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Research Paper

Quantification of material recovery from meat waste incineration – An approach to an updated food waste hierarchy

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ABSTRACT

The meat industry generates a significant amount of hazardous waste, containing phosphorus, calcium, and other elements which could be the basis for other products. This work presents the results of research on the thermal utilisation of bone meat waste and the use of the ash thus obtained as a substitute for phosphorus raw materials. Material Flow Analysis was used to quantify and assess the option with the highest material productivity. Such a solution can be in line with an updated pyramid of food waste hierarchy already proposed in the literature, distinguishing surplus food and a new category for recycling of materials, in analysed case food waste, in the circular economy. The research is based on the example of real data from a Polish meat producer. The quantity of waste from primary production and meat manufacturing containing waste bone in Poland was estimated to be 232,000 t/y (24.0% of the total quantity of meat waste). Its thermal utilisation potentially allows 71,118 t/y of hydroxyapatite ash, a substitute for phosphorites, to be obtained. The high quality hydroxyapatite ash could be used for the production of food grade phosphoric acid and also for the production of food grade mono- and dicalcium feed phosphates.

1. Introduction

One third of the food produced globally is lost or wasted corresponding to an annual generation of roughly 1.3 billion tonne of food waste. In Europe this figure is estimated to about 88 Mt corresponding to ca. 173 kg per capita; in economic terms, this incurs a loss of 143 billion € each year (Tonini et al., 2018; FAO, 2018). Among the UN Sustainable Development Goals (SDGs) there is one specifically addressed to food waste reduction losses along the production and supply chains by 2030 (United Nations, 2020). The European Union (EU) has adopted a target of a 30% reduction in food waste by 2025 and 50% by 2030 (European Commission, 2019). Food preparation, for households and food service sectors, also provided an important contribution to the Global Warming impacts, while waste management partly mitigated the overall impacts by incurring significant savings when landfilling was replaced with anaerobic digestion and incineration (Tonini et al., 2018).

In literature and practice the reduce, re-use, recycle (3Rs) principle, Life Cycle Assessment (LCA), sustainable consumption and production, and the circular economy (CE) framework have already been proposed to identify and define the best environmental option for the food waste hierarchy and to close the loop in the supply chain. Waste should be avoided, and if not possible, treated to recycle materials and then adopt nutrient and energy recovery to minimise landfilling The food waste hierarchy has been redefining by including materials recycling due to the economic potential of unavoidable food waste, with nutrient and energy recovery as separate categories due to the importance of addressing nitrogen flows and other nutrients (Eriksson et al., 2015; Teigiserova et al., 2020). The food waste generated should be treated as a raw material for industry to produce various high-value biomaterials or bioenergy. However, making beneficial use of food waste and by-products as a resource is quite recent, therefore inventory data on innovative recovery processes are currently lacking (Caldeira et al., 2019), also in case with meat waste.

The average global consumption of all meat has been estimated to be 122 g/day per capita (347.334 Mt consumed per year by 7.8 billion people) of which pork and poultry are a third each, a fifth is beef, and the remainder comes from sheep, goats, and other animals (Godfray et al., 2018). At the global level, the total amount of meat consumed is rising, driven by increasing average individual incomes and by population growth. Meat production is one of the most important ways in which

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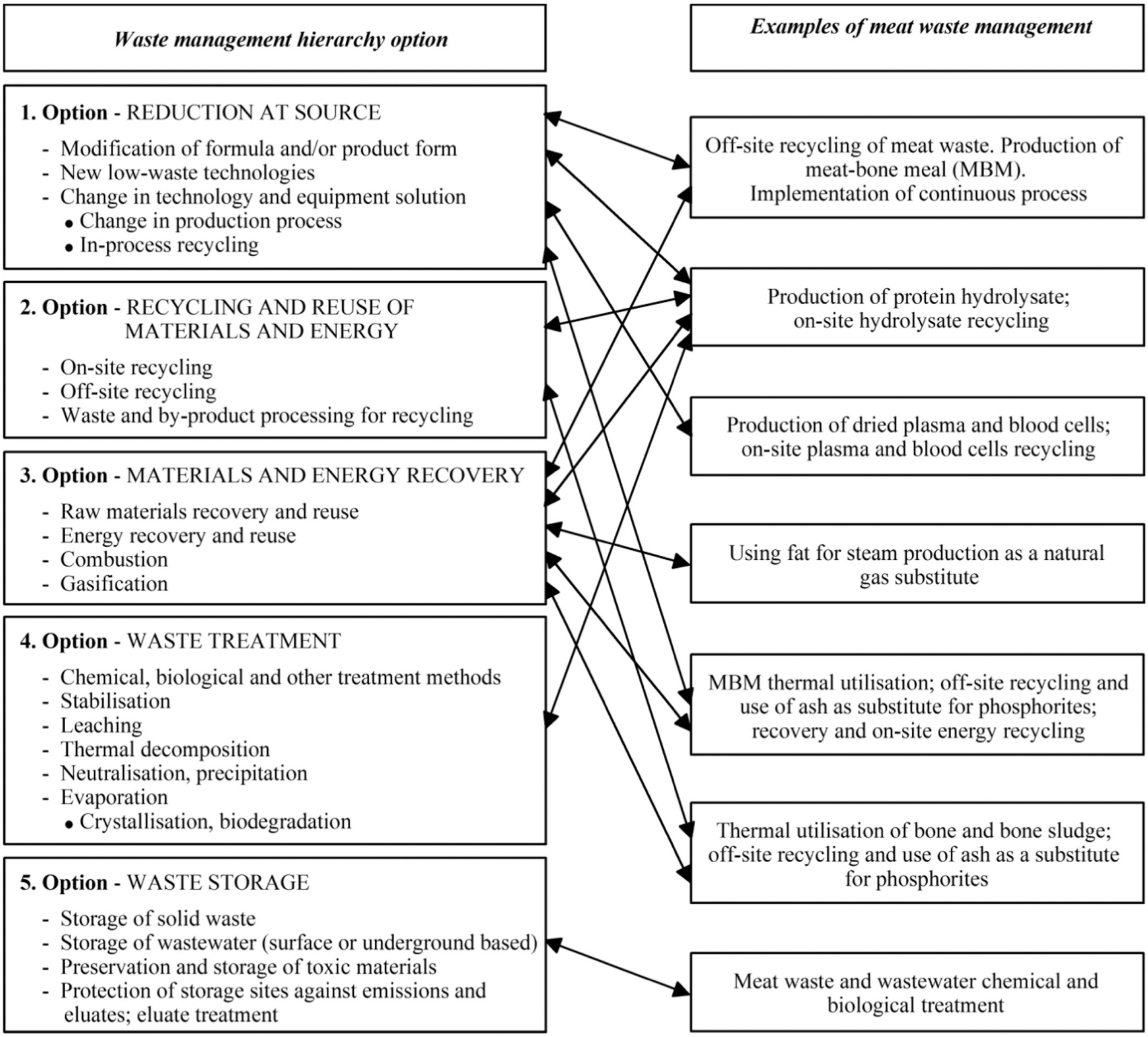
humanity affects the environment. Livestock production is a major source of greenhouse gases (GHGs) and other pollutants (Makara et al., 2019), in some areas making major demands on scarce water resources, and can also exacerbate soil erosion (Tonini et al., 2018; Costello et al., 2016).

A systematised food waste accounting system at macro level was developed for Europe (Caldeira et al., 2019). The meat available in the EU and the meat waste calculated for the meat supply chain for 2011 were as follows [Mt/y]: EU available meat 61.7; total meat waste 14.2 (23%), of which: primary production 0.5 (0.81%), processing and manufacturing 2.9 (4.7%), retail and distribution 1.7, consumption in households 7.3, food services 1.7. The majority of waste in the meat industry is produced during slaughtering, including the gut contents, bones, tendons, skin, blood and internal organs. Meat waste generated in the EU is mainly processed into meat-bone meal (MBM) (Ariyaratne et al., 2014).

