

Article

Improving the Quality of Hydroxyapatite Ashes from the Combustion of Meat-Bone Meal in an Industrial Rotary Kiln

Zygmunt Kowalski ^{1,*}, Agnieszka Makara ², Agnieszka Generowicz ³ and Józef Ciuła ⁴

- ¹ Mineral and Energy Economy Research Institute, Polish Academy of Sciences, 31-261 Kraków, Poland
- ² Faculty of Chemical Engineering and Technology, Cracow University of Technology, 31-155 Kraków, Poland; agnieszka.makara@pk.edu.pl
- ³ Department of Environmental Technologies, Cracow University of Technology, 31-155 Kraków, Poland; agnieszka.generowicz@pk.edu.pl
- ⁴ Institute of Engineering, State University of Applied Sciences in Nowy Sącz, 33-300 Nowy Sącz, Poland; jciula@pwsz-ns.edu.pl
- * Correspondence: zkow@meeri.pl; Tel.: +48-12-617-16-33

Abstract: Research on the properties of hydroxyapatite ashes from an industrial unit burning meat and bone meal in an industrial rotary kiln is presented. High carbon content (10%), relatively low phosphorus (34%), and sulfides were found. The ash obtained was unsuitable for producing superphosphate fertilizer due to the emission of hydrogen sulfide in the reaction of the raw material with sulfuric acid. The research showed that decreasing the meat-bone meal calcining temperature below 950 °C and recycling the ashes, reusing them after mixing in a 1:1 ratio with dosed meat and bone meal, allows reducing the carbon content in the hydroxyapatite ash to the level of <0.2%, increases the P₂O₅ content in the ash to 39%, and eliminates hydrogen sulfide emissions. The improved parameters allow the production of hydroxyapatite ash that could be a substitute for phosphorites used in the production of fertilizers. Incineration of the meat-bone meal allowed the production of bioenergy and hydroxyapatite. This is an example of implementing a very profitable circular economy solution.

Keywords: meat-bone meal; rotary kiln; combustion; hydroxyapatite ash; calcining parameters



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1. Introduction

The world meat-bone meal (MBM) market has been increasing by an average of 3.5%/y in recent years, reaching USD 1.2 billion by 2030 [1]. The growth of this market can be attributed to the increasing demand for meat and poultry products in emerging economies such as China and India, which are witnessing an increase in disposable income levels and changing lifestyles. The growing population, coupled with rising awareness about animal welfare, has also led to increased demand for meat products from animal-based sources such as beef, pork, chicken, and fish. The global meat-bone meal market is segmented by type into 60% protein MBM and 65% protein MBM for application in poultry feed and pet food.

In Poland, over 1 Mt/y of meat waste is processed into 250,000 t of MBM, used mainly as biofuel co-combusted with coal and for pet food production [2,3].

Meat bone meal is mostly applied as fuel, and also calcium and phosphorus fertilizer, containing also some amount of nitrogen [4,5]. MBM could be an interesting option for mineral fertilizer and for organic production [6].

MBM is a CO₂-neutral biofuel substituting for non-renewable fuels like coal burned in rotary kilns, especially in many cement plants [7]. Models of MBM combustion and MBM and coal co-combustion in a rotary cement furnace have been worked out and presented by Ariyaratne et al. [8]. MBM is also utilized as a renewable fuel source in electricity generation,

especially in the UK [9]. Combustion of MBM eliminates pathogens and pollutants. MBM has about 70% heat value of coal.

The ash from a UK industrial incinerator used for electricity generation with MBM as the only fuel has a high content, 13.48% of P, and a low concentration of heavy metals. The ash contains hydroxyapatite as the main P compound. Applying MBM ash for P-containing wastewater treatment offers the profit of waste remediation, enabling the possibility of applying hydroxyapatite ash for phosphorus recovery [10].

Calcium phosphates contained in hydroxyapatite ash can be used for the production of inorganic coating raw material (reuse and off-process recycling according to circular economy CE) [11]. Hydroxyapatite bone ash is also used as an additive in porcelain sintering [12].

Characterization of meat bone meal co-fired with coal was presented by Senneca [13]. Cascarosa et al. [9] reviewed research on the incineration, pyrolysis, and gasification of MBM and the most important possibilities of the use of HA ashes generated in these thermal methods. The thermal decomposition of MBM was investigated, too [14–16].

The co-incineration of MBM with coal was also examined by Fryda et al. [17] and Gulyurtlu et al. [18]. The incineration of MBM/feather mixtures was examined by Staroń et al. [19]. These solutions are examples of applications in the industrial practice of CE methods, emphasizing the potential to apply the value contained in materials to the greatest extent [20]. According to CE, applying MBM biofuel in combustion for energy recovery is treated as a useful alternative, due to the product life cycle value chain keeping the high value and quality, and is as energy efficient as long as feasible [21].

MBM is increasingly used as a biofuel. It is envisaged that the thermal decomposition products of MBM may be used as a substitute for phosphorites. The parameters of the thermal treatment of MBM have been determined. It can be burned in both stationary and rotary kilns at temperatures of 600–950 °C [3,19]. The developed production of renewable energy from biofuel meat-bone meal incinerated in rotary kilns allows the transformation of existing district heating in Piła city (currently using coal) into a fourth-generation district heating system, predicting the use of heat (hot water) from the incineration of MBM. The use of 52,000 t/y of MBM (962,000 GJ/y) for district heating production allows the closure of the coal-fired heating plant eliminating the consumption of 44,000 t/y of coal and emissions of 93,720 t/y CO₂. Currently, the fees for the purchase of such CO₂ emission permits amount to over 5.588 million €/y [3].

Due to the medium-high heating value of MBM, approximately 18 MJ/kg the use of MBM as a secondary fuel in a fluidized bed combustor has been the most frequently evaluated option. Pyrolysis and gasification have been investigated to a lesser degree than co-combustion [13,15,17]. The use of MBM as a secondary fuel in thermochemical processes [9] could result in a noticeable saving. For example, the amount of MBM produced in Spain during a year is 400,000 tons. The coal consumed in thermal units in Spain is 44 million tons per year. MBM wastes could be burnt in thermal plants by replacing 0.91 wt.% of the total coal used in these plants.

Greenhouse gases (GHG) accounting of the MBM use for energy production showed that overall GHG savings in the order of 600–1000 kg CO₂-eq. per Mg of MBM treated, mainly as a consequence of avoided fossil fuel consumption in the energy sector [22].

Energy balances of MBM production and MBM incineration were presented in the example of industrial units of the Polish agri-food consortium in [3].

The main component of MBM combustion ashes is hydroxyapatite. The phosphorus content in hydroxyapatite ash (within 16–17% P) is maintained at this level in very good phosphorus raw materials. It contains trace amounts of heavy metals and other impurities. This confirms the usefulness of these ashes as high-quality feedstock for producing phosphorus compounds [23].

