

THE INFLUENCE OF CaO AND P₂O₅ OF BONE ASH UPON THE REACTIVITY AND THE BURNABILITY OF CEMENT RAW MIXTURES

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The influence of CaO and P₂O₅ upon the reactivity of cement raw meal was investigated in this paper. Ash of bone meal containing Ca₃(PO₄)₂ - 3CaO·P₂O₅ was used as the source of P₂O₅. Two series of samples with different content of the ash of bone meal were prepared. In the first series, the ash of bone was added into cement raw meal. The second series of samples were prepared by considering ash as one of CaO sources. Therefore, the total content of CaO in cement raw meal was kept constant, while the amount of P₂O₅ increased. These different series of samples were investigated by analyzing free lime content in the clinkers. The XRD analysis and Electron Micro Probe Analyzer analysis of the clinkers were also carried out. Two parameters were used to characterize the reactivity of cement raw meal: content of free lime and Burnability Index (BI) calculated from free lime content in both series of samples burnt at 1350 °C, 1400 °C, 1450 °C and 1500 °C. According to the first parameter, P₂O₅ content that drastically makes worse the reactivity of cement raw meal was found at 1.11 wt.% in the first series, while this limit has reached 1.52 wt.% in the second one. According to the BI, the limit of P₂O₅ was found at 1.42 wt. % in the first series and 1, 61 wt.% in the second one. Furthermore, EPMA has demonstrated the presence of P₂O₅ in both calcium silicate phases forming thus solid solutions.

INTRODUCTION

The main concerns of cement industry and cement researchers are and will remain the energy savings, environmental protection and pollution control [1-5]. To achieve these goals, cement industry and relative sectors are developing constantly the concept of use of alternative fuels and raw materials in the production of clinkers and final cements. The use of industrial wastes energy bearing to replace partially fossil fuel is well known. They are used mainly for their calorific values and also because of the similarity between chemical composition of their ashes and raw materials or clinkers. Many studies have dealt with the use of different kinds of wastes and by-products energy bearing for incineration, co-pyrolising or burning in cement rotary kiln during clinker firing [6-11]. Therefore, new burners and pyrolysing equipments as Hot-discs were installed in order to enhance the effective use of alternative fuels in cement production. Some alternative fuels can also be considered as alternative raw materials, since their ash component will end up as an integral part of cement clinker. The ash, an inorganic part of wastes energy bearing after burned, is incorporated into clinker or reacts with raw materials to form clinker minerals or their solid solutions.

Ones of these alternative fuels that could be considered as alternative raw materials are the meat bone meal, referred as Meal Bone Meat (MBM) or other processed veterinary wastes of animal origin. The cement rotary kiln reaches high temperature needed to effective degradation of biological wastes combined with chemical binding of the ash into the clinker. The ash of the meat bone meal is composed mainly of P₂O₅ and CaO, mostly in the form of calcium phosphate (Ca₃(PO₄)₂) of modified hydroxyapatite (Ca₅(PO₄)₃OH). Therefore, the investigation upon the influence of P₂O₅ or other calcium phosphate forms becomes urgent and necessary, since the combustion of phosphorus containing biowastes is today highly actual. The combustion of these wastes in cement rotary kiln helps to prevent the spread of infectious diseases (BSE) and also to lower the amount of wastes deposited in a landfills and lower the amount of greenhouse gas emissions (CO₂, CH₄).

It was reported that P₂O₅ has an important impacts upon the melting properties of cement raw meal; it enters the clinker minerals forming solid solutions and affects the phase composition of the clinker[12,13]. Until now, cement industry uses limited biological wastes as alternative fuels in order to prevent the negative effect of resulted ash containing P₂O₅ upon the clinker properties.

The quantity of MBM to incinerate in rotary kiln is in a such manner to ensure the total P₂O₅ content in clinker under 1 wt.%. The existence of this limited amount of P₂O₅ in clinker is the disadvantage of present state, since it makes impossible to increase the amount of wastes calcium phosphate bearing.