The meat available in Poland was 4.204 Mt/y (Statista, 2021). Total meat waste calculated on the basis proposed by (Caldeira et al., 2019) was estimated to be 0.967 Mt/y processed into MBM, of which 400,000 t/y was produced and used as a biofuel (Stokłosa et al., 2019; Kowalski and Makara, 2021a). Such solutions, depending on technology, permit the production of energy and provide overall GHG savings of the order of 600–1000 kg CO_2-eq. per 1 t of MBM treated, mainly as a consequence of fossil fuel consumption avoided in the energy sector (Cascarosa et al., 2013).

Meat waste mainly contains organic parts, water and phosphorus compounds (Pham et al., 2017; Rahimpour Golroudbary et al., 2019). Research on phosphorus recovery from waste has been conducted for many years (Tan and Lagerkvist, 2011; Lee and Oa, 2016; Mayer et al., 2016) and supported by many different EU programmes (Horizon 2020, Life, Knowledge and Innovation Community (KIC) Raw Materials). These activities are included in the waste and agricultural policy and CE strategy of many countries (Cordell et al., 2011). EU waste hierarchy including reduce, reuse, recycle (3 R) principles, cleaner production, resource efficiency, zero waste policy. The basic concepts and definitions related to waste management in the EU have been proposed in the Waste Framework Directive, including general rules for the application of end of waste criteria and by-products. Basic meat waste utilisation


Waste management hierarchy option

1. Option - REDUCTION AT SOURCE
- Modification of formula and/or product form
- New low-waste technologies
- Change in technology and equipment solution
  - Change in production process
  - In-process recycling

2. Option - RECYCLING AND REUSE OF MATERIALS AND ENERGY
- On-site recycling
- Off-site recycling
- Waste and by-product processing for recycling

3. Option - MATERIALS AND ENERGY RECOVERY
- Raw materials recovery and reuse
- Energy recovery and reuse
- Combustion
- Gasification

4. Option - WASTE TREATMENT
- Chemical, biological and other treatment methods
- Stabilisation
- Leaching
- Thermal decomposition
- Neutralisation, precipitation
- Evaporation
  - Crystallisation, biodegradation

5. Option - WASTE STORAGE
- Storage of solid waste
- Storage of wastewater (surface or underground based)
- Preservation and storage of toxic materials
- Protection of storage sites against emissions and eluates; eluate treatment

Examples of meat waste management

Off-site recycling of meat waste. Production of meat-bone meal (MBM). Implementation of continuous process

Production of protein hydrolysate; on-site hydrolysate recycling

Production of dried plasma and blood cells; on-site plasma and blood cells recycling

Using fat for steam production as a natural gas substitute

MBM thermal utilisation; off-site recycling and use of ash as substitute for phosphorites; recovery and on-site energy recycling

Thermal utilisation of bone and bone sludge; off-site recycling and use of ash as a substitute for phosphorites

Meat waste and wastewater chemical and biological treatment

Fig. 1. Hierarchy of pollution prevention options and examples of meat waste management.

techniques, pollution prevention and reference processing methods are briefly presented in (BREF, 2005). Moreover, in the case of animal by-products the Regulation (EC) No 1069/2009 lays down more rules for processed products, however the question of waste/non-waste status for specific animal by-products still has to be addressed for the promotion of the CE. The CE business model and practice in the meat industry provide some examples of how the priority order in waste management planning can be achieved (Fig. 1).

Thermal methods can be used to prevent environmental pollution by reducing the amount of hazardous waste from the meat industry (Kowalski and Makara, 2021a). One good idea is to process wastes from the meat industry using calcining (Coutand et al., 2008; Leng et al., 2019). Thermal utilisation of bone, resulted in production high purity hydroxyapatite (HA) ash, containing on average 16% P. Phosphate rock contain 13.2–17.2% P (Staroń et al., 2010, 2016). HA is a naturally occurring mineral form of calcium apatite with the formula $Ca_5(PO_4)_3(OH)$, crystallised in the hexagonal crystal system. Pure hydroxyapatite powder is white. Up to 50% by volume and 70% by weight of human bone is a modified form of hydroxyapatite, known as bone mineral.

Bones consist of organic and inorganic compounds in the proportion of 30% and 70% respectively. The mineral parts of bones provide stiffness and proper mechanical properties. Biological HA is a component of bones and also pathological tissue (urolith, tooth scale and mineralised soft tissue) (Vallet-Regí and González-Calbet, 2004). The model compound corresponding to the mineral phase of bones is nonstoichiometric HA with a molar ratio of calcium to phosphorus of 1.67. In enamel and dentine, the Ca/P molar ratio is greater than 1.67. Due to its chemical and structural similarity to bone minerals, HA is a good candidate for bone substitutes. Carbonated calcium-deficient hydroxyapatite is the main mineral of which dental enamel and dentin are composed. HA is biocompatible, osteoconductive, non-toxic, with no inflammatory and no immunogenic agents, and bioactive, i.e. it has an ability to form a direct chemical bond with living tissues (Hu et al., 2017; Fathi et al., 2008).

Waste hierarchies serve as guidelines in environmental policy in many industrialised countries (Redlingshöfer et al., 2020), but in combination with Material Flow Analysis (MFA) and economic appraisal (Net present value (NPV), Cost-benefit analysis (CBA)), they can also be applied by industry to create strategic planning to minimise legislative and environmental risk. MFA is a methodology adopted by Eurostat in 2001 and mainly used at a macro and mezo level to promote sustainability, resource efficiency, and the improvement of performance, but also for decisions related to legislation and policy practice (Bringezu, 2006; Brunner and Rechberger, 2004), the development of the CE (Millette et al., 2019) or decoupling (UNEP, 2011). Often combined with LCA, it helps to assess and quantify the impacts of waste flows. For example, based on a Norwegian case study, it has been shown that with food waste prevention, the theoretical potential for systems-wide energy savings would be 16%, and for phosphorous savings 21%, whereas food waste recycling saves 8% for energy and 9% for phosphorus respectively (Hamilton et al., 2015). Focusing on the UK situation, it was shown from an analysis of four treatment methods (anaerobic digestion, in-vessel composting, incineration and landfilling) that incineration is currently the most sustainable option per tonne of waste treated, whereas anaerobic digestion is the best option based on the annual volume of waste treated (Slorach et al., 2019).

MFA allowed for the identification and determination of the quantity of material flows as well as the accumulation of materials in a waste management system (Kosińska et al., 2013). It is based on the principle that "materials cannot be lost" which corresponds to the first law of thermodynamics implying conservation of mass and energy by drawing a system boundary within time and space. The total mass of inputs must be equal to a sum of outputs plus a storage term that considers accumulation or depletion of materials in the process. It is described by the Eq. (1), presented below (Brunner and Rechberger, 2004).

$$\sum_{k_i} \dot{m}(\text{input}) = \sum_{k_0} \dot{m}(\text{output}) + \dot{m}(\text{storage}) \quad (1)$$

where k_i and k_0 represent input and output flows respectively and $\dot{m}$ stands for the flow or flux. MFA can be performed at the level of goods or substances. In the current study, meat waste is involved and considering the assumptions of MFA, it is treated as a good.

When it comes to waste management, it is important to know and understand the flow of materials in the system, which will give a better picture of the problem and also is extraordinarily helpful in the preparation of appropriate strategies. Therefore, MFA allows the evaluation of the proposed solutions in terms of solving problems, as well as achieving the assumed goals related to waste utilisation. In this paper a novel waste hierarchy based on MFA has been proposed for the assessment of solutions that minimise the environmental impact of the waste generated by meat producers. The zero waste technology, using the meat bones incineration process with valuable material recovery (HA) has been analysed.

This work presents the results of research on the thermal utilisation of bone meat waste and the use of the ash thus obtained as a substitute for phosphorus raw materials. The concepts of a waste hierarchy, end of waste criteria, technological assessment (calcining of bone sludge from various types of bones) and MFA were used to quantify and analyse the flow of materials and to minimise the environmental impact of the waste generated.

