Manufacturing of phosphoric acid from hydroxyapatite, contained in the ashes of the incinerated meat-bone wastes

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The results of the investigations concerning phosphoric acid manufacturing, by the extraction method, from the ashes containing hydroxyapatite, obtained through the thermal treatment of bone sludge have been presented. The incinerated bone sludge with ~16% P content and the minimal amount of impurities can be an alternative source for phosphoric acid production. The process consists in two stages. In the 1st stage, reaction of hydroxyapatite with phosphoric acid resulting in monocalcium phosphate formation in the solution obtained is carried out. The tests revealed that overall hydroxyapatite dissolution in phosphoric acid takes place when the concentration is 37% H_3PO_4. In the 2nd stage monocalcium phosphate is converted into calcium sulphate using concentrated sulphuric acid at the recommended temperature of 95°C. The principles of the technological idea of the process of phosphoric acid manufacturing from HA-containing ashes, obtained by bone wastes incineration, as well as a preliminary economic analysis for the production of 10 000 t/year of food-grade phosphoric acid have been developed.

Keywords: meat waste, hydroxyapatite, phosphoric acid.

INTRODUCTION

About 18mln t/year of meat wastes, containing phosphorus compound, are generated by the meat industry in the European Union countries. That sort of waste can be an alternative source of phosphorus, while the amount of natural phosphate rock is in continuous depletion[1–5]. According to the „cleaner technology" rules, more considerations has been given to the substitution of natural raw materials for wastes and for preventing the waste release in the environment[1, 2].

Practical processing of meat industry wastes is regulated by the European Union law[5, 6]. According to the law, the wastes are divided into categories depending on the risk of infectious disease. The wastes such as meat-bone crushes and all kind of animal parts that may generate potential risk of CJD disease belong to the 1st category of high risk[5, 6].

The only possible method, enabling neutralisation of these wastes, is thermal treatment at temperatures higher than 850°C. The wastes of the 2nd category are by-products derived from animals (droppings, enteron content), sludge from slaughterhouse sewage utilisation, and animal products containing veterinarian medicines. The wastes of this category have to be utilised in incinerating plants, too. Bone sludge (protein-free and fat-free bones) – skin, hoofs, horns, pigs bristle, feathers, blood recovered from other than ruminant animals, parts of the animals suitable for consumption, and those, though discarded by the people, estimated as no causing danger of a disease transfer from animal to human being belong to the 3rd category of wastes. They can be utilised thermally or processed into biogas or compost.

In the paper, the results concerning the extraction of phosphoric acid from the ashes obtained by thermal processing of bone sludge have been presented.

EXPERIMENTAL PART

Bone tissue, beside the meat tissue, is the main constituent of the wastes generated by slaughterhouses[5, 7]. The bones, after initial preparation, removing metallic pieces, and crushing, are subjected to hydrolysis[8, 9], yielding „protein hydro-lysate" and bone sludge. Chemical composition of sludge, obtained from different sorts of bone, does not differ much (Table 1)[5].

Table 1. Chemical composition of bone sludge

Sludge of bone as below	Content [mass %]				
	H_2O	P	Ca	Fat	Proteins
Ox	7.07	14.12	25.8	2.37	20.38
Pig	6.53	14.09	22.8	3.13	24.04
Pig legs	7.06	13.98	20.6	2.89	18.69

The phosphorus content (~ 14 %) is at the level of that in phosphate rocks. The tested bone sludge (a mixture 1 : 1 : 1 by weight), composed of pig legs, pig bones and ox bones contained pieces from a few to dozens cm in large. The composition (wt.%) of the sludge was: H_2O ~ 7.0; organic matter ~ 16.1 (in wet mass), ~ 17.3 (in dry); fat = 3.0; protein = 14.3; phosphorus P ~ 13.1 (in wet mass), ~ 14.1 (in dry); CaO ~ 35.7 (in wet mass), 38.4 (in dry)[5]. The combustion energy determined using the calorimeter KL-12Mn (Precyzja-Bit Company) was 7.9 MJ/kg (in comparison, the heat of coal combustion is 20.66MJ/kg)[5, 11].

The X-ray diffraction analysis (XRD) of the sludge was performed with the Philips X'Pert diffractometer equipped with the graphite monochromator PW 1752/00 and anode copper. The result obtained revealed that hydroxyapatite, (HA), was the only crystalline phase in bone sludge (Figure 1). The thermogravimetric analysis in air, (TGA), using the simultaneously recorded DTA-DTG system SDT 2960 TA Instruments, presented in Figure 2, demonstrates three steps of bone sludge decomposition, while the temperature is increasing. The combustion of the organic matter is performed up to ~ 600°C. The fourth endothermic effect around 800°C is likely to be associated with $CaCO_3$ decomposition.