The low phosphorous concentrations (analytically expressed like P₂O₅) in the clinker markedly impact the quality of cements. Increased amount of P₂O₅ in the raw meal lower the burnability of clinker [14]. The overall view from the work [15] reported on the incorporation of phosphorous compounds in Portland cement clinker is that, up to 0.3 per cent (or slightly more), P₂O₅ enters the C₂S and improves its hydraulic properties and can give a modest lengthening of the setting times by perhaps 20 min. This is compatible with the normal range of P₂O₅ contents which are from 0.03 to 0.22 per cent in the natural raw materials. When higher amounts of P₂O₅ are present, the C₂S is stabilized to an extent that its reaction with C to form C₃S is inhibited. The addition of small amounts of fluorine-containing compounds prevents this effect and permits the formation of C₃S to proceed. Kwon W.-T. et al. [16] explored the possibility of effective reutilization of sewage sludge in cement kiln process. The characterization of clinkering reaction was carried out with various amounts of P₂O₅ and Cl⁻ content. Their results indicate that free lime content is increased, while alite, ferrite and aluminate mineral contents are decreased with P₂O₅ addition. The Cl⁻ presence exhibits opposite properties to P₂O₅ addition. The authors claim that chlore compound plays an accelerator role for the liquid-solid reaction of clinkering reaction since its product turns into liquid phase at low temperatures.

It has been shown that phosphate takes an active part in the reactions occurring during clinker burning process and shifts the stability limits of individual phases [14]. Phosphate is firstly fixed by calcium in the form of hydroxyl apatite, which gets unstable at higher temperatures, reacting with silicon to form an isomorphous mixture made up of dicalcium silicate and tricalcium phosphate (C₂S–C₃P) first, which can be mixed with β-C₂S continuously. If the CaO supply is sufficient, this isomorphous mixture containing phosphate can react further to form alite containing phosphate. The viscosity of the clinker melt is diminished as a result of phosphate input, which is conducive to alite growth. As phosphate input increases, C₂S–C₃P isomorphous mixtures having a structure of α'-C₂S and α-C₂S are formed. As a consequence, alite formation is increasingly impeded.

Halicz L., Nathan Y. and Ben-Dor L. [12] prepared synthetic clinkers similar to high-silica Portland cement clinkers from raw material containing at times more than 50% oil shale from Har-Tuv area to which phosphate rock and laboratory grade CaCO₃ and SiO₂ were added. Although some clinkers contained more than 3% P₂O₅, their mineralogical composition was satisfactory (50 to 60% C₃S). This result was obtained by taking into account

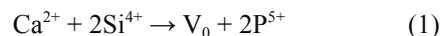
in the Silica Modulus formula the P₂O₅ concentration. The resultant relatively high silica concentrations raise the melting point of the raw meal, causing a non-equilibrium state which allows the formation of C₃S and its preservation.

The influence of phosphorous upon the formation of tricalcium silicate was studied by other authors [17-19]. They showed that the limit of phosphate ions amount in tricalcium silicate solid solution is about 1.1 wt.% P₂O₅. Higher amounts inhibit C₃S crystallization and lead to preferential formation of phosphate solid solution of dicalcium silicate with stabilization of high temperature polymorph modifications α'- and α-C₂S [12, 20, 21].

The P₂O₅ concentrations in belite as well as in alite increase markedly with its growing overall content in clinker. It preferentially enters the structure of belite and for a total P₂O₅ content in clinker ≥0.5% its content is more than two times higher in belite than in alite. P₂O₅ also influences the size of alite crystals. In the raw meals with high content of P₂O₅, the form of alite crystals delay or is completely blocked [13].

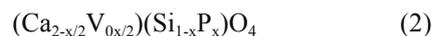
Systematic study of the effect of phosphorus addition on pure C₃S in the range 0.1 to 0.9 wt.% P₂O₅ is presented in the literature [22]. The authors showed that adding phosphorus (alone) from 0.1 wt.% P₂O₅ causes a partial decomposition of C₃S into α'-C₂S and C phases. This indicates a low solubility limit of phosphorus in T1 C₃S (≤ 0.1 wt.% P₂O₅) and supports the idea that phosphorus impurity stabilizes α'-C₂S polymorph. The content of phosphorus in the α'-C₂S(P) phase is more than 1 wt.% P₂O₅. As P₂O₅ content increases, the α'-C₂S(P) phase appears as layer covering more and more C₃S grains.