2. Materials and methods

2.1. Raw materials used

2.1.1. Bone waste

Grinded pork bones with the following properties were incinerated: the particles with the dimension 1–3 cm, H_2O content 35–45.0%; content in dry mass of [%]: organic matter 34–39, fat 14–16, protein 18–23, P 10–14, Ca 28–30. Their bulk density was 0.655 kg/dm^3 and specific density 1.12 kg/dm^3.

2.1.2. Bone sludge

Meat tissue and bone tissue are a basic component of bone waste. Bones, after pre-treatment, removal of metal parts and fragmentation, are subjected to a hydrolysis process resulting in protein hydrolysate and bone sludge. Bone sludge used in calcining process contained in average [%]: H_2O 42.5 and in dry mass: P 14.0; Ca 24.5; fat 4.5; organic matters 16.0; inorganic matters 87.0. Its bulk density was 0.85 kg/dm^3 (Kowalski et al., 2011, 2017).

2.1.3. Recycled hydroxyapatite (HA) ash used in calcining process

In the process of calcining of bone waste recycled HA ashes were used. The main crystalline phase of which is $Ca_5(PO_4)_3OH$. These ashes are a homogeneous high purity raw material (practical absence of heavy metals) in terms of chemical composition and chemical properties. X-ray analysis also shows the presence of small amounts of $Ca_3(PO_4)_2$, $CaCO_3$, SiO_2, Fe_2O_3 in the product. Molar ratio of Ca/P is 1.67. Bulk density 1.2–1.3 kg/m^3. Ash contained [%]: P-17.03 (P_2O_5-39.0); Ca-46.43 (CaO-65.0). A fraction of 0.01–0.5 mm will be the product. Undersize fraction < 0.01 mm – share 39.8% and oversize fraction > 0.5 mm – share 16.9% were recycled (in-process recycling) into rotary kiln and reused.

2.2. Description of calcining method used in laboratory tests

Hydroxyapatite ash was obtained by calcining of bone sludge in a chamber kiln with electric heating, in an air atmosphere, for 3 h at 600 °C to 950 °C with temperature interval of 50 °C. The first phase of the process is the evaporation of moisture from the meat waste. The next stage is its thermal decomposition, during which the organic compounds, mainly proteins and fats included in the meat and bone mass, are combusted. As designed, the process of thermal treatment of meat and bone tissue includes the complete combustion of the organic part of the waste in a complete process carried out with at least 20% of excess air. In the kiln the thermal decomposition processes of bone waste take place, including drying-degassing, incineration and combustion of carbonised organic matter, and calcination of calcium phosphates.

The preparation of bone sludge took place in two stages. First, sludge from pig bones, bovine bones and pig legs were dried at 105 °C and then mixed together in a 1:1:1 mass ratio. About 150 g of the mixture was calcined in a chamber kiln for 3 h in an air atmosphere. The sieve fraction below 0.063 mm was used in all the tests.

2.3. Analytical methods

Chemical composition of raw materials and products determined on the basis of appropriate methods (Polish Committee for Standardization, 2016). The phosphorus content was established based on the spectrophotometric method with a Marcel Media UV–VIS spectrophotometer after prior mineralisation in a mixture of concentrated hydrochloric and nitric acids. Calcium was determined via the titration method. The phase composition was analysed using the X-Ray method with a Philips X′Pert diffractometer with graphite monochromator. The contents of heavy metals such as Cu, Co, Ni, Cr, Cd, Pb, Hg and As were determined by the Atomic absorption spectrometry (AAS) method using an Analyst 300 Perkin Elmer Spectrometer PW 1752/00 after prior mineralisation in concentrated nitric acid. The effect of calcining temperature on the microstructure of samples was examined using a Hitachi S-4700 scanning electron microscope (SEM). Chemical analysis was carried out using an energy dispersive X-ray spectroscope (EDS) at 20.0 kV and 15.0 mA. The specific surface of powders was evaluated by the Brunauer-Emmett-Teller (BET) method using a Micrometrics Inc. USA ASAP 2405 apparatus. The surface and volume of pores were also tested. The combustion heat of bone was determined using a KL-12Mn calorimeter from Precyzja-Bit. Thermogravimetric analyses were performed in an air atmosphere using TA Instruments SDT 2960 Simultaneous DTA-DTG apparatus.

3. Results and discussion

3.1. Bone sludge properties

Characteristic of bone sludge used in the study were presented in Table 1. Meat tissue and bone tissue are a basic component of bone waste. Bones, after pre-treatment, removal of metal parts and fragmentation, are subjected to a hydrolysis process resulting in protein hydrolysate and bone sludge (Kowalski et al., 2011, 2017).

Table 1 shows that the chemical composition of the sludge from various types of bones is comparable. The phosphorus content varies around 14% P. The content of heavy metals: cadmium, mercury, arsenic, chromium, lead, copper is lower than the sensitivity of the AAS method (0.1 ppm). The combustion heat of the bone sludge is 7.9 MJ/kg, dimension 1–3 cm, bulk density 0.8–0.9 kg/dm^3.

Pork bones characterised in point 2.2.1 used in calcining was additionally tested. X-ray analysis showed that the only one crystalline phase of bone sludge is hydroxyapatite (Fig. 2).

Thermogravimetric analysis (TGA) (Fig. 3) showed that bone sludge decomposes in four stages. Below 200 °C water is desorbed. Thermal decomposition of proteins takes place at temperature about 440 °C. The process of burning the organic part of the sample occurs at about 600 °C. The fourth peak visible on the curve probably corresponds to the endothermic distribution of calcium carbonate contained in the ash, at about 800 °C. This TGA are important for this study. The calcining temperatures (especially 600 °C) was selected based on the TGA data.

3.2. Physic-chemical properties of ash calcined in a stationary chamber kiln

Fig. 4 present X-ray diagrams of ash from the calcining of bone sludge at 600 °C and 950 °C. Analysis of the phase composition of ashes obtained showed that the only crystalline phase identified by X-ray analysis is hydroxyapatite.

The morphology of ash samples was studied to determine the effect of bone waste calcining temperature on changes in the surface properties of the ash. The ashes of bone sludge mixture calcined at 600 °C and 950 °C were compared. Fig. 5 showed the distribution of elements on the surface of the ashes tested. These images showed very good homogeneity of their surface. The distribution of Na, Mg, Al, Si, P and Ca is almost even in both cases.

Fig. 6 show SEM images of ash samples calcined at 600 °C, 650 °C, 900 °C and 950 °C in an air atmosphere for 3 h. All microphotographs were taken at 1800x magnification. These images show a large amount of fine crystallites, the dimension of which can be estimated at about 5–10 μm, and larger crystallites of about 25–30 μm which appear individually. The surface images of ash calcined at 950 °C also show insignificant amounts of lighter crystallite edges, which may indicate a slight melting of the crystallites due to sample overheating.

Fig. 7 show the results of EDS analysis of the chemical composition of ashes calcined at 600 °C and 950 °C.

In both cases, the two highest peaks derived from phosphorus and calcium, the main constituents of the HA previously identified by X-ray analysis. From their dimensions it can be concluded that they are the main component of the ashes. Small peaks from sodium, aluminium and silicon indicate that these elements are impurities in the samples tested.

The results of the grain analysis of the ashes obtained are presented in Table 2, with their chemical composition in Table 3.

Table 3 data show that the calcium and phosphorus contents in the ash samples are of a similar level, and the increase in P content with an increase in temperature is insignificant. The same is seen to be the case with calcium. The content of Ca and P in the ashes obtained (within 18.5% P and 38.5% Ca) are higher than the content of P and Ca in typical phosphate rock raw materials. An image of the ash is shown in Fig. 8.

Ash after the calcining of bone sludge at 950 °C consists of white coarse particles. The light, uniform ash colour suggests the absence of the unburnt organic parts of this material. The analyses of Cu, Co, Ni, Cr, Cd, Pb, Hg and As content made by the AAS method showed that the level of these heavy metal content in the test samples calcined at 950 °C was below the threshold of the method sensitivity, which was equal to 0.1 ppm.

The specific surfaces the powders obtained were characterised by the BET method. The surface and volume of pores were also investigated.

Table 1
Composition of meat bones.