The bone sludge was incinerated in a stationary chamber oven at 600 and 950°C for 3 hours in air atmosphere[5, 12]. Phosphorus and calcium concentration, in the ashes obtained, were analysed according to standards[10, 13]. The chemical composition of the ashes is summarised in Table 2. The XRD patterns of the ashes, presented in Figure 4, indicate that hydroxyapatite is the only crystalline phase in the ashes.
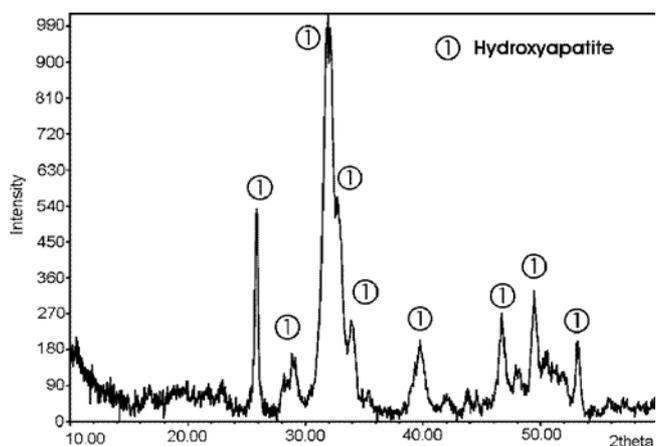
Figure 1. X-ray diffraction pattern, (XRD), of bone sludge
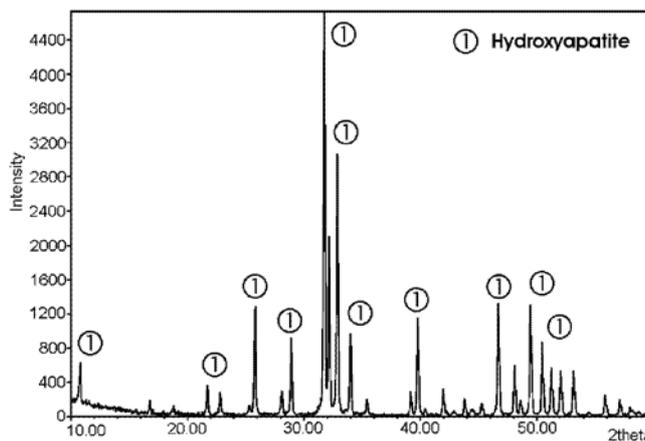
Figure 3. XRD of the ash obtained through bone sludge incineration in the stationary chamber oven at 950°C
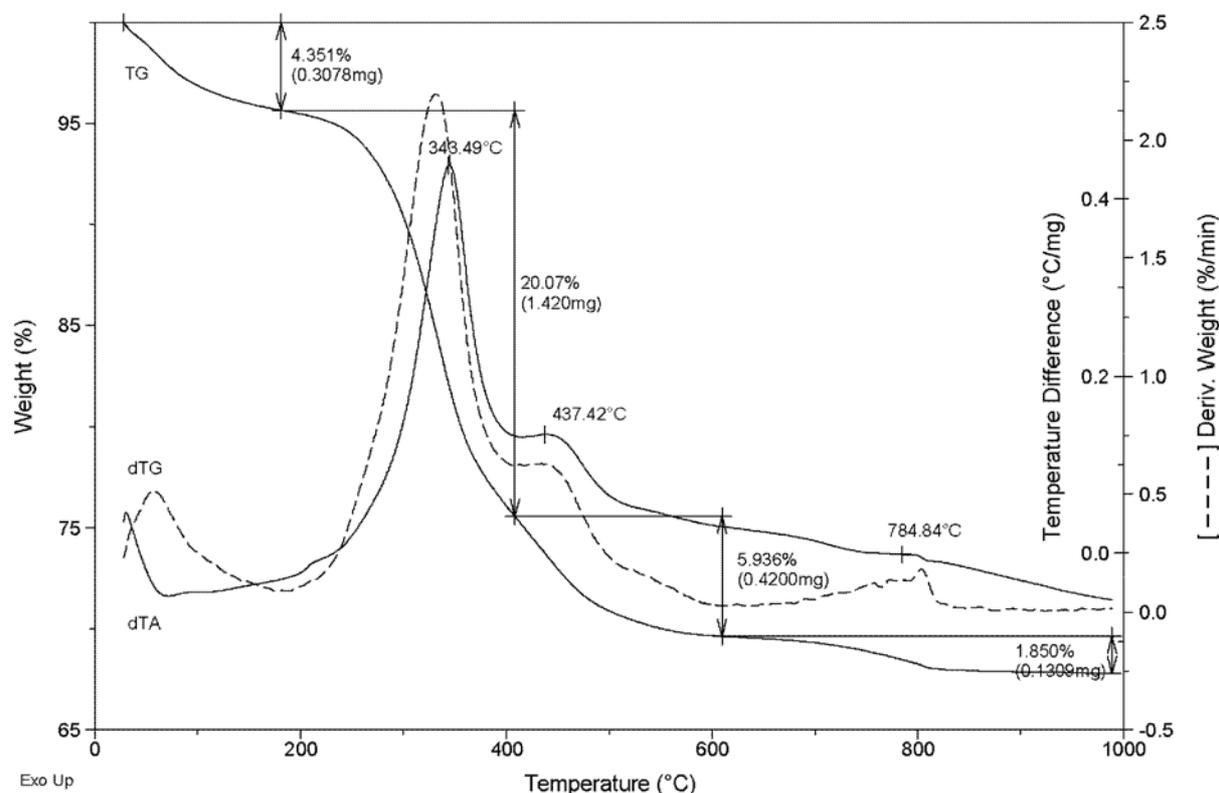
Figure 2. DTA-DTG curves of bone sludge TGA analysis in the air