Studies carried out on a laboratory rotary kiln have confirmed the advisability of using recycled ash in the process of burning meat and bone meal [24]. The characteristic of

industrial and laboratory MBM ashes containing hydroxyapatite and their potential use was presented in [23].

The optimization of MBM and sewage sludge co-incineration was presented in [25,26]. The sustainable development of MBM biofuel incineration in terms of the use of the obtained renewable energy to transform city district heating into sustainable energy systems is described in [3].

The goal of our research was to analyze the quality of hydroxyapatite ashes obtained by the combustion of MBM in an innovative industrial unit operating in one of the Polish industrial plants and to propose technological solutions for the production of a high-quality product that could be a full-value substitute for phosphorus ores used in the production of superphosphate fertilizers.

2. Materials and Methods

Research on new calcining parameters was realized to improve the quality of hydroxyapatite ash. The tests of the new solution of MBM incineration with re-use of the recycled ash were made in a chamber kiln with the variable parameters: ratio of MBM to ash, temperature, and calcining time.

Table 1 presents the incineration parameters and characteristics of inputs of the feed-stock samples used in the combustion tests. Sample 0 was taken from an industrial rotary kiln. Samples 1–5 were obtained by calcining in an electric-heated laboratory chamber kiln. The goal of these tests was to determine the possibility of reducing the carbon content in the ashes by selecting the appropriate temperature and applying in-process recycling of hydroxyapatite ashes.

Table 1. Production parameters of meat-bone meal MBM and/or hydroxyapatite ash HA and MBM mixtures in a laboratory chamber kiln and an industrial rotary kiln.

Sample	Mass Ratio HA */MBM	Calcining Parameters	
		Temperature (°C)	Time (h)
0 *	MBM only	~1150	4
1	1:1	800	1
2	1:1	800	2
3	1:1	900	1
4	1:1	900	2
5	HA * only	900	2

* HA ash from an industrial rotary kiln.

Inductively coupled plasma atomic emission (ICP-AE) and a Perkin Elmer spectrometer, OPTIMA 7300 DV, were used to determine the Ca, K, Na, Mg, S, Fe, Cr, Hg, Pb, and Zn contents in the ashes. P content was determined with a spectrophotometric method according to proper Polish standards [27].

A Philips X'Pert diffractometer with a graphite monochromator, PW W 1752/00, Cu K α radiation, and a Ni filter was used to identify the phase composition of the analyzed samples. The analyses of carbon, hydrogen, and nitrogen content in the ashes were made on a Perkin Elmer type 2400 CHN elemental composition analyzer.

The study of ash surface morphology was made using a Hitachi TM 3000 scanning electron microscope (SEM) equipped with an SE secondary electron detector, a backscattered electron detector (BSE), and an energy-dispersive spectrometer (EDS), Bruker Quantax 70 X-ray with a silicon drift detector (SDD). The samples were sputtered with palladium and gold.

The odor emissions were tested in the gas samples emitted from treated ash, with an olfactometric method [28–30].

3. Results and Discussion

3.1. The Basic Technology of the MBM Incineration Process

The study [31] provided the results of MBM burning in a classic rotary kiln. A typical rotary kiln is an ordinary tube (with appropriate lining) rotating on rollers. Technically, it is a rather simple device and easy to use. In classic rotary kilns, the diameter-to-length ratio is 1:10. MBM incineration is a technologically uncomplicated process.

This unit would allow the production of cheap bioenergy for use in MBM and meat product production (in-site energy recycling), and the hydroxyapatite ash could be used as a substitute for natural phosphorites [3,26].

A flow sheet of the thermal process of MBM into hydroxyapatite ash is shown in Figure 1. Meat bone meal is dosed with a screw transporter to a co-current rotary kiln. The calcining product is collected from the dust chamber after the rotary kiln and transported to the storage tank. It is also possible to partially recycle it to the rotary kiln dosing screw. The exhaust gases from the rotary kiln are incinerated in the afterburning chamber. The flue gas heat is used for the production of steam in the steam boilers. The flue gas from the steam boiler is de-dusted in bag filters and next directed through the chimney to the air. The hydroxyapatite (HA) dust obtained is recycled into a rotary kiln dosing screw.

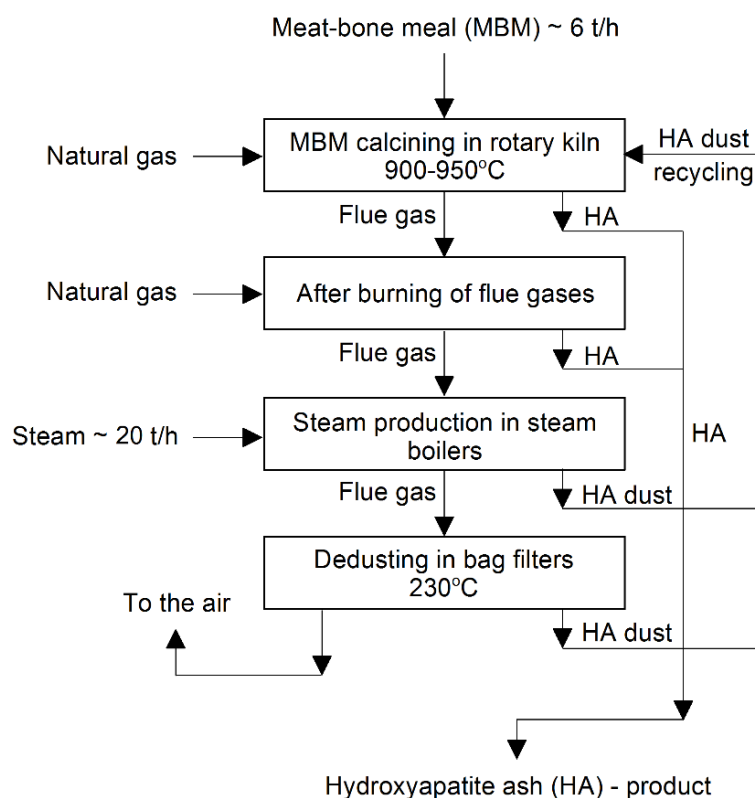


Figure 1. Flow sheet of the meat-bone meal thermal processing into hydroxyapatite ash.

P content in the product is at a level that is typical in phosphorus raw materials, 13.2–17.2% P. The product grain sizes (fraction size in mm) are as follows: >0.25–65%; 0.16–0.25–15%; 0.10–0.16–7%; <0.10–13%. The bulk density is 0.7 kg/dm³ [32].