Bone sludge from	H_2O	Content in dry mass (%)				
		P	Ca	Fat	Organic matters	Inorganic matters
Bovine bones	7.07	14.12	25.8	2.37	20.38	85.0
Pig bones	6.53	14.09	22.8	3.13	24.04	86.0
Pig legs	7.06	13.98	23.6	2.89	18.69	88.0
Bone sludge used in calcining process	35.0–50.0	12.0–16.0	23.0–26.0	4.0–5.0	12.0–18.0	85.0–89.0

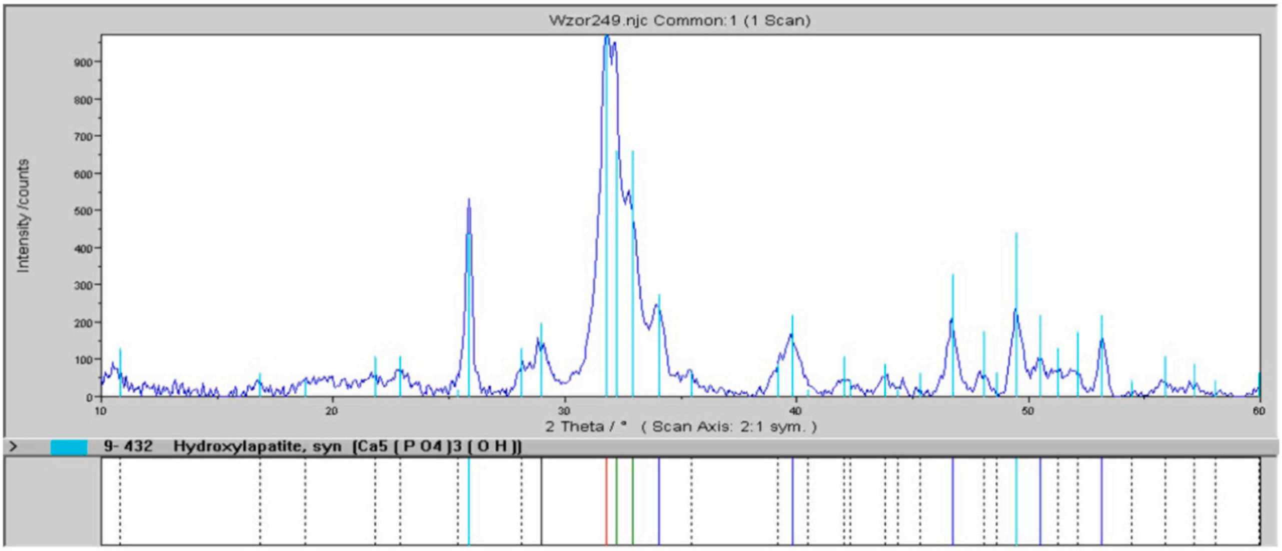


Fig. 2. X-ray analysis of bone sludge.

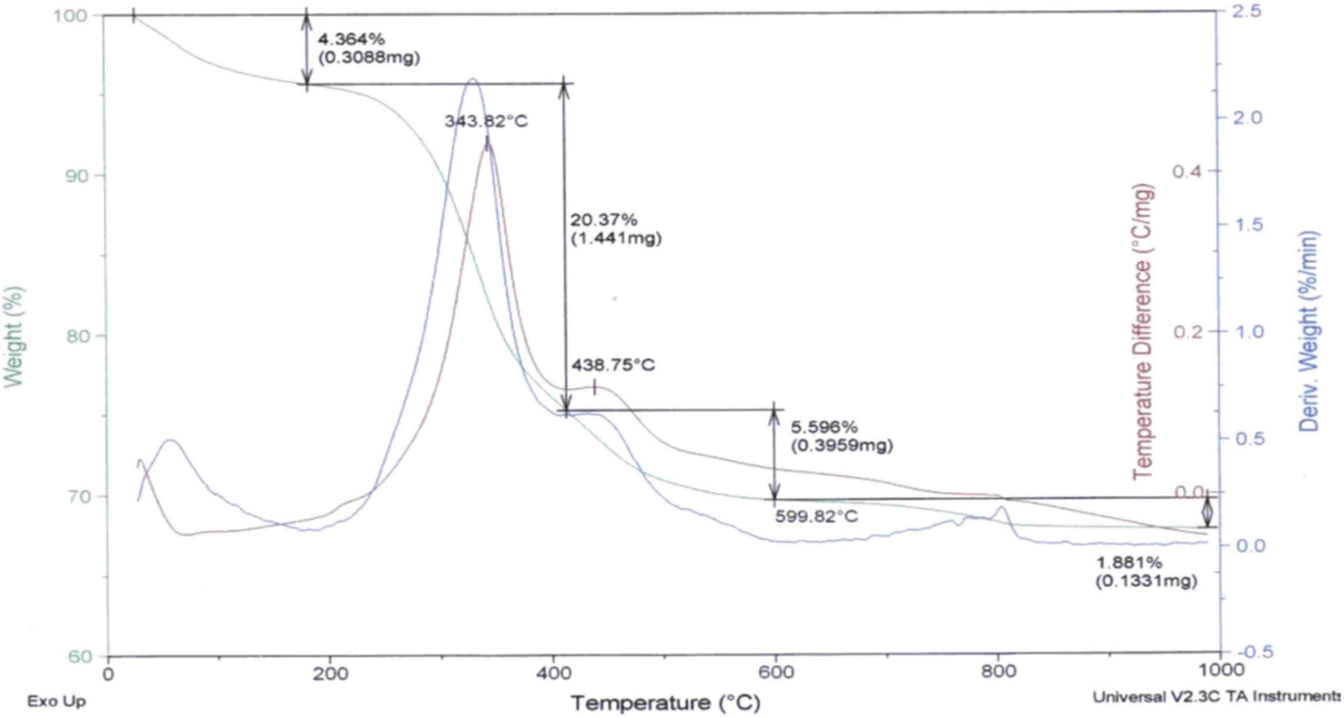


Fig. 3. Thermogravimetric analysis of bone sludge.

The results are presented in Table 4 and the average diameters were calculated and proved to be 20.54 nm and 7.536 nm for material calcined at 650 °C and 950 °C.

BET tests showed that the surface of material following calcining at 650 °C was nearly twenty times bigger than the surface of ash obtained at 950 °C. This could be the result of carbon residue in the material obtained at 650 °C. The decrease in the specific surface and average pore diameter with increase in calcining temperature confirmed that the grains of powder were sintered.

The content of heavy metals: cadmium, mercury, arsenic, chromium, lead and copper is lower than the sensitivity of the AAS method used (0.1 ppm).

3.3. Description of the industrial process that has been developed and MFA analysis

Total meat waste calculated on the basis proposed by (Caldeira et al., 2019) was estimated to be in Poland 0.967 Mt/y from which waste from primary production and meat processing and manufacturing contributed 0.232 Mt/y (24.0% of the total quantity of meat waste). These type of meat waste contained mainly bones presented in Table 5. In analysed case calculation was made for one from biggest Polish meat plants. Developed capacity of production unit for processing bone waste will be 24,000 t/y and amount of hydroxyapatite ash produced 7357 t/y.