The study of Ca₂SiO₄–Ca₃(PO₄)₂ system at high temperatures shows that Ca₂SiO₄ receives certain amount of P₂O₅. The P⁵⁺ ion fills Si⁴⁺ position [23]. During the P⁵⁺ ion substitution for Si⁴⁺ ion the vacancies is built up as a result of need to maintain neutrality.



The substitution of two atoms P⁵⁺ for two atoms Si⁴⁺ causes that Ca²⁺ atom must leave its position and so the vacancies is created.

General formula of dicalcium silicates solid solutions with stabilized P₂O₅ is following [24]:



where 0.02 ≤ x ≤ 0.10

It follows that during the synthesis of stabilized dicalcium silicate from pure dicalcium silicate and P₂O₅, certain amount of CaO must be released. P₂O₅ is present in the form of apatite, which contains CaO. Therefore, it is comprehensible that the free lime content increases with increasing amount of added apatite that could be considered as secondary raw materials substituting partially limestone.

Staněk and Sulovský [13] showed that P enters the structure of both calcium silicates at least partially through the so called berlinite substitution: $Al^{3+} + P^{5+} \leftrightarrow 2Si^{4+}$, where $AlPO_4$ (the berlinite component), isostructural with quartz, substitutes SiO_4 tetrahedrons. The berlinite substitution is the more important, the higher is P_2O_5 content in the clinker. This finding led the authors to experiments with clinker composed of only three main oxides, i.e. without either Al_2O_3 or without Fe_2O_3 . In the clinkers without Fe_2O_3 the negative impact of P_2O_5 on alite formation manifested itself at the theoretical content of 3 wt.% P_2O_5 in the clinker.

Benarchid et al. [25] examined the simultaneous influence of iron and phosphorus inclusions on the $CaCO_3$ decarbonation and the C_2S formation in $CaCO_3$ - SiO_2 mixtures around the molar ratio $CaCO_3/SiO_2 = 2$. In these reacting mixtures, the onset temperature of decarbonation decreased with Fe_2O_3 and P_2O_5 additions of, respectively, less than 9.50 wt.% and 8.45 wt.%. The corresponding reduction of decarbonation temperature was about 85°C. The mineralogical analysis of the synthesized solid solutions $(Ca_{2-2x}Fe_xV_{0x})(Si_{1-x}P_x)O_4$ (V_0 : cationic vacancy of Ca^{2+}) with $0 \leq x \leq 0.20$ showed that at room temperature the iron and phosphorus doped C_2S is stabilized in the β , α' and α forms for additions less than 9.50 wt.% Fe_2O_3 and 8.45 wt.% P_2O_5 . For the only (Fe_2O_3 2.33 wt.% - P_2O_5 2.07 wt.%) composition, the presence of iron oxide inhibited the stabilizing effect of P_2O_5 on the α' - C_2S formation. Beyond this composition, the phosphorus effect was predominant.

Another authors [26] studied the effect of combination of manganese and phosphorus elements on the formation of solid solutions, by heterovalent substitution of corresponding ions in C_3S lattice, at air atmosphere. The X-ray analysis showed that the M3 polymorph of C_3S was undoubtedly formed at Mn and P inclusions less than 0.69 wt.%, Mn_2O_3 and 0.62 wt.% P_2O_5 . At higher amounts of these order, the alite phase was not formed and solid solutions of C_3S take a place with $2CaO.MnO_2$ and CaO compounds. The observed mineralogical evolution of C_3S phase agreed with the reported effect of P_2O_5 [21]; the increasing amount of P_2O_5 leads to the stabilization of C_3S polymorphs according to the order: $\beta \rightarrow \alpha' \rightarrow \alpha$. The presence of manganese did not influence this stabilization accompanied by the inhibiting effect on C_3S crystallization. The Electron Paramagnetic Resonance investigations of synthesized monoclinic C_3S showed that Mn ions are in octahedral site as Mn^{2+} oxidation state. The solid solutions were formed by simultaneous substitutions $Mn^{2+} \rightarrow Ca^{2+}$ and $(PO_4)^{3-} \rightarrow (SiO_4)^{4-}$ and were described with the following cationic vacancies formula: $(Ca_{3-5x}Mn_{4x}V_{0x})(Si_{1-2x}P_{2x})O_5$ with $x \leq 0.005$.