All types of MBM can be combusted in a rotary kiln. The average MBM composition is as follows: maximum moisture, 10.0%; phosphorus, 5.5–6%; calcium, 7–8%. The average heat value of MBM is 18.5 MJ/kg, and the bulk density is 0.6 kg/dm³. X-ray analysis showed that the main component of MBM is hydroxyapatite (Figure 2).

Thermal analysis (Figure 3) shows that MBM undergoes thermal decomposition in three stages, during which ignition and decomposition of the organic part of the samples take place, as evidenced by the high exothermic effect. Three different zones can be

distinguished in the curves obtained in these analyses. The sample dehydration occurs up to 148 °C. The weight loss from 148 to 225 °C is attributed to the evaporation of low molecular weight compounds and decomposition reactions. The highest weight loss rate is estimated in the temperature range of 200–400 °C and is due to degradation reactions in which the organic intermediates are destroyed. The peaks observed at 360–500 °C, probably correspond to the thermal degradation of the bones. The total decomposition of the organic phase follows up to a temperature of about 550 °C [9]. The weight loss related to the burning of the organic part of the sample is 76%. The fourth peak visible in the curve shows that the final decomposition is set from 600 to 900 °C. In [13], the DTG curves produced in the pyrolysis of MBM under oxidative conditions (7–21% O₂ in He). The main stage of weight loss at temperatures higher than 550 °C occurs under oxidative atmospheres.

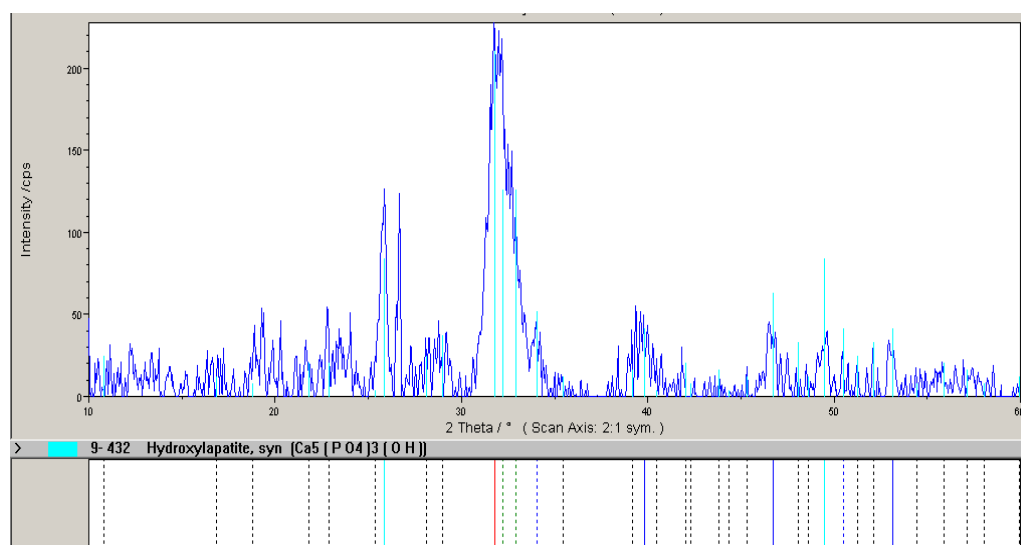


Figure 2. X-ray graph of the meat bone meal.

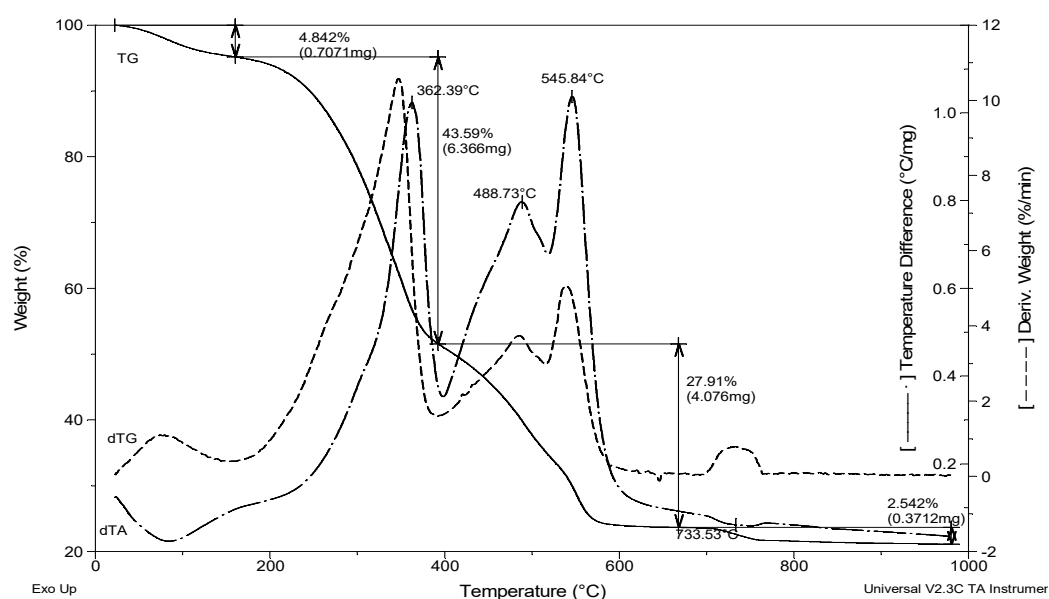


Figure 3. Thermal analysis of the meat bone meal.

MBM incineration provides 25–30% (based on the amount of MBM burned) of the calcining product; the main crystalline phase is hydroxyapatite. Hydroxyapatite ash is a homogeneous product in terms of its composition and chemical characteristics. The high purity, especially the absence of heavy metals, is essential, too.

Calcining parameters of MBM in a rotary kiln are as follows [26]:

- The calcining time is 30–60 min for a rotary kiln load charge of $\sim 50 \text{ kg/m}^2/\text{h}$.
- The temperature of the material in the rotary kiln is less than $950 \text{ }^\circ\text{C}$.
- The co-current work system has a variable speed of 1–2 rpm.
- The exhaust gas flow velocity in the rotary kiln is up to 4 m/s ; the oxygen content in the exhaust gases after the rotary kiln is 11%.
- Possible hydroxyapatite recycling assumes a 1:1 mass ratio of recycled hydroxyapatite and dosed MBM. The recycled hydroxyapatite ash could be fed to the rotary kiln dosing screw. It is also possible to dose the MBM itself.
- For afterburning in the afterburner chamber, combustion gases are supplied at a temperature of about $850 \text{ }^\circ\text{C}$ with an afterburning time of 3 s; the temperature in the afterburner is $850\text{--}900 \text{ }^\circ\text{C}$.
- Steam production in a steam boiler-steam is at a pressure of 6 bar.
- The exhaust gas flow rate is $\sim 2 \text{ m/s}$ for dedusting in bag filters, and the working temperature is $200\text{--}250 \text{ }^\circ\text{C}$.