The morphology of the ashes obtained was investigated by the scanning electron microscopy method (SEM), using the S-4700 Hitachi, equipped with the EDS analyzer[5]. It has been found (Figure 4) that the ash resulted from bone sludge incineration at the temperature of 950°C in the stationary chamber oven in air atmosphere is of homogeneous structure. The oval-shaped grains of the crystallites of about 0.5 – 1.0 μm large can be seen in the picture. The absence of agglomerates indicates the lack of agglutination. The white shades, shown in the picture, may indicate the melted areas of the sample resulted from overheating. That may indicate that the incineration temperature was too high.

The tests on incineration indicated that the ash obtained was almost pure hydroxyapatite. The homogenous chemical composition and the chemical properties, especially its pu-

Table 2. Chemical composition of the ashes obtained by incineration of bone sludge in the stationary chamber oven at temperatures of 600°C and 950°C[5]

Temperature of incineration	Weight loss [%]	Phosphorus content [mass %]	Calcium content [mass %]
600°C	34	15.8	39.1
950°C	35	16.4	39.2

rity and lack of heavy metals, facilitates its processing when it is used as a source of phosphorus[5, 12]. The incinerated bone sludge can be used for food-grade phosphoric acid production.
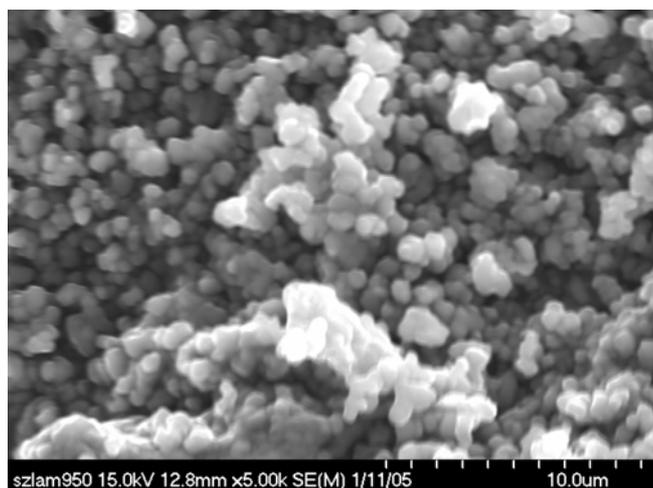
Figure 4. Microphotograph of the surface of the ash, obtained by bone sludge incineration at 950°C in the air

PHOSPHORIC ACID MANUFACTURING

Phosphoric acid was obtained by the extraction of H_3PO_4 from hydroxyapatite with the concentrated sulphuric acid[14 – 16].

$$2Ca_5(PO_4)_3OH + 10H_2SO_4 + 18H_2O =$$
$$6 H_3PO_4 + 10 CaSO_4 \cdot 2H_2O \qquad (1)$$
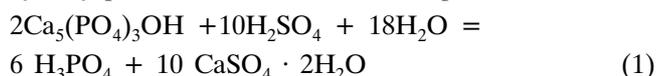
The process was carried out in two stages. In the 1st stage hydroxyapatite was treated with phosphoric acid to obtain a solution of monocalcium phosphate $Ca(H_2PO_4)_2$. In the 2nd stage calcium sulphate was precipitated using sulphuric acid[5, 16]. The goal the first part of the investigations was to determine the amount of phosphoric acid sufficient for the total dissolution of the hydroxyapatite at 75°C. The reaction was carried out for 4h in a glass reactor equipped with the heating jacket, reflux condenser, and a mechanical stirrer[5]. The results are shown in Table 3.