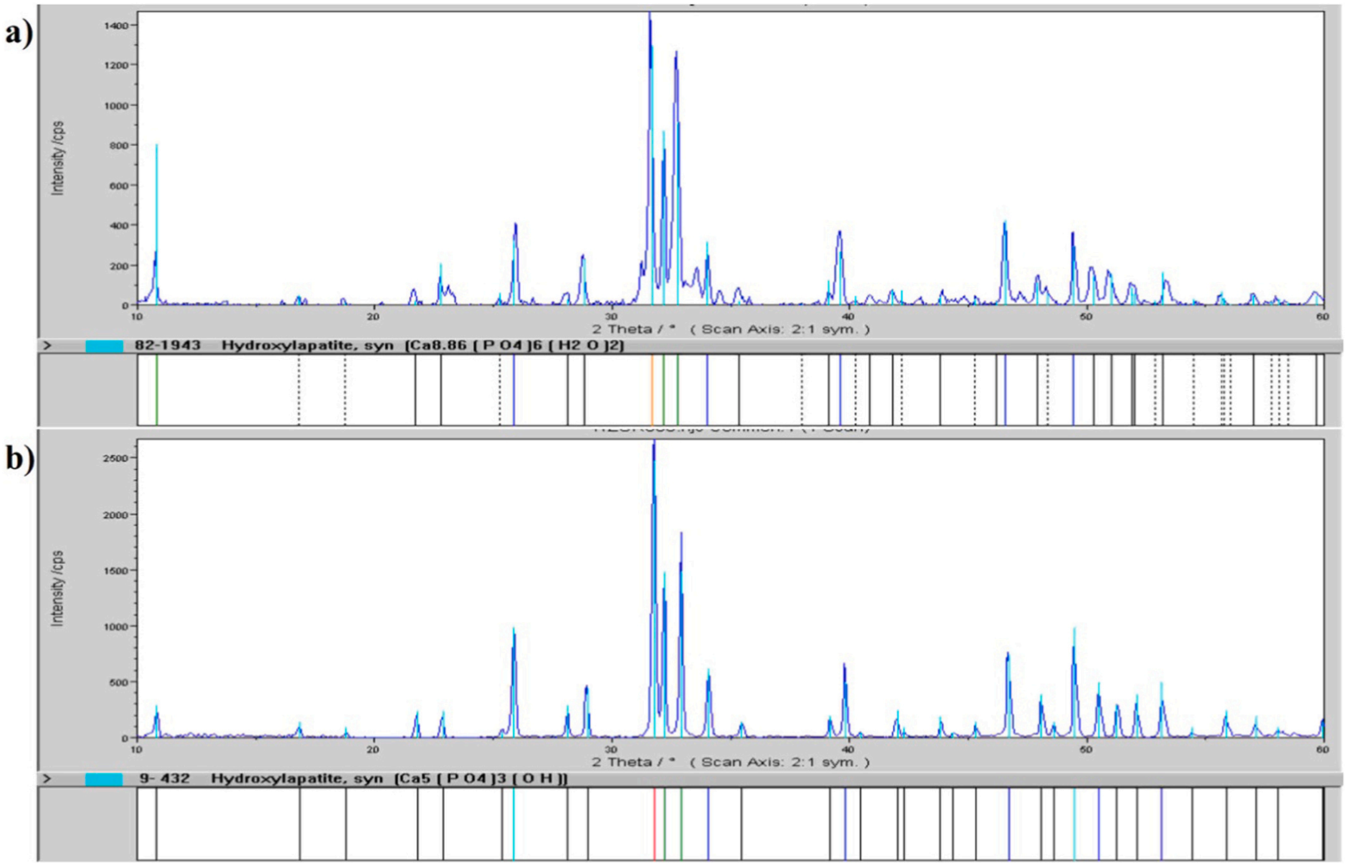


Fig. 4. X-ray diagram of ash obtained by calcining bone sludge at: a) 600 °C and b) 950 °C.

3.4. *Characteristics of product - HA ash*

In the process of calcining of bone waste, ashes in form of white powder (bulk density 1.2–1.3 kg/dm^3) were obtained, the main crystalline phase of which is $Ca_5(PO_4)_3OH$. These ashes are a homogeneous raw material in terms of chemical composition and chemical properties. Their high purity is also important, and especially the practical absence of heavy metals. X-ray analysis also shows the presence of small amounts of $Ca_3(PO_4)_2$, $CaCO_3$, SiO_2, Fe_2O_3 in the product. Molar ratio of Ca/P is 1.67.

Chemical composition of ash is [%]: P-17.03 (P_2O_5-39.0); Ca-46.43 (CaO-65.0) and fraction share: $<$ 0.01 mm - 39.8%; 0.01–0.16 mm - 15.2%; $>$ 0.16–0.25 mm - 18.1%; 0.25–0.5 mm – 16.9%; $>$ 0.5 mm 10.5%. A fraction of 0.01–0.5 mm will be the product. Oversize and undersize will be recycled to the calcining process (in-process recycling).

3.5. *Characteristic of raw materials*

The charge used contained grinded pork bones with dimension 1–3 cm, containing 35.0–45.0% H_2O and in dry mass of [%]: organic matter 34.0–39.0, fat 14.0–16.0, protein 18.0–23.0, P 10.0–14.0, Ca 28.0–30.0. Their bulk density was 0.655 kg/dm^3. Second component of charge was bone sludge with dimension 1–3 cm, containing 35.0–50.0% H_2O and in dry mass of [%]: organic matter 12.0–18.0, fat 4.0–5.0, P 12.0–16.0, Ca 23.0–26.0. Its bulk density was 0.85 kg/dm^3.

The content of heavy metals: Cd, Hg, As, Cr, Pb, Cu is in bone waste and bone sludge lower than the sensitivity of the AAS method (0.1 ppm).

Third component of charge was recycled part of product HA ash. The mass ratio of recycled HA and dosed mixture of bone waste and bone sludge was equal to 1:1. The quantitative composition of the charge is presented in Table 5.

3.6. *Flow-sheet of bone waste incineration*

It is assumed that in a rotary kiln thermal processing of bone sludge and grinded bone wastes will be carried out. Flow-sheet of bone calcining in co-current rotary kiln is shown in Fig. 9. As designed, the process includes the complete combustion of the organic part of the waste in a complete process carried out with at least 20% of excess air. The gas products are burned in the afterburner. The ash obtained from the thermal decomposition of meat bone waste is almost pure HA.

The installation includes the following basic stages of production: mixing of grinded bones with bone sludge, thermal treatment of the bone mixtures in rotary kilns, sieving of the HA ash produced, after-burning of flue gas coming from a rotary kiln, heat generation and steam production in steam boilers, and dust removal from the flue gases. Bone waste intended for processing is delivered to an intermediate tank. From there, it is transported to a co-current rotary kiln where it is calcined, ground and sieved. Grains with a dimension of 0.1–0.5 mm - the calcining product, are stored in a feed tank. Ash contained fraction of 0.01–0.5 mm will be the product. Undersize fraction $<$ 0.01 mm – share 39.8% and oversize fraction $>$ 0.5 mm – share 16.9% were recycled (in-process recycling) into rotary kiln and reused as filler of charge.

The exhaust gas from the rotary kiln is burned in the after-burning chamber, and the heat of the exhaust gases is recovered in a heat recovery steam generator. Flue gas from the boilers has its dust removed in bag filters and then is released through a chimney to the atmosphere. Dust from the bag filters and the boiler is directed to the calcining stage (in-process recycling and reuse). Content of impurities in flue gases emitted were [ppm]: inert dust - 30; SOx - 50; NOx - 150; organics as C – 10; $\sum$ Pb, Zn, Cr, As, Co, Ni - traces; PCDD/PCDF - 0.05 ppb; Hg – none; HCl, HF – traces (Kowalski and Makara, 2021b).