Consumption figures per 1000 kg of hydroxyapatite produced are as follows: 4000 kg MBM; electricity, 80 kWh; technological water 0.1 m^3 ; natural gas 90 m^3 .

3.2. Operating Parameters of an Industrial Rotary Kiln Used for MBM Combustion

The industrial kiln consists of two short 7 m tubes with a diameter of 3.5 m (total length 14 m, diameter to length ratio = 1:4) working in a counter-rotating system at 1–6 rph. This is a unique solution (unknown before in the literature). It is complicated and challenging to operate. Both kilns rotate at minimum speed, and the sinter has practically no mechanical mixing. These are essentially two stationary combustion chambers connected. Bujak et al. [31] presented results of the MBM incineration in this rotating burning chamber, but there are no data on the quality of hydroxyapatite ash obtained. It is not known what the technical justification for such a solution is. It does not result from the technology of the MBM combustion process.

This solution can be highly emergency (this especially applies to the contact of two counter-rotating short kilns). It is also not known why a poured concrete lining was used, which is very troublesome in operation, especially during replacement. In classic rotary kilns, linings of appropriate brick are used, but the lining should be added to withstand the process temperature used, up to $1150 \text{ }^\circ\text{C}$.

In classic rotary kilns, the diameter-to-length ratio is 1:10, and a rotation speed of 1–2 rpm is usually used. In the kilns used according to [31], it is practically impossible to adjust the residence time of the material in the furnace by changing its rotation. Low revolutions of the kiln do not ensure the mechanical mixing of the ashes.

The rotary kiln implemented operates typically in a co-current system with a charge load of 2.9 t/h MBM ($22 \text{ kg/m}^2/\text{h}$, kiln area is 140 m^2). With a combustion efficiency of 75%, this gives a steam production of 48 GJ/h of steam, i.e., under the design assumptions. With 8000 h of operation a year, it enables a capacity of about $23,000 \text{ t/y}$ of MBM. The efficiency of the combustion process is low; with the correct technological and design solutions for the MBM combustion process, it should be about 90%.

The MBM combustion time in the applied solution is 4–6 h. It is not known what the technical justification for such a solution is. It does not result from the technology of the MBM combustion process. The typical incineration time of MBM in classic rotary kilns is 30–60 min. According to the obtained data, the level of O_2 in the exhaust gas is observed at 12%, indicating this parameter's correct level.

The material temperature of the MBM combustion process is up to $1150 \text{ }^\circ\text{C}$ and is too high (in typical MBM combustion technologies, it is $<950 \text{ }^\circ\text{C}$). A high (up to 10%) amount of carbon in the HA ash is also observed, resulting in incomplete oxidation of MBM during combustion products, and due to too high calcining temperature results in the carbothermic reduction of small amounts of calcium and sodium sulfates contained in MBM to sulfides [33]. HA ash could be used for the production of superphosphate, formed

as a result of the reaction of hydroxyapatite with sulfuric acid [34]. Contamination of the hydroxyapatite with sulfides, however, resulted in the emission of hydrogen sulfide.

Stabilizing the combustion parameters at a lower temperature level was the first goal of the technological process. The second one would be recycling the ashes, with a 1/1 mass ratio of MBM/HA. The filler will increase the access of oxygen to the MBM grains and accelerate oxygen diffusion through the feet formed during combustion. It will also be possible to increase the load on the furnace to 50 kg/m²/h or even more (currently 22 kg). These solutions allow the reduction or even complete elimination of the C content in the HA ash. For the HA to be a top-quality product, the carbon content of the HA ash should be traceable.

3.3. Analysis of Combustion Parameters Used in an Industrial Kiln and Proposal for Improvement

Table 2 presents the analyses of HA ashes from the incineration of MBM, and HA and MBM mixtures in laboratory chamber kiln, and industrial rotary kiln.

Table 2. Results of elemental analysis of hydroxyapatite ashes (HA) from meat-bone meal MBM combustion and HA and MBM mixtures in laboratory chamber kiln and industrial rotary kiln.

Component	Unit	Sample of Hydroxyapatite Ashes **						
		0 *	1	2	3	4	5	
Ca	%	30.65	31.45	36.50	33.27	30.08	30.15	
P ₂ O ₅		34.98	37.72	37.51	38.94	39.35	39.20	
K		0.45	0.79	0.79	0.63	0.60	0.55	
Na		1.39	1.84	1.87	1.68	1.78	1.71	
Mg		0.70	0.64	0.84	0.76	0.71	0.73	
S		0.40	0.28	0.46	0.43	0.23	0.33	
Fe		0.22	0.13	0.29	0.27	0.18	0.21	
C		10.06	0.38	0.26	0.24	0.16	0.18	
H		0.03	0.10	0.14	0.16	0.17	0.18	
N		0.21	0.23	0.20	0.19	0.10	0.10	
Cr		mg/kg	43.36	54.33	77.49	83.55	72.7	113
Hg			<5.31	<4.97	<5.31	<4.96	<4.99	<4.91
Pb			<5.31	<4.97	<5.31	<4.96	<4.99	<4.93
Zn			4.15	88.30	77.49	23.62	14.57	18.43

* HA ash from an industrial rotary kiln; ** Numbered as in Table 1.

Elemental analysis of the ashes showed that the greatest differences in the analyzed samples occur in the content of carbon. Very high C content (10%) was found in the ash sample 0 obtained in a rotary industrial furnace by burning MBM for 4 h at a temperature of about 1150 °C. The carbon content of sample 0 (>10%) is extremely high. The calculated C content in MBM is 50%. Hence, it follows that 20% of the dosed MBM is not completely burned in the case of sample 0. Too high a temperature and longer calcination time resulted in such increased carbon content.

Re-calcination of this ash for 2 h at 900 °C (sample 5) in a laboratory rotary kiln significantly reduced the carbon content down to 0.18%. In samples 1–4, in which the ash obtained in an industrial furnace was mixed with MBM in a mass ratio of 1:1 and calcined at 800 °C or 900 °C for 1 or 2 h, a significant reduction in carbon content, to the level below 0.38%, was also visible. Very high P content (~39% P₂O₅) is observed in samples calcined at 900 °C containing only 0.16–0.24% C. These results show the possibility of reducing the carbon content in the ashes by selecting the appropriate temperature and applying in-process recycling of hydroxyapatite ashes. There is an additivity between the decrease in carbon content (even by over 65 times) and an increase in phosphorus content (by 4.37% P₂O₅) in samples from 0 to 4, visible also in characteristic changes in the color of samples depending on the calcining temperature and time (Figure 4). Figure 4 below shows images of ash samples from MBM combustion.