The cement industry itself is estimated to emit about 5 % of the total global anthropogenic carbon dioxide (CO_2) emissions [27]. One of the ways to make Portland cement with less CO_2 emissions can be to produce clinker by supplementing partially limestone by another calcium source than carbonate.

The aim of the present investigation is to show that the bone meal can be utilized not only as alternative fuel but also as the source of material (alternative material). The ash of bone meal contains CaO so it can be used as partial substitution of limestone. The calculation of CaO fraction from the ash of bone meal into the total CaO account balance in the cement raw meal will enable to combust higher amount of the bone meal, to reduce the CO_2 emission and to save one of the basic raw material in production of cement – limestone.

EXPERIMENTAL

The ash of bone meal preparation

The bovine bone was used to ash of bone meal preparation. This bone was boiled out in the water (app. 4 hours) to separate rest of meat and fat. After boiling out process the bone was cleaned from rest of meat and in consequence the bones were annealed app. 1 hour at different temperatures in order to follow the influence of temperature upon the bone calcination. The ash calcinated at 700°C was used in the preparation of cement raw meal. The ash of bone meal was before using grinded and sieved (sieve 0.6 mm). The obtained fracture below 0.6 mm was used.

Chemical analysis of starting raw materials and ash of bone was realized by X-Ray Fluorescence Analysis (XRF) Spectro 2000.

STOE Powder Diffraction System (STADI P) using CoK radiation with a wavelength of $\lambda = 1.788$ nm, operating at 40 kV and 30 mA was used to identify the phase evolution of calcined bone at different temperatures. Before the analysis, samples of each composition were milled into fine powder. All patterns were collected in the range of 10° to 60° 2θ with a scan speed of $2^\circ/\text{min}$ and step size 0.02. Also, Electron Probe Micro-Analyzer analysis (EPMA JEOL JXA-840A, EDS parameters- 15KV, Takeoff Angle 40.0°) was useful to detect the presence of P_2O_5 in different clinker minerals.

Chemical analysis of free lime (f- CaO) in samples was achieved according to the standard ethylene glycol extraction method.

The preparation of clinker samples

The calcined ash of bone meal, lime, marl and Fe-addition with determined chemical composition were used for preparation of raw mixtures. Two series of samples with different content of ash (resp. P_2O_5) were set.

1. series: ash of bone was added to the mixtures without computing its CaO into the total CaO needed to react with hydraulic oxides (SiO_2 , Al_2O_3 and Fe_2O_3). The lime factor may be higher than that of mixture without ash addition.

2. series: the CaO from the bone meal ash was considered in the calculation of total CaO in the mixture (CaCO₃ content aliquotly is reduced). The lime saturation remains constant, but the content of limestone decreases.

The water was added into prepared raw mixtures and the beads with diameter app. 1 cm were formed. These beads were dried at laboratory temperature for 24 hours. After drying process the burning process at temperatures 1350°C, 1400°C, 1450°C and 1500°C follows. The temperature rise in used electric elevator furnace was set to 10°C/min and holding time at final temperature to 1 hour. The samples were kept out and rapidly air-cooled to laboratory temperature.

RESULTS AND DISCUSSION

The ash of bone meal annealed at different temperatures was analyzed by XRD method. As it is seen in Figure 1, the main products of ash calcinated at 700°C and 1000°C are hydroxyapatite (JCDD 24-0033). At 1450°C hydroxyapatite is partially decomposed in other calcium phosphate form, Ca₃(PO₄)₂ identified as mineral whitlockite (JCDD 3-0713). Considering the results of chemical composition given in Table 1, one can affirm that the main inorganic component of the bone is hydroxyapatite Ca₅(PO₄)₃OH. Hydroxyapatite in the form of P₂O₅ or also in the form of calcium phosphate is considered as raw materials that react with other oxide during the burning process to form different solid solutions of clinker minerals.