Table 3 demonstrates that the lowest phosphoric acid concentration sufficient for the total dissolution of $Ca_5(PO_4)_3OH$ is 27.5% H_3PO_4, and that does not depend on the ratio of $Ca_5(PO_4)_3OH /H_3PO_4$. However, while the

Table 3. Results on hydroxyapatite dissolution in phosphoric acid of different H_3PO_4 concentration

H_3PO_4 [%]	Weight ratio $Ca_5(PO_4)_3OH$ / H_3PO_4	Dissolution	Acid conc. after dissolution [% H_3PO_4]	Phase composition of the solid	Soluble in water P remained in the solid after dissolution [% H_3PO_4]
10	1:15	Not total dissolved	13.5	$Ca_5(PO_4)_3OH$	4.3
10	1:14	Not total dissolved	13.3	$Ca_5(PO_4)_3OH$	4.2
10	1:13	Not total dissolved	13.7	$Ca_5(PO_4)_3OH$	4.0
10	1:12	Not total dissolved	13.7	$Ca_5(PO_4)_3OH$	4.0
10	1:11	Not total dissolved	13.6	$Ca_5(PO_4)_3OH$	3.9
20	1:15	Not total dissolved	24.1	$Ca_5(PO_4)_3OH$	4.0
20	1:14	Not total dissolved	24.1	$Ca_5(PO_4)_3OH$	4.0
20	1:13	Not total dissolved	24.6	$Ca_5(PO_4)_3OH$	4.1
20	1:12	Not total dissolved	25.0	$Ca_5(PO_4)_3OH$	3.9
20	1:11	Not total dissolved	22.5	$Ca_5(PO_4)_3OH$	3.8
30	1:15	Dissolved	35.6	No solid	0
30	1:14	Dissolved	35.5	No solid	0
30	1:13	Dissolved	35.0	No solid	0
30	1:12	Dissolved	35.0	No solid	0
30	1:11	Dissolved	35.1	No solid	0
25	1:15	Not total dissolved	28.6	$Ca_5(PO_4)_3OH$, $CaPO_3(OH) \cdot 2H_2O$	3.7
25	1:14	Not total dissolved	28.9	$Ca_5(PO_4)_3OH$, $CaPO_3(OH) \cdot 2H_2O$	3.9
25	1:13	Not total dissolved	29.0	$Ca_5(PO_4)_3OH$ $CaPO_3(OH) \cdot 2H_2O$	4.0
25	1:12	Not total dissolved	29.0	$Ca_5(PO_4)_3OH$, $CaPO_3(OH) \cdot 2H_2O$	4.0
25	1:11	Not total dissolved	28.6	$Ca_5(PO_4)_3OH$, $CaPO_3(OH) \cdot 2H_2O$	3.9
27,5	1:15	Dissolved	32.0	No solid	0
27,5	1:14	Dissolved	32.5	No solid	0
27,5	1:13	Dissolved	33.0	No solid	0
27,5	1:12	Dissolved	32.0	No solid	0
27,5	1:11	Dissolved	32.0	No solid	0

clear solution obtained was left to stay, after a few hours secondary hydroxyapatite started to precipitate. A similar effect was observed when phosphoric acid, containing 30% H_3PO_4, was used. Further dissolution was carried out for 2 and 4h at 75°C, while the weight ratio of the solid/liquid was 1/15, 1/11 and the concentration of the acid was 10; 20; 25; 27.5; and 30 % H_3PO_4 (Table 4). In the case of the 2-hour reaction with 10% H_3PO_4, the dissolution of $Ca_5(PO_4)_3OH$ was not completed. Also, the concentration of 20 and 25% H_3PO_4 was not sufficient for the total hydroxyapatite dissolution, additionally, the system reached some rate of over-saturation and a secondary precipitate of $CaHPO_4.2H_2O$ was formed[5]. Total hydroxyapatite dissolution was achieved in the acid of 27.5% H_3PO_4 within 17 minutes.

Table 4 demonstrates that time is not significant for the hydroxyapatite dissolution under the investigated conditions.

To evaluate the optimal parameters (concentration, temperature, weight ratio of liquid/solid phases) of hydroxyapa-

tite dissolution in phosphoric acid a set of experiments was carried out according to the second order rotatable design in three factors Z_1, Z_2, Z_3 (Tables 5 and 6). The choice of the limiting concentrations of H_3PO_4 for the experiment was based on phase diagram of $H_2O – P_2O_5 – CaO$ [14], so that calcium sulphate was hydrated to the solid phase of the final product.

The tests on hydroxyapatite dissolution in phosphoric acid at different concentrations revealed that overall dissolution, without secondary precipitation, takes place only when the acid concentration was 37% H_3PO_4. In the acid of 24% H_3PO_4 the hydroxyapatite was dissolving incongruently. In the acid of 50 and 59% of H_3PO_4 the secondary precipitate was formed.