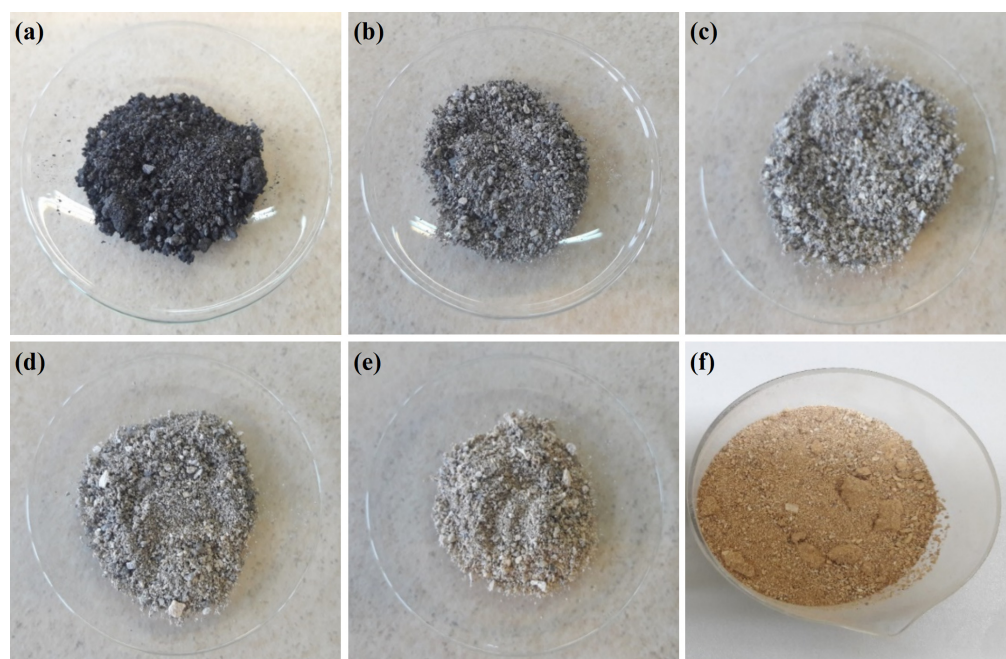


Figure 4. Images of ash samples from MBM combustion. (a) sample 0—hydroxyapatite ash HA from industrial rotary kiln; (b) sample 1—HA mixed with MBM (1:1) calcined at 800 °C for 1 h; (c) sample 2—HA mixed with MBM (1:1) calcined at 800 °C for 2 h; (d) sample 3—HA mixed with MBM (1:1) calcined at 900 °C for 1 h; (e) sample 4—HA mixed with MBM (1:1) calcined at 900 °C for 2 h; (f) sample 5—HA after calcining at 900 °C for 2 h. Samples 1–5 were calcined in a laboratory chamber kiln.

The ash sample 0, from the industrial rotary kiln, was grey with visible black carbon inclusions. Samples 1–4 were dark grey to light grey with no visible traces of carbon. On the other hand, sample 5 (sample 0 from an industrial rotary kiln, after calcining 2 h at 900 °C) was slightly brown, with no traces of carbon.

3.4. Tests of Samples for the Emission of Hydrogen Sulfide from Hydroxyapatite Ash

A significant problem with using hydroxyapatite ash from an industrial rotary kiln for producing superphosphate fertilizers was the emission of hydrogen sulfide after adding inorganic acids to hydroxyapatite. This made it practically impossible to sell hydroxyapatite ash from an industrial furnace as a substitute for phosphorites.

Hydrogen sulfide emission tests were performed after adding 50% sulfuric acid or 75% phosphoric acid to the sample (in a 1:1 weight ratio). A positive test result is confirmed by the evolution of hydrogen sulfide (which indicates the presence of calcium sulfides in the sample). H₂S has a characteristic smell of rotten eggs, and its detection threshold is low, 1.4 mg/m³.

Odor concentrations were measured using the dynamic olfactometric method and appropriate procedures were followed [28–30]. The assumed minimum velocity in the measuring chamber was 0.1 m/s (this corresponds to the so-called “atmospheric silence”) and the surfaces of samples tested in the laboratory were 0.063 m². The 3-person assessing the odor intensity of the gases emitted from the sample at the designated point was set at a distance of 1 m from the tested sample and, for 3 min, measured the time with an electronic stopper every 1 min and recorded the intensity of the perceived odor (on a 5-point scale). The scale of the intensity of the smells (in this case, the smell of rotten eggs) was as follows: 4—very strong; 3—strong; 2—perceptible; 1—hardly perceptible; 0—not perceptible. The test (Table 3) shows that the maximum values of the emitted hydrogen sulfide intensity were 4 on the odor intensity scale for sample 0 (from an industrial rotary kiln). HA samples calcined at 900 °C showed no hydrogen sulfide odor in the tests.

Table 3. Results of hydrogen sulfide emission tests from hydroxyapatite ashes obtained by combustion of meat bone meal MBM, and hydroxyapatite ash HA and MBM mixtures in laboratory chamber kiln and industrial rotary kiln.

Sample	Mass Ratio HA */MBM	Smell Intensity after Dosing into HA **			
		H ₂ SO ₄		H ₃ PO ₄	
0 *	MBM only	4	4	4	4
1	1:1	1	1	1	1
2	1:1	1	1	1	1
3	1:1	0	0	0	0
4	1:1	0	0	0	0
5	HA * only	0	0	0	0

* HA ash from an industrial rotary kiln; ** The scale of smell intensity: 4—very strong; 3—strong; 2—perceptible; 1—faintly perceptible; 0—not perceptible; numbered as in Table 1.

3.5. Research on Hydroxyapatite Ashes by Scanning Electron Microscopy

SEM image of HA from an industrial rotary kiln (Figure 5a) indicates that the ash consists of very fine hydroxyapatite grains, ranging in size from a few to about 50 μm . The degree of thermal crystallization of the ash and the small size of the grains indicates the necessity for improving thermal crystallization. The fine-grained ash increases the dust lifting and the frequency of cleaning the boilers. The lack of larger agglomerates and agglomerates proves the correct conditions for the calcining process. The images of HA samples 1–4 after calcining in a laboratory chamber kiln, without mixing (Figure 5b–e), show that the ash consists of larger hydroxyapatite grains. Ash from an industrial rotary kiln additionally calcined for 2 h at 900 $^{\circ}\text{C}$ (in a chamber kiln, without mixing) also contains larger grains of hydroxyapatite (Figure 5f). Therefore, the degree of thermal crystallization of the ashes is much better. The lack of larger agglomerates and lumps proves the correct conditions for the calcining process.

