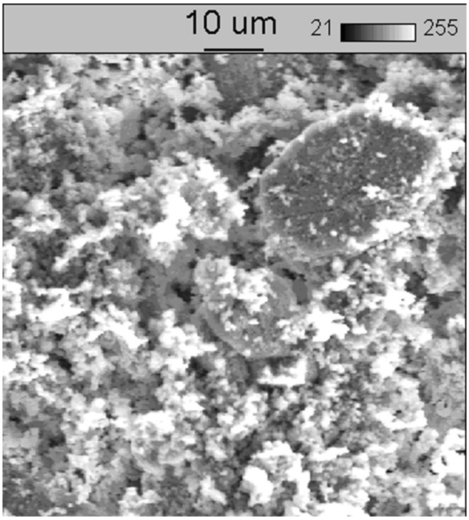

FIGURE 6 Images of ash surface obtained by combustion at the temperature of 1173 K.

show microimages of ashes obtained by combustion at temperatures ranging from 873 K to 1173 K in air atmosphere in a chamber kiln within 3 hours, enlarged 1,800 times. The images present a lot of small crystallites of a size estimated at 5–10 μm as well as bigger crystallites of 25–30 μm appearing occasionally. For ash obtained at the temperature of 1173 K one may observe insignificant amounts of brighter edges of crystallites, which can be a sign of slight melting of crystallites caused by overheating of a sample.

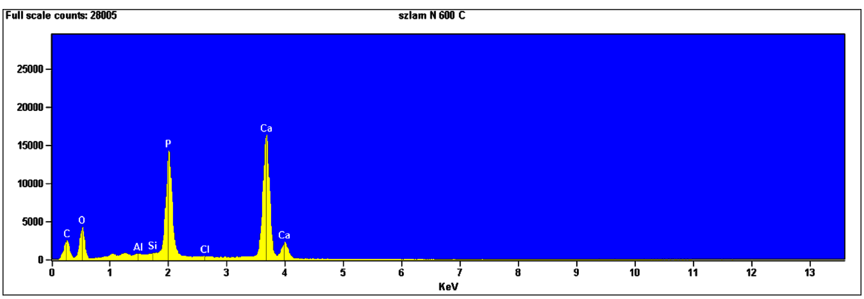

FIGURE 7 Chemical composition analysis of ash obtained by combustion of bone sludge at the temperature of 873 K in air atmosphere within 3 hours.

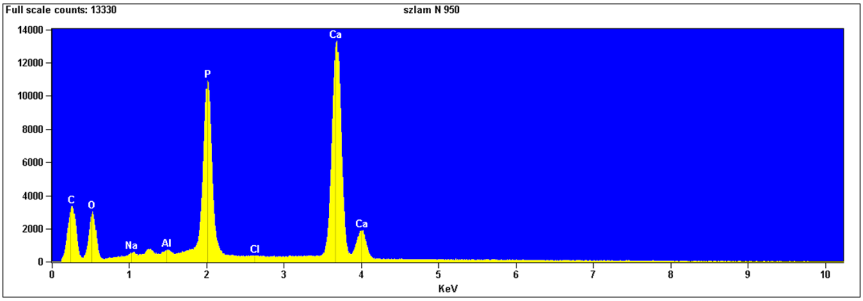

FIGURE 8 Chemical composition analysis of ash obtained by combustion of bone sludge at the temperature of 1223 K in air atmosphere within 3 hours.

Figures 7 and 8 present the results of analysis of chemical composition of obtained ashes at 873 K and 1223 K by the EDS method. In both cases two highest peaks come from phosphorus and calcium, main components of hydroxyapatite. Low peaks from sodium, aluminium and silicon mean that these chemical elements are impurities in the tested samples [16].

CONCLUSIONS

The research on physicochemical properties of bone-waste from meat industry showed that phosphorus content is around 14%, which is the level of phosphorus content in typical phosphorites used for phosphoric acid production; however, calcium content amounts to 23% on average.

The conducted research on bone-waste calcining in a laboratory chamber kiln at the temperatures of 873–1223 K confirmed that thermal utilization of deproteinized bone-waste was possible. The obtained ashes contained mainly hydroxyapatite with low amounts of sodium, aluminium and silicon.

The research on ashes morphology at different temperatures showed that calcination temperature did not affect their properties in any significant way. In all cases fine-crystalline products of a similar shape and grain size were obtained. Only the ashes calcined at the temperature of 1223 K were characterised by slightly melted crystallites.

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