The aim of the second stage of the experiments was to determine the most preferable for calcium sulphate precipitation conditions. In the experiment, the concentration of phosphoric acid, (37% H_3PO_4) was maintained constant, while the temperature and sulphuric acid concentrations were variable parameters. First, hydroxyapatite was dissolved in phosphoric acid (37% H_3PO_4) solution at the temperatures [°C] of 75, 80, 85, 90, 95. The molar ratio of $Ca_5(PO_4)_3OH$ to H_3PO_4 was 1 : 47.4 (by weight, 8g : 100g). Afterwards, calcium sulphate precipitation from the obtained solution was carried out by sulphuric acid (concentration: 15 – 60% H_2SO_4) addition. The amount of H_2SO_4, taken for the precipitation, was equivalent to the amount of calcium introduced with $Ca_5(PO_4)_3OH$. The introduction of H_2SO_4 into the solution, containing $Ca(H_2PO_4)_2$, resulted in white precipitate formation. The hot precipitate was filtered off immediately. In the obtained phosphoric acid phosphorus and calcium and ions were analyzed (Table 7). The precipitate

Table 4. The rate of hydroxyapatite dissolution in phosphoric acid obtained for the lowest (1 : 11) and highest (1 : 15) ratio of the solid/liquid phase. Dissolution time 2 hours

Concentration H_3PO_4 [%]	1:15 ratio of the solid/liquid phase		1:11 ratio of the solid/liquid phase	
	Rate of HA dissolution %		Rate of HA dissolution	
	2h	4h	2h	4h
10	21.5	23.2	18.7	19.3
20	88.3	88.6	40.3	41.9
25	98.6	99.5	60.8	65.7
27,5	100.0	100.0	100.0	100.0
30	100.0	100.0	100.0	100.0

Table 5. Parameters of the designed experiments

Parameter	Coded values				
	-1.682	-1.000	0	+1.000	+1.682
Z_1 [% H_3PO_4]	15	24	37	50	59
Z_2 temperature [ºC]	75	79	85	91	95
Z_3 HA: H_3PO_4	1:10	1:11	1:12,5	1:14	1:15

Table 6. Matrix of the experiment designed

N°	Coded values						
	Z_1		Z_2		Z_3		H_3PO_4 content in solution, [%]
1.	+1	50	+1	91	+1	1:14	52.0
2.	+1	50	-1	79	+1	1:14	51.8
3.	-1	24	+1	91	+1	1:14	28.5
4.	-1	24	-1	79	+1	1:14	31.9
5.	+1	50	+1	91	-1	1:11	51.9
6.	+1	50	-1	79	-1	1:11	51.7
7.	-1	24	+1	91	-1	1:11	30.4
8.	-1	24	-1	79	-1	1:11	30.2
9.	-1.682	15	0	85	0	1:12.5	24.2
10.	+1.682	59	0	85	0	1:12.5	37.7
11.	0	37	-1.682	75	0	1:12.5	39.6
12.	0	37	+1.682	95	0	1:12,5	39.9
13.	0	37	0	85	-1.682	1:10	40.1
14.	0	37	0	85	+1,682	1:15	39.8
15.	0	37	0	85	0	1:12.5	39.2
16.	0	37	0	85	0	1:12.5	39.8
17.	0	37	0	85	0	1:12.5	39.8
18.	0	37	0	85	0	1:12.5	39.9
19.	0	37	0	85	0	1:12.5	40.1
20.	0	37	0	85	0	1:12.5	40.2

was subjected to X-ray diffraction and for water and phosphorus content analysis.

The data in Table 7 indicate that when the concentration of the sulphuric acid is increasing, introduced for calcium sulphate precipitation, calcium concentration in the obtained phosphoric acid is decreasing, but sulphate-ion concentration is increasing. The X-ray diffraction analysis (Figure 5) of the precipitates obtained in the process of phosphoric acid formation identified gypsum in the precipitate obtained at 85 – 95°C, while in the precipitate obtained at 75 – 80°C, hemihydrate $CaSO_4.0.5H_2O$ was additionally found[5].

The ciagram of the technological idea of phosphoric acid production from hydroxyapatite obtained by bone wastes incineration is shown in Figure 6. Part of the phosphoric acid, recycled from the filtration section, part of the mixture of phosphoric acid with calcium sulphate, recycled before calcium phosphate was filtered off, and the suspension of hydroxyapatite in water are directed to the reactor equipped with the heating jacket. After the hydroxyapatite was dissolved, sulphuric acid, diluted with the washings from the filtration section, was added. The suspension, containing calcium and phosphoric acid, is filtered off with the use of

Table 7. Result of analysis of phosphoric acid obtained from hydroxyapatite at different temperature