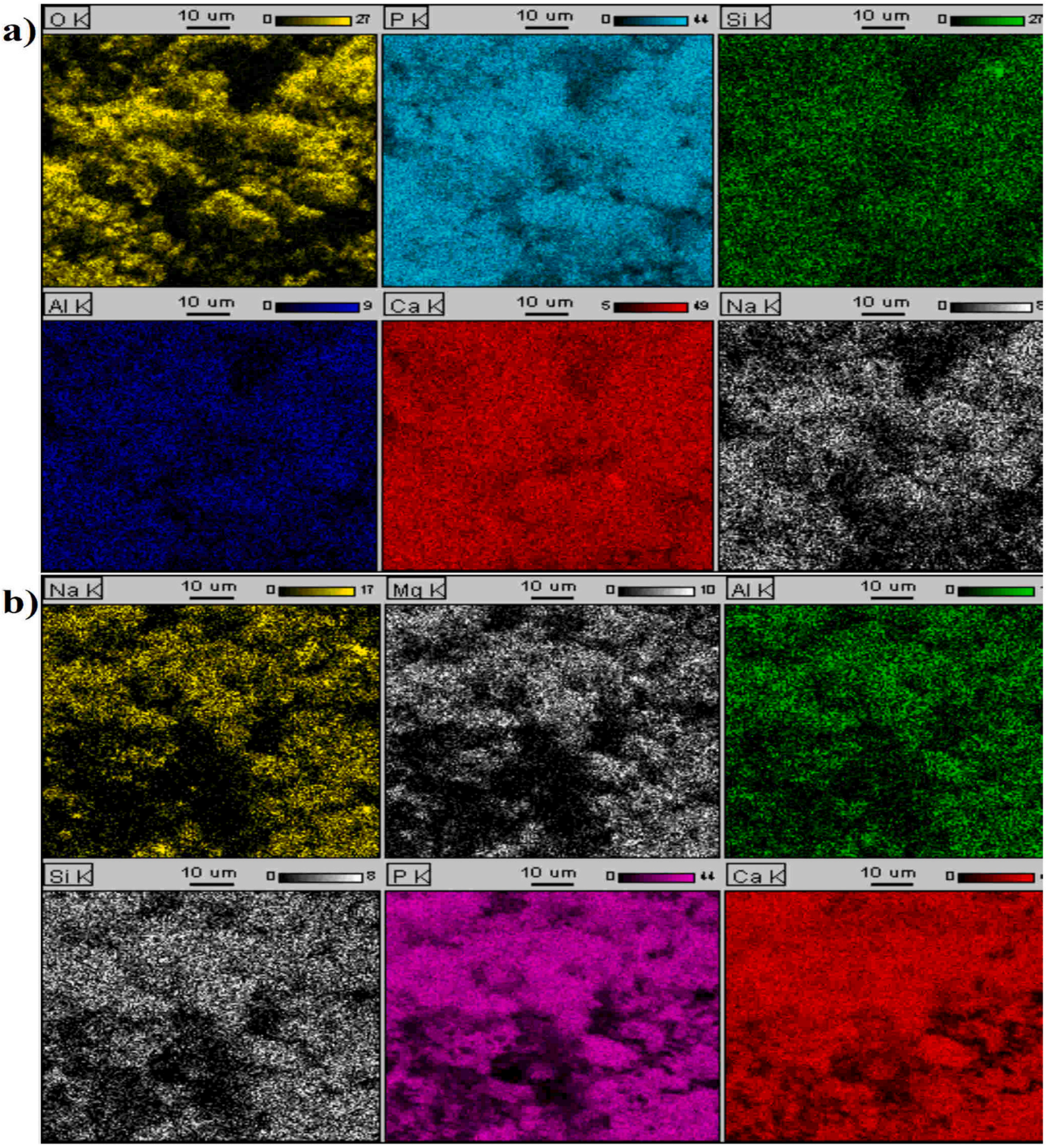


Fig. 5. Distribution of elements on the surface of ash obtained after calcining at a) 600 °C and b) 950 °C.

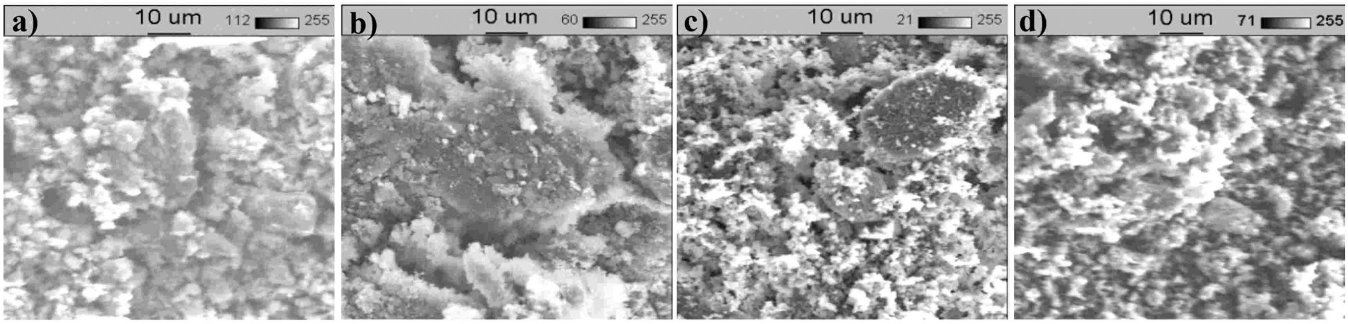


Fig. 6. SEM image of ash surface calcined at a) 600 °C, b) 650 °C and c) 900 °C, d) 950 °C.

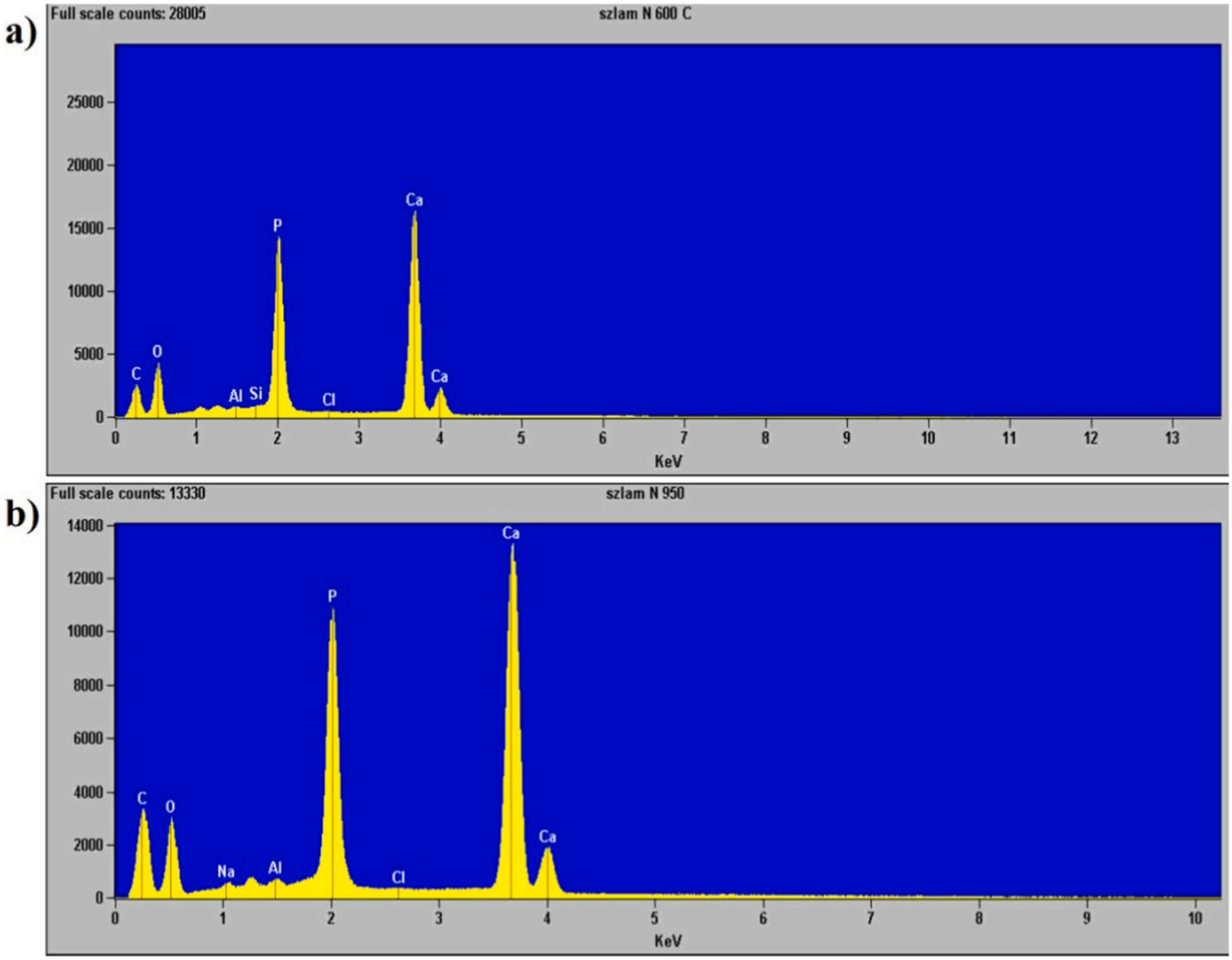


Fig. 7. EDS analysis of the composition of ash from bone sludge calcined at a) 600 °C and b) 950 °C.