Chemical analysis of free lime

The results of chemical analysis of unreacted lime, so-called free lime (f-CaO) as function of ash addition or P₂O₅ are depicted in Tables 3 and 4.

Table 1. Chemical composition of used raw material.

Composition (wt.%)	Marl	Limestone	Fe addition	Ash of bone meal
CaO	18.88	53.674	8.836	54.14
SiO ₂	41.8	3.654	3.197	0.819
Al ₂ O ₃	11.9	0	0.688	0
Fe ₂ O ₃	3.82	0	80.91	0.00995
P ₂ O ₅	–	–	0.2004	38.03

Table 2. Adjusted basic chemical parameters.

Raw materials	Raw material composition	Characteristics of cement raw meal		Mineralogical composition	
Marl	28.50 %	Lime saturation	93.84	C ₃ S:	2.69 %
Lime	70.25 %	Silica modulus	2.64	C ₂ S:	18.58 %
Fe- addition	1.25 %	Aluminate modulus	1.62	C ₃ A:	8.63 %
Ash of BM	0 %			C ₄ AF:	10.11 %

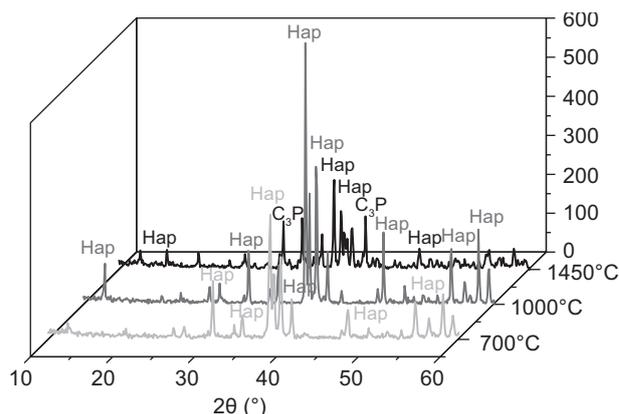


Figure 1. XRD analysis of the bone meal ashes burnt at 700 °C, 1000 °C and 1450 °C.

Table 3. First series of samples (without CaO account balance in raw mixture).

Annealing at temperature: 1350°C 1400°C 1450°C 1500°C					
Ash of bone meal (wt.%)	P ₂ O ₅ (wt.%)	f-CaO (wt.%)	f-CaO (wt.%)	f-CaO (wt.%)	f-CaO (wt.%)
0	0	2.25	0.02	0.05	0.07
0.99	0.38	3.43	0.47	0.22	0.05
1.96	0.75	5.25	1.45	0.97	0.36
2.91	1.11	5.6	2.59	2.1	1.31
3.85	1.46	5.57	3.66	3.03	2.23
4.76	1.81	5.55	4.14	4.08	3.86

Table 4. Second series of samples (with CaO account balance in raw mixture).

Annealing at temperature: 1350°C 1400°C 1450°C 1500°C					
Ash of bone meal (wt.%)	P ₂ O ₅ (wt.%)	f-CaO (wt.%)	f-CaO (wt.%)	f-CaO (wt.%)	f-CaO (wt.%)
0	0	2.02	0.13	0.05	0.02
1	0.38	2.58	0.58	0.05	0.05
2	0.76	4.03	1.56	0.68	0.43
3	1.14	4.49	2.28	1.5	1.02
4	1.52	4.39	2.85	2.17	2.09
5	1.9	4.27	3.27	3.08	3

The free lime content increases with increasing ash of bone meal addition and decreases with increasing burning temperatures in both series of samples. The increase in f-CaO content in clinker is due to the fact that P₂O₅ enters C₂S and stabilizes it. As it was mentioned by [25], P₂O₅ can be used to stabilize high temperature form of C₂S against their transformation

to the thermodynamically stable b-C₂S. Unfortunately, this form is without hydraulic properties. Once P₂O₅ stabilizes C₂S, it becomes hard to react with CaO to form C₃S. The increasing content of P₂O₅ causes that the formation of alite is increasingly retarded or later totally blocked.