Concentration H_2SO_4 [%]	Phosphoric acid analysis, [%]			Precipitate analysis [%]	
	Concentration H_3PO_4	Calcium content	Sulphate content	Water content	Phosphorus content
Temperature 75°C					
15	29.90	0.143	0.725	34.90	4.90
20	31.70	0.108	0.720	33.50	4.75
25	32.70	0.108	0.820	36.40	3.20
30	33.50	0.102	0.810	34.30	5.20
35	34.30	0.101	0.840	32.00	5.80
40	38.20	0.100	0.840	22.90	4.60
45	38.20	0.093	0.940	22.40	3.80
50	38.80	0.085	0.940	22.20	2.70
55	39.40	0.084	0.940	21.80	1.80
60	41.00	0.074	0.940	20.40	1.60
Temperature 80°C					
15	29.60	0.129	0.83	25.0	4.5
20	31.60	0.127	0.82	24.3	4.0
25	32.40	0.114	0.84	23.7	3.7
30	35.40	0.107	0.92	23.6	3.3
35	35.60	0.102	0.92	22.6	3.2
40	37.50	0.097	0.90	22.2	3.1
45	37.50	0.093	0.93	18.9	3.1
50	38.80	0.088	0.95	18.3	3.0
55	39.90	0.085	0.99	18.0	2.6
60	40.00	0.075	1.02	17.9	2.5
Temperature 85°C					
15	28.1	0.143	0.80	19.9	5.1
20	33.1	0.131	0.82	19.8	4.0
25	33.5	0.120	0.88	18.5	3.7
30	35.9	0.119	0.97	18.0	3.5
35	36.5	0.094	0.99	17.5	3.2
40	38.5	0.090	0.99	14.6	3.0
45	38.5	0.084	1.00	14.0	2.9
50	39.1	0.079	1.03	13.6	2.5
55	39.2	0.075	1.02	12.9	2.5
60	39.9	0.073	1.03	12.2	2.3
Temperature 90°C					
15	28.2	0.138	0.79	20.7	5.1
20	33.0	0.132	0.89	19.6	4.4
25	34.5	0.129	0.96	18.7	3.9
30	35.6	0.108	0.99	14.1	3.7
35	37.7	0.108	0.99	14.0	3.5
40	37.7	0.098	1.00	13.9	3.3
45	40.1	0.097	1.20	13.8	2.6
50	40.6	0.096	1.22	7.0	2.2
55	40.9	0.090	1.22	7.0	2.0
60	41.2	0.084	1.29	6.3	1.9
Temperature 95°C					
15	30.3	0.129	0.88	20.9	4.4
20	31.3	0.116	0.90	19.5	3.4
25	31.3	0.110	0.93	18.3	3.0
30	35.4	0.109	0.97	14.3	2.9
35	37.9	0.107	0.82	12.6	2.5
40	39.5	0.108	0.94	11.5	2.3
45	41.3	0.104	0.96	10.1	2.0
50	39.8	0.107	0.88	9.6	1.8
55	41.9	0.106	0.84	8.8	1.8
60	41.9	0.097	0.88	7.2	1.6
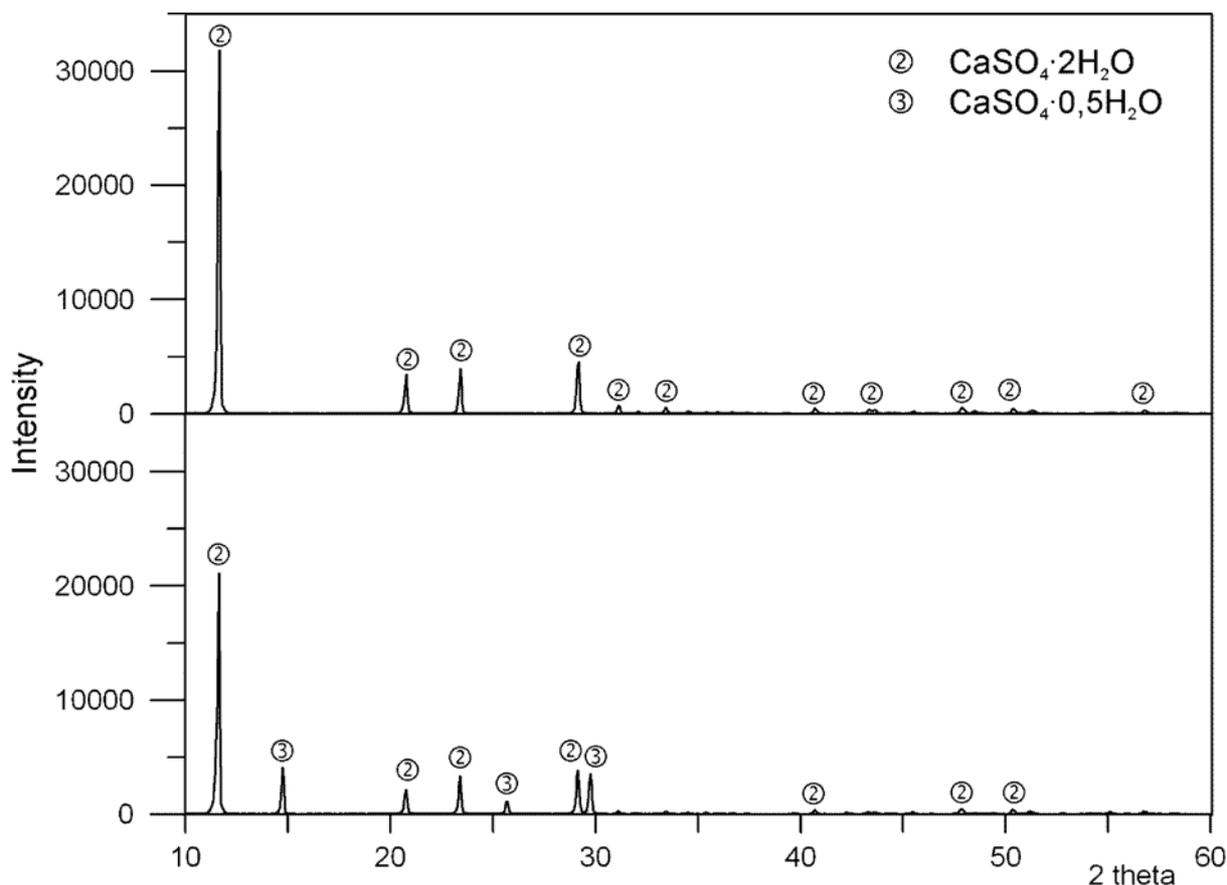
Figure 5. XRD of the precipitate obtained in the process of H_3PO_4 formation at temperature of 95 (A) and 75°C (B). Concentration of sulphuric acid used was 50 – 60% H_2SO_4