Table 2
The grain dimension of ash after calcining of bone sludge.

Fraction (cm)	Content of ash calcined temperature (%)		
	600 °C	800 °C	950 °C
< 0.01	58.9	53.0	57.8
0.1–0.16	9.5	6.0	5.2
0.16–0.25	24.4	29.2	20.1
> 0.25	7.1	11.8	16.9

Table 3
Chemical composition of ash after calcining of bone sludge at 600–950 °C.

Ash calcined at temperature (°C)	Loss of weight (%)	P content (%)	Ca content (%)
600	33.6	17.8	38.7
650	33.6	17.9	38.7
700	33.8	18.0	38.8
750	33.8	18.1	38.6
800	33.8	18.2	39.0
850	34.0	18.3	39.3
900	34.0	18.4	39.4
950	34.2	18.6	39.4

Fig. 8. Ash after the calcining of bone sludge at 950 °C.

3.7. Process parameters

a) Initial storage of by-products - Bone sludge and grinded bone waste will be transported to a transitional tank and temporarily stored there.
b) Calcining in a co-current rotary kiln: calcining time ~ 1 h; temperature 950 °C, material > 900 °C; variable rotation speed

Table 4
Surface parameters of the products of calcining.

Parameter	Unit	Ash calcined at temperature (°C)	
		650	950
BET surface area	(m^2/g)	44.1026	2.6868
Cumulative adsorption surface area of mesopores	(m^2/g)	44.8185	3.3124
Cumulative adsorption surface area of micropores	(m^2/g)	7.4745	0.6250
Cumulative adsorption surface volume of mesopores	(cm^3/g)	0.309106	0.006160
Cumulative adsorption surface volume of micropores	(cm^3/g)	0.003374	0.000283
Average pore diameter	(nm)	20.54	7.536

Table 5
Quantitative composition of the charge.

Input raw material	(kg/h)	(%)
Bone material	3000	50.0
- bone waste	2000–2500	33.3–41.7
- bone sludge	500–1000	8.3–16.6
Recycled hydroxyapatite	3000	50.0
Total	6000	100.0

0.2–2.0 rpm; kiln load with the charge: 10–40 kg/m^2h; recycling of HA was assumed with the mass ratio of HA and dosed bone waste equal to 1:1.

c) Afterburning in the afterburner chamber: input flue gas at a temperature of about 900 °C; afterburning time > 2 s, temperature - 1000 °C.
d) Steam production capacity up to 10 t/h. Two boilers will be installed alternately, which will enable continuous operation of the rotary kiln (the boilers can be cleaned every week).
e) Dedusting in the bag filter after the steam boiler: temperature 150–200 °C, under pressure as indicated by the filter supplier.

3.8. Material flow analysis

Using MFA, material flow diagrams were developed for the research sites showing both the total quantity of waste materials processed per year, as well as the use of these materials per ton of HA ash produced. A presentation was also made of the quantity of emissions into the air from the incineration plants examined.

The material balance of the calcining process is presented in Table 6. Operation time of production unit was specified to be 24 h/d during 8000 h/y (333 d/y). Calculated amount of biomass processed was 3.00 t/h (72 t/d; 24,000 t/y) and amount of HA ash produced 0.942 t/h (22.6 t/d; 7357 t/y). Conservation of mass should be satisfied by the flows in the data structure. This requirement is fulfilled for the sample case analysed.

Fig. 10 presents a Sankey diagram of the process being analysed

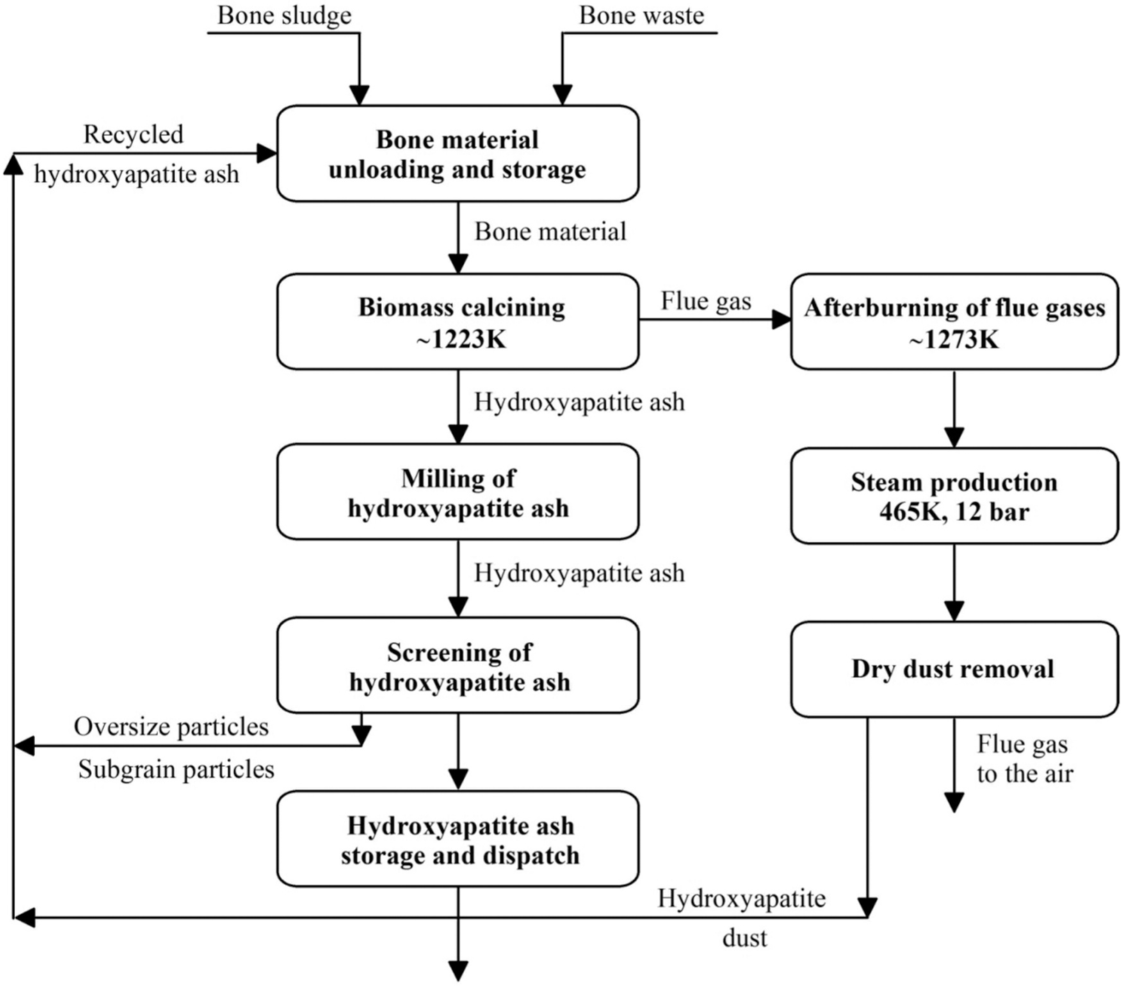


Fig. 9. Flow-sheet of bone calcining into hydroxyapatite in rotary kiln.

Table 6
The material balance of the meat bone calcining process.