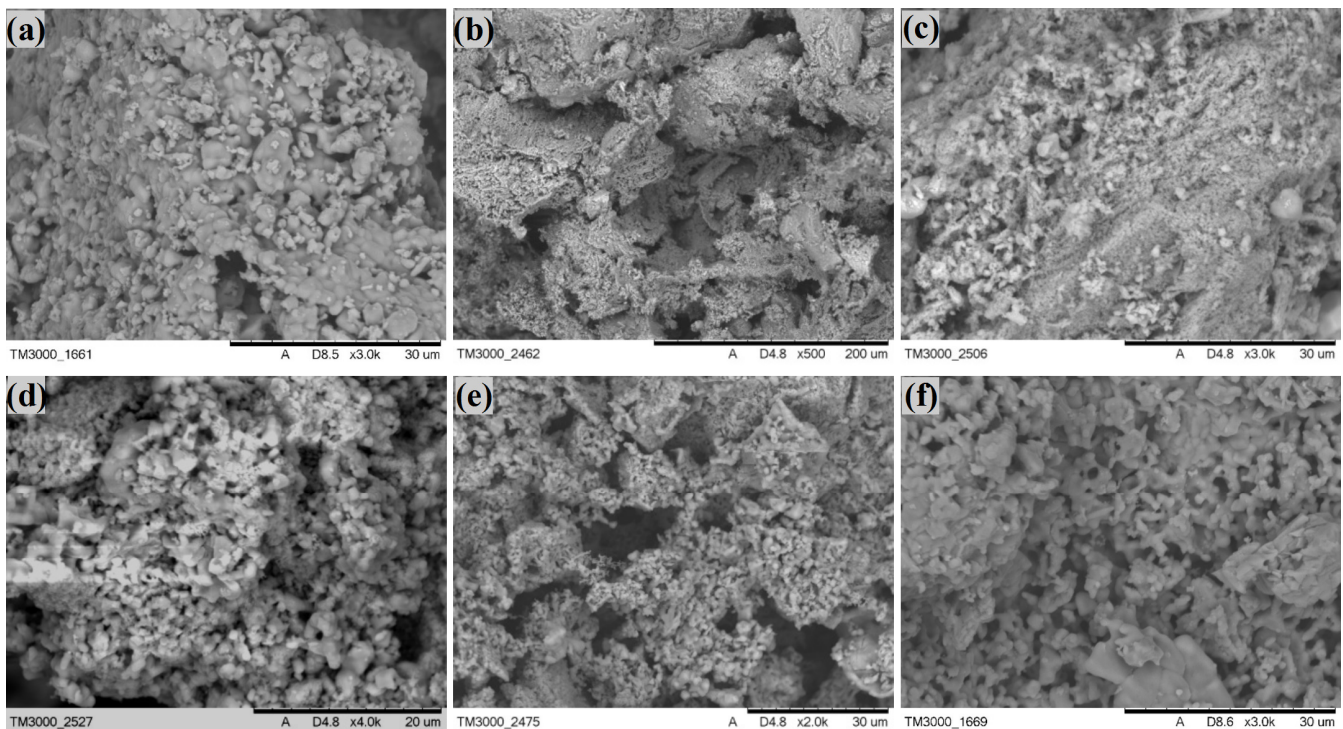


Figure 5. SEM images of ash samples from MBM combustion. (a) sample 0—hydroxyapatite ash HA from industrial rotary kiln; (b) sample 1—HA mixed with MBM (1:1) calcined at 800 $^{\circ}\text{C}$ for 1 h; (c) sample 2—HA mixed with MBM (1:1) calcined at 800 $^{\circ}\text{C}$ for 2 h; (d) sample 3—HA mixed with

MBM (1:1) calcined at 900 °C for 1 h; (e) sample 4—HA mixed with MBM (1:1) calcined at 900 °C for 2 h; (f) sample 5—HA calcined at 900 °C for 2 h. Samples 1–5 were calcined in a laboratory chamber kiln.

Figure 6 shows the EDS analysis of a sample of hydroxyapatite ash obtained from an industrial rotary kiln (sample 0), while Figure 7 shows the mapping made with the use of the BSE method of calcium and sulfur. The results of the analysis show a relatively low content of phosphorus, <14%. The carbon content is very high (7.7%), which indicates that the combustion process is incorrect. The sulfur content of 0.6% is high. Under the reductive reaction conditions (high C content), the formation of calcium sulfide is possible, which can be confirmed by the mappings in Figure 7. The reaction of CaS_2 with sulfuric acid leads to the release of hydrogen sulfide.

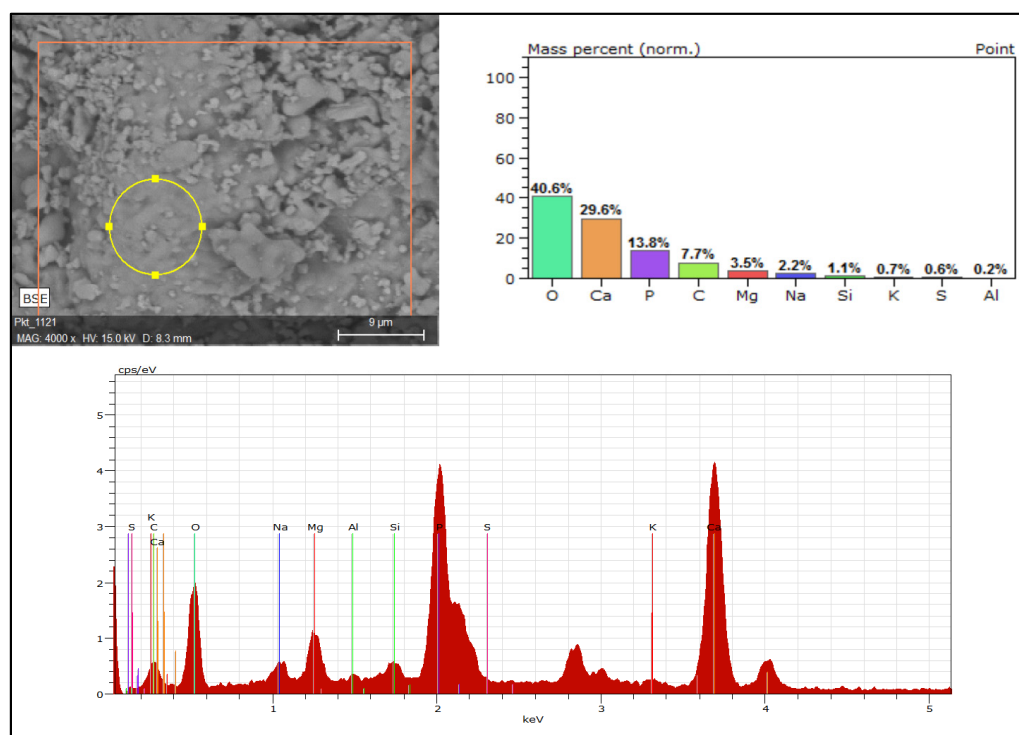


Figure 6. EDS analysis of hydroxyapatite ashes from industrial rotary kiln (sample 0).