the filter-press. Part of the phosphoric acid obtained has been recycled to the reactor, the rest is directed to the concentrating section. The concentrated phosphoric acid (75% $H_3PO_4 \sim 54$ P_2O_5) can be commercialized or used for the production of phosphoric acid salts by the company. The vapours from the reaction and from the acid concentrating section are condensed. The condensate is used in the filtration section for phosphogypsum washing. The phosphogypsum is temporarily stored and then sold.

In Table 8 the parameters of the phosphoric acid manufacturing from apatite in Wizow Chemical Works plant in comparison to the manufacturing (to be made) from hydroxyapatite, derived from bone wastes has been presented. The assessed cost of the phosphoric acid (100% H_3PO_4) production from hydroxyapatite is $\sim$\$500/t. The current cost of the commercial food-grade phosphoric acid is on the level of \$1200. A comparison of these two numbers indicates that the expected profit of phosphoric acid production from the incinerated bone wastes could be high[5].

Table 8. Parameters of phosphoric acid technology carried out in ZCH Wizow plant in comparison to the manufacturing (to be made) from hydroxyapatite, derived from bone wastes [17]

Parameter	Technological parameters of 1 t phosphoric acid manufacturing in ZCH Wizow, Poland			Parameters of 1t phosphoric acid manufacturing (to be made) from bone-hydroxyapatite (100 % H_3PO_4)
	100% P_2O_5	100% H_3PO_4	75% H_3PO_4	
Theoretical consumption of P_2O_5 [t]	1.146	0.830	0.623	
Theoretical consumption of sulphuric acid (100 %) [t]	2.301	1.667	1.250	
Practical consumption of P_2O_5 from apatite [t]	1.146	0.830	0.623	
Practical consumption of hydroxyapatite, containing 39 % P_2O_5 [t]				1.334
Practical consumption of sulphuric acid (100 %) [t]	2.733	1.980	1.485	1.854