Material balance				
Specification	(t/t)	(kg/h)	(kg/d)	(t/y)
I. Mixing of raw materials				
Input:				
1. Bones and bone sludge	3.184	3000	72,000	24,000
2. Recirculated hydroxyapatite from III.	3.184	3000	72,000	24,000
Total	6.369	6000	144,000	48,000
Output:				
1. Feedstock	6.369	6000	144,000	48,000
II. Calcining				
Input:				
1. Feedstock	6.369	6000	144,000	48,000
Output:				
1. Hydroxyapatite for III	3.900	3675	88,192	29,397
2. Gases and vapours	2.184	2057	49,373	16,458
3. Dust for IV	0.285	268	6435	2145
Total	6.369	6000	144,000	48,000
III. Grinding				
Input:				
1. Hydroxyapatite from II	3.900	3675	88,192	29,397
2. Afterburner dust from IV	0.142	134	3217	1072
3. Steam boiler dust IV	0.071	67	1609	536
4. Bag filter dust from IV	0.070	66	1593	531
Total:	4.184	3942	94,610	31,537
Output:				
1. Product HA ash for sale	1.000	942	22,610	7537
2. Hydroxyapatite for recirculation to I	3.184	3000	72,000	24,000
Total:	4.184	3942	94,610	31,537
IV. Flue gas dust removal				
Input:				
1. Dust from II	0.285	268	6435	2145
Output:				
1. After burner dust for III	0.142	134	3217	1072
2. Steam boiler dust for III	0.071	67	1609	536
3. Bag filter dust from III	0.070	66	1593	531
4. Emission to the atmosphere	0.001	0.670	0.016	5
Total:	0.285	268	6435	2145

Input-output analysis.

created using Sankey software. A Sankey diagram presents a snapshot of a system's behaviour at a given time. It is a directional flow chart where the magnitude of the arrows is proportional to the flow rate (Gonzalez Hernandez et al., 2018). Therefore, it validates the mass balance and reveals the effectiveness of the process described, in this case the yield of phosphorus compound from the calcined biomass.

The developed method allows in analysed case the utilisation of 24,000 t/y of bone waste. The environmental effect is the substitution of 7357 t/y of phosphorites used for the production of phosphoric fertilisers with ashes from bone waste incineration.

The quantity of waste from primary production and meat processing and manufacturing containing waste bone in Poland was estimated to be 232,000 t/y (24.0% of the total quantity of meat waste). Its thermal utilisation potentially allows 71,118 t/y of HA ash, a substitute for phosphorites, to be obtained. The economic effects of selling HA ash could be significant. The already-developed capacity allows the production of 7357 t/y of ash amounting to 1.155 million USD. The maximum potential value of 71,118 t/y HA amounts to 11.165 million USD. The price adopted for the calculation corresponds to the current price of phosphorites on the Polish market of 156 USD/t at Polish ports (based on Money.pl).

The quality of meat bone ashes obtained was compared with the quality of Senegal LamLam phosphate rock (Table 7) used for the production of phosphoric acid (Kowalski et al., 2021).

The BPL value of HA ashes could be considered to represent a high-quality material, with a BPL 85. The MER value for phosphorite was 16.8 and for MBA 0.36. This high quality hydroxyapatite ash does not contain fluorine compounds and during their processing into phosphoric acid there is no need for a complicated phosphorite de-fluorination stage. This HA could be used also for the production of food grade mono- and dicalcium feed phosphates (Smol et al., 2019).

4. Conclusions

In this paper using real data obtained from meat producers and slaughter-houses in Poland, MFA analysis and a waste hierarchy was developed to assess the incineration process of creating hydroxyapatite ash from meat bone waste. Technical and technological characteristic of different types of bone waste and produced hydroxyapatite ash and parameters of thermal processing of bone waste were presented. Using the method of MFA material flow diagram was developed in the analysed plant, showing both the quantity of bone waste incinerated as well as the amount of produced hydroxyapatite ash. In the case analysed, it was shown that 1.0 t of crystalline HA can be obtained from 3.2 t of meat bone waste.

The quantity of waste from primary production and meat manufacturing containing waste bone in Poland was estimated to be 232,000 t/y (24.0% of the total quantity of meat waste). Its thermal utilisation potentially allows 71,118 t/y of hydroxyapatite ash, a substitute for phosphorites, to be obtained. This HA could be used for the production of food grade phosphoric acid and also for the production of food grade mono- and dicalcium feed phosphates.

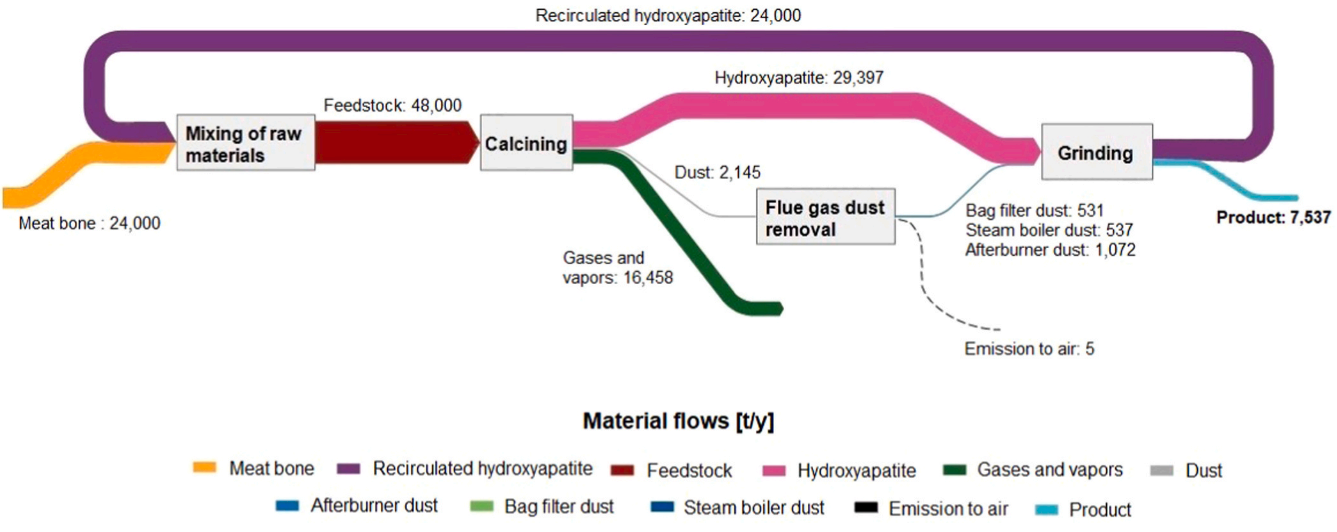


Fig. 10. Sankey diagram of the calcining process (t/y).

Table 7
Content of P_2O_5 and impurities in Senegal LamLam phosphate rock (Kowalski et al., 2021) and in ashes from the combustion of meat bones (MBA).

Phosphorite type	Content (%) or ratio (%)								
	P_2O_5	Al_2O_3	Fe_2O_3	$(Fe_2O_3 + Al_2O_3)$ /P_2O_5	MgO	BPL[b]	MER[a]	Cd (ppm)	X_{Cd} (mg Cd/kg P_2O_5)
Senegal LamLam	33.3	3.59	1.62	0.16	0.38	73	16.8	52	156
MBA	39.0	0.0	0.01	0.0003	0.13	85	0.36	0.01	0.026

[a] Minor Element Ratio MER = 100 * ($\sum$ (Al_2O_3, Fe_2O_3, MgO))/ P_2O_5 (%))
[b] BPL bone phosphate of lime = 2.1852 P_2O_5

The economic effects of selling HA ash could be significant. The potential value of 71,118 t/y HA amounts to 11.165 million USD. The price adopted for the calculation corresponds to the current price of phosphorites on the Polish market of 156 USD/t.

The worked out MFA may help to resolve environmental problems related to the utilisation of meat waste. It was shown that the recovery of raw materials, during an incineration process could be an efficient option for hazardous waste.

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CRediT authorship contribution statement

Zygmunt Kowalski: Conceptualization, Methodology, Investigation Conducting, Writing - original draft preparation, Preparation, Writing - review & editing. **Joanna Kulczycka:** Methodology, Formal analysis, Writing - original draft preparation, Resources, Data curation, Writing - review & editing. **Agnieszka Makara:** Investigation, Formal analysis, Resources, Data curation, Visualization, Preparation, Editing. **Paulina Harazin:** Visualization, Preparation, Editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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