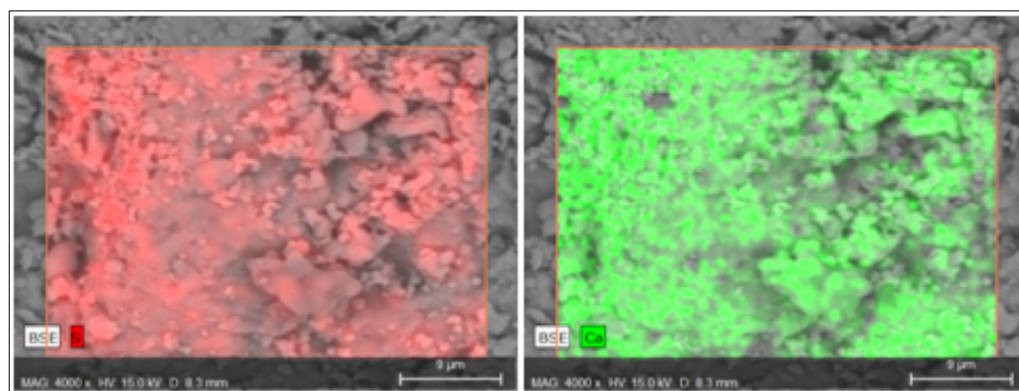


Figure 7. Sulphur and calcium mappings from the BSE method. Sample 0—hydroxyapatite ash HA from industrial rotary kiln.

Figures 8 and 9 show the EDS analysis of sample 4 (mass ratio HA/MBM = 1:1, calcination at 900 °C for 2 h) and sample 5 (hydroxyapatite from an industrial rotary kiln

calcined again in a laboratory chamber kiln at 900 °C for 2 h) containing images of the analyzed samples, the elemental composition of the tested surfaces, and the spectra of the identified elements.

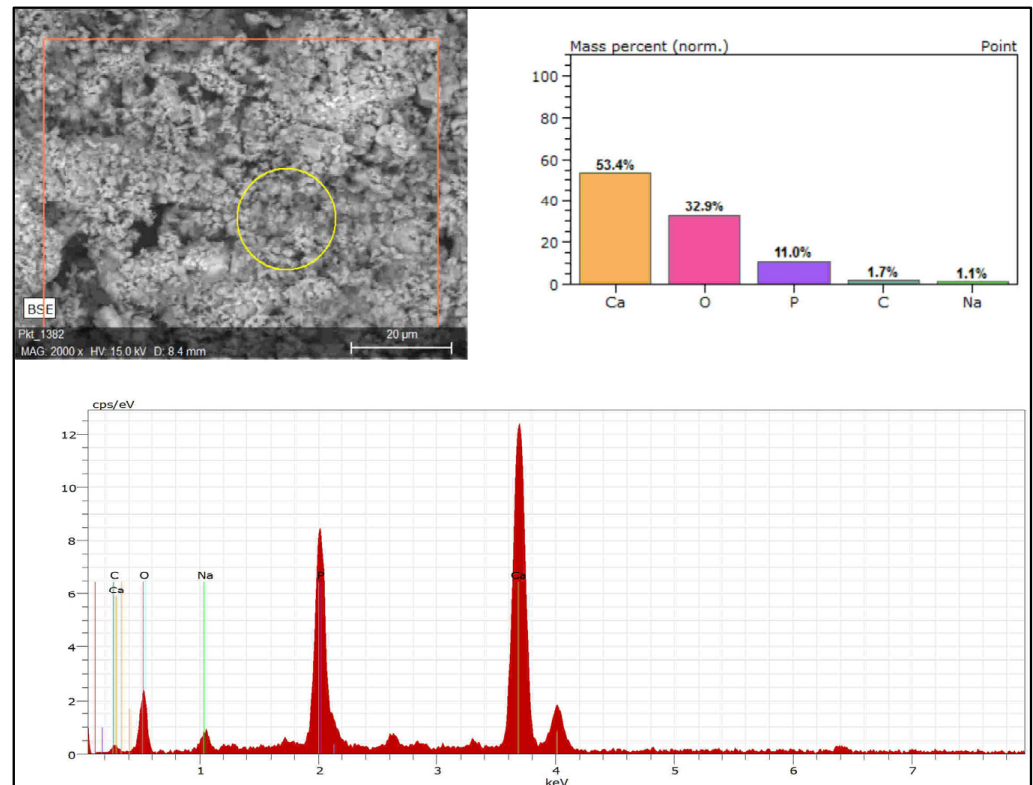


Figure 8. EDS analysis of hydroxyapatite ashes from calcining: at 900 °C for 2 h (sample 4).

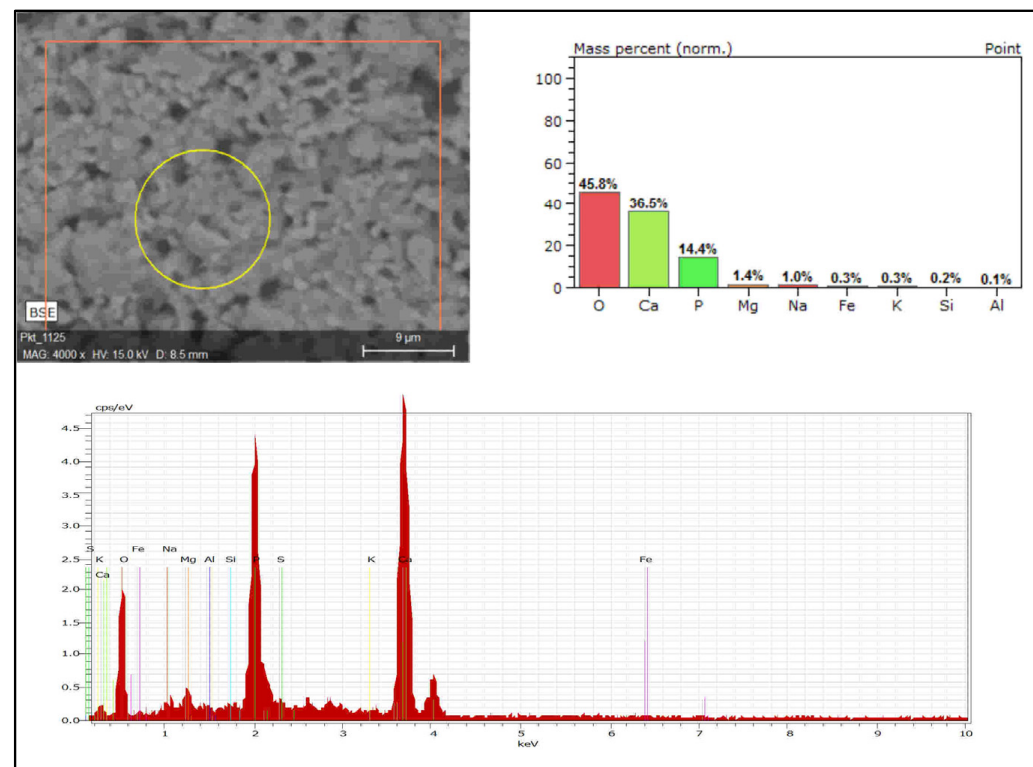


Figure 9. EDS analysis of hydroxyapatite ashes from an industrial rotary kiln calcined again in a laboratory chamber kiln at 900 °C for 2 h (sample 5).