Practical consumption of sulphuric acid (96 %) [t]	2.847	2.063	1.547	1.932
Consumption of soda [t]	0.054	0.039	0.029	
Consumption of deterlon [t]	0.004	0.003	0.002	0.003
Industrial water [m^3]	99	72	54	
Technological water [t]				2.203
Electric energy [kWh]	207	150	113	
Steam [GJ]	0.6	0.4	0.3	6.407
Gypsum (20 % water) – waste [t]	5.494	3.980	2.985	3.292
Amount of liquid acidic wastes [m^3]	26	19	14	
Amount of liquid neutral wastes [m^3]	39	28	21	
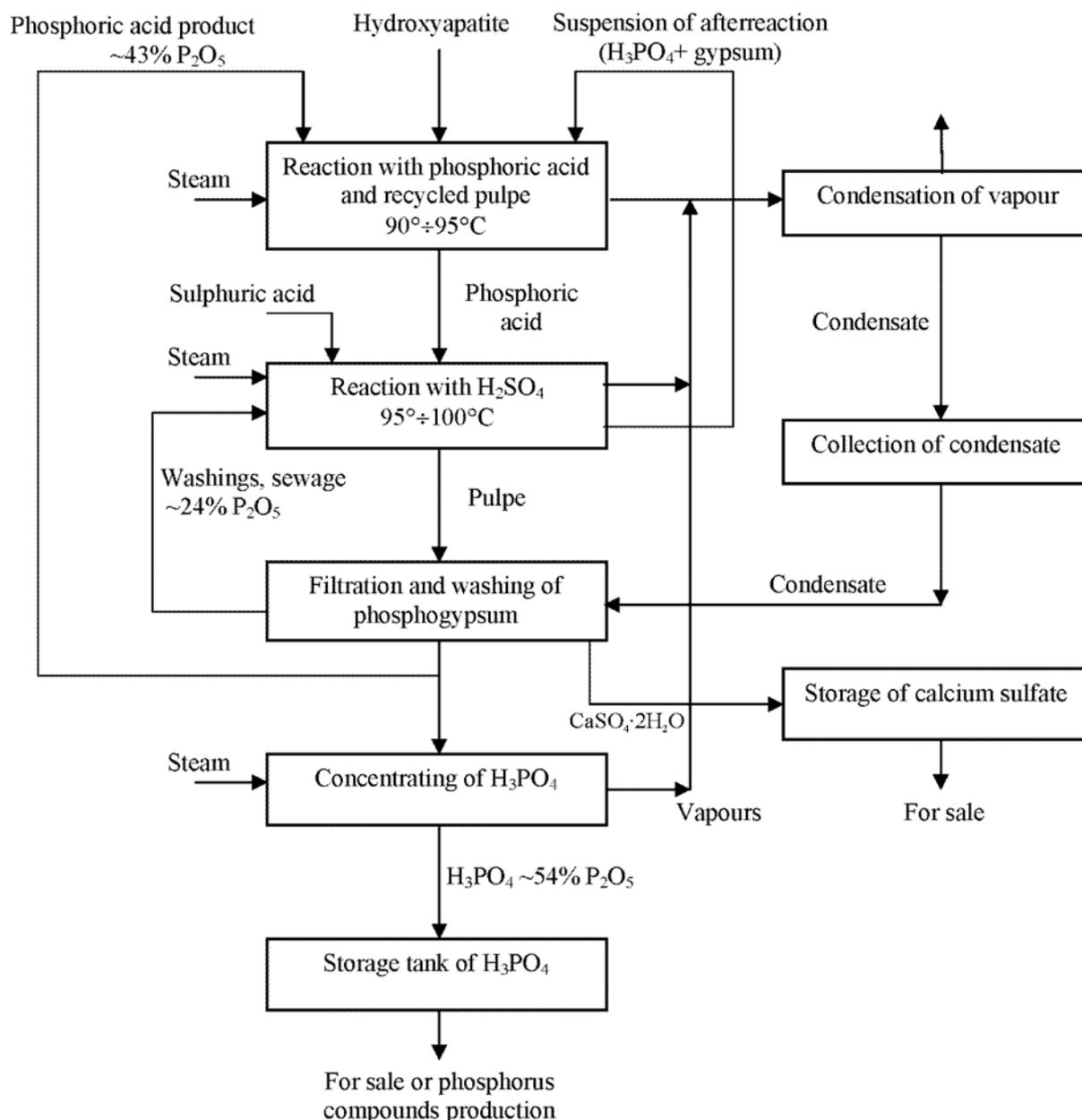
Figure 6. Diagram of the technological idea of phosphoric acid production from hydroxyapatite obtained by bone wastes incineration

CONCLUSION

The results that led to the elaboration of phosphoric acid production method from the ashes obtained through the incineration of bone wastes from meat industry have been presented. The ash is a valuable alternative source for food-grade phosphoric acid production. It is characterised by high phosphorus concentration (the level of 16% P) and traces of impurities.

On the basis of the research, carried out on the laboratory scale, the technological parameters of two-stage phosphoric acid processing from hydroxyapatite obtained through the incineration of bone wastes have been evaluated. In the 1st stage hydroxyapatite is dissolved in phosphoric acid to yield mono-calcium phosphate in solution. The overall hydroxyapatite dissolution takes place in phosphoric acid with the 37% H_3PO_4 content. In the 2nd stage calcium phosphate is converted into calcium sulphate using concentrated sulphuric acid.

A preliminary economic analysis of the production of 10 000 t/year of food-grade phosphoric acid (100% H_3PO_4) enabled an assessment of the cost of around ~ \$500 /t. In comparison to the current cost of the commercial food-grade phosphoric acid (~ \$1200 /t) the expected profit could be high.

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