Analyses of sample 4 show a slightly higher phosphorus content and a much lower carbon content (Figure 8). The almost three-fold decrease in the C content in the ash after increasing the calcining temperature to 900 °C is noticeable. Also, sulfur was not identified on the surface of the analyzed sample. The carbon content analyses from the CHN analyzer are more reliable.

The results of the analysis of sample 5 show a slightly higher content of phosphorus, about 14.4% (Figure 9). There is no carbon in the ash, which proves the complete course of the combustion process. The presence of sulfur was also not found. Still, it should be borne in mind that the quantitative composition refers to a point covering a variable surface with a diameter from a few to a dozen μm (the diameter of the circle marked in the SEM images). Under highly oxidizing reaction conditions, it is possible to fully oxidize sulfur to sulfur oxides and form a calcium sulfate phase.

The elemental analysis results show a high content of P_2O_5 , 39.2%. There is <0.2% C in the ash, which proves the right course of the combustion process.

3.6. X-ray Analyses of Hydroxyapatite Ashes

The results of the phase composition analysis (semi-quantitative analysis) of hydroxyapatite ashes (samples 0–5) are presented in Table 4.

Table 4. The phase composition of hydroxyapatite ashes according to X-ray structural semi-quantitative analysis.

Phase Name	Sample of Hydroxyapatite Ashes **					
	0 *	1	2	3	4	5
Hydroxyapatite, Cl-bearing $\text{Ca}_{4.905}(\text{PO}_4)_3\text{Cl}_{0.3}(\text{OH})_8$	+	-	+	-	-	+
	(86.9%)		(80.4%)			(83.73%)
Chlorapatite, OH-bearing, syn $\text{Ca}_5(\text{PO}_4)_3(\text{Cl}_{0.53}(\text{OH})_{0.26})$	-	+	-	+	+	-
		(84.7%)		(78.06%)	(74.61%)	
Whitlockite, syn $\text{Ca}_{2.71}\text{Mg}_{0.29}(\text{PO}_4)_2$	-	-	+	-	-	-
			(14.8%)			
Whitlockite, syn $\text{Ca}_{2.89}\text{Mg}_{0.11}(\text{PO}_4)_2$	+	-	-	+	+	+
	(12.3%)			(15.59%)	(21.18%)	(15.6%)
Whitlockite, syn $\text{Ca}_3(\text{PO}_4)_2$	-	+	-	-	-	-
		(11.0%)				
Czochralskite $\text{Na}_4\text{Ca}_3\text{Mg}(\text{PO}_4)_4$	-	+	-	-	+	-
		(4.3%)			(4.21%)	
Buchwaldite, syn $\text{NaCa}(\text{PO}_4)$	-	-	+	-	-	-
			(4.8%)			
β -NaCaPO ₄ , rhenanite NaCaPO_4	-	-	-	+	-	-
				(6.34%)		
Silicon oxide SiO_2	+	-	-	-	-	+
	(0.80%)					(0.67%)

* HA ash from an industrial rotary kiln; ** Numbered as in Table 1.

The main component of the ash obtained in the industrial rotary kiln (sample 0*) is hydroxylapatite (approx. 87%). Whitlockite ($\text{Ca}_{2.89}\text{Mg}_{0.11}(\text{PO}_4)_2$), is present in a much smaller amount (approx. 12%), while SiO_2 content is below 1%. Re-calcining of sample 0* in a stationary laboratory kiln (sample 5, temperature 900 °C, time 2 h) caused only slight quantitative changes in the determined phase components. In samples 1 and 2 calcined at 800 °C (mass ratio HA*/MBM equal to 1:1, calcination time, respectively, 1 and 2 h), the main component is chloroapatite (approx. 85%, sample 1) and hydroxyapatite (approx. 80%, sample 2). The remaining components are calcium phosphates, i.e., $\text{Ca}_3(\text{PO}_4)_2$ and $\text{Na}_4\text{Ca}_3\text{Mg}(\text{PO}_4)_4$ in sample 1 and $\text{Ca}_{2.71}\text{Mg}_{0.29}(\text{PO}_4)_2$ and $\text{NaCa}(\text{PO}_4)$ in sample 2. In ash samples 3 and 4 calcined at 900 °C, the main component is chloroapatite, which content is 78% and 75%, respectively. Whitlockite ($\text{Ca}_{2.89}\text{Mg}_{0.11}(\text{PO}_4)_2$) content in both samples is about 15.6% in sample 3 and about 21% in sample 4. Rhenanite content is lower about 5% (sample 3) and Czochralskite about 4% (sample 4). Analyzing the phase composition of

ash samples 1–4, it can be concluded that the extension of both the calcining time from 1 h to 2 h and the increase in temperature from 800 °C to 900 °C causes a lower content of hydroxyapatite and higher content of other calcium phosphates.

4. Conclusions

The results of research on the properties of hydroxyapatite ashes from an industrial unit burning meat bone meal MBM in a rotary kiln indicated a high (10%) content of carbon and the presence of sulfides in the ash. The test resulted in the proposal of calcining parameters of MBM in a rotary kiln as follows: the calcining time is 30–60 min, the load charge of ~50 kg/m²/h, and the temperature of the material in the rotary kiln is less than 950 °C. The co-current work rotary kiln should have a variable speed of 1–2 rpm. Possible hydroxyapatite recycling assumes a 1:1 mass ratio of recycled hydroxyapatite and dosed MBM. The exhaust gas flow velocity in the rotary kiln should be up to 4 m/s; the oxygen content in the exhaust gases from the kiln should be about 11%. This allows for reducing the carbon content in the hydroxyapatite ash to the level of <0.2%, increasing the P₂O₅ content in the ash to 39%, and eliminating sulfide from the ash. The hydroxyapatite ash obtained could be used as a high-quality substitute for the phosphorites used in producing superphosphate fertilizers. Incineration of the meat-bone meal allowed the production of bioenergy and hydroxyapatite ash in a waste-free process, an example of implementing a very profitable circular economy solution into industrial practice.

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