The highest free lime content was found out in samples burned by 1350°C. With increasing P₂O₅ content in cement raw, the f-CaO seems to decrease. These results could be explained by the detection limit of this analytical method. At higher temperatures, the f-CaO content increases proportionally to P₂O₅ content, but the formation of C₃S is well advanced in sample without ash addition at 1400°C, the value f-CaO is negligible due to the laboratory burning conditions (heat transfer, sample quantity etc.). But, the addition of ash into cement raw meal at this temperature lowers the formation of C₃S and increases the f-CaO in clinker. Burning clinker at 1400°C limits the addition of P₂O₅ to less than 1 wt.%. By burning cement raw meal at industrial burning temperature in cement rotary kiln (1450°C), the standard limit of f-CaO

in clinker is reached with 1.14 wt.% P₂O₅. This result is in agreement with that referred by many authors and that kept in cement industry using MBM as alternative fuels. The need to increase MBM in co-pyrolysing requires that cement industry has to consider bone ash as alternative raw materials for partial replacement of limestone. At 1500°C, the f-CaO increases with P₂O₅ content, but at lower extent than at lower temperatures. The limit of f-CaO is reached with 1.46 wt.% P₂O₅ (see Table 3). Clinkering at 1500°C can enable to use more MBM, but it will require an additional energy and this can contract with economic effect.

The dependence of f-CaO content in the clinkers burnt at different temperatures with ash addition as raw material is depicted in the Figure 3. The standard limit of f-CaO required (2 wt.%) is reached at higher P₂O₅ content compared with the results reported in the Figure 2. Except for the temperature 1350°C that is much lower than the industrial burning temperatures, the P₂O₅ content in the clinker can be more than 1 wt.% at all temperatures. These results confirm the necessity to consider ash of bone as alternative raw material and then to compute its CaO content into the total CaO of the raw mixtures for the clinker preparation.

The comparison of free lime content in the 1st and 2nd series of samples burned at the same temperatures (Figures 4-7) shows that the free lime content is lower in the case of 2nd series at each temperature. It means that the CaO account balance in the raw mixture allow to burn a higher amount of meat bone meal in cement rotary kiln without negative influence to clinker properties. The highest difference in the values of free lime in both series of samples was found at burning temperature 1350°C. The lowest difference was found at temperature 1500°C. Higher content of calcium oxide can lower chemical resistance of cement and it can cause calcium hydroxide expansion. Therefore, the free lime content in the clinker over 2.5 wt.% is not accepted in cement practice [28]. The comparison of 1st and 2nd series of samples burned at 1450 °C shows that, in the first series the maximum content of P₂O₅ is 1.11 wt.% while the maximum P₂O₅ content in the 2nd series was found at 1.52 wt.%. Higher contents of P₂O₅ are inconvenient because of high content of free lime.

Burnability index calculation

The burnability index (BI) can be calculated with free lime contents in the samples burnt at 1350°C, 1400°C, 1450°C and 1500°C [29]. This parameter expresses the reactivity of individual raw meals. The value of burnability index is obtained from the formula:

$$BI = 3.75 \frac{(A + B + 2C + 3D)}{\sqrt[4]{A - D}} \quad (3)$$

where *A*, *B*, *C* and *D* are free lime contents in the clinkers burnt at 1350°C, 1400°C, 1450°C and 1500°C.

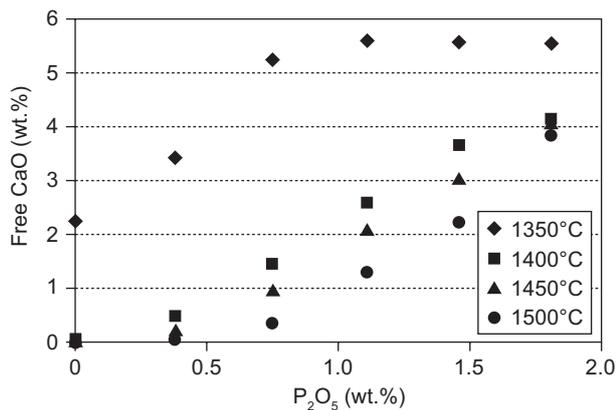


Figure 2. Influence of P₂O₅ upon the reactivity of cement raw meal at different burning temperatures - bone meal was added without consideration of CaO in bone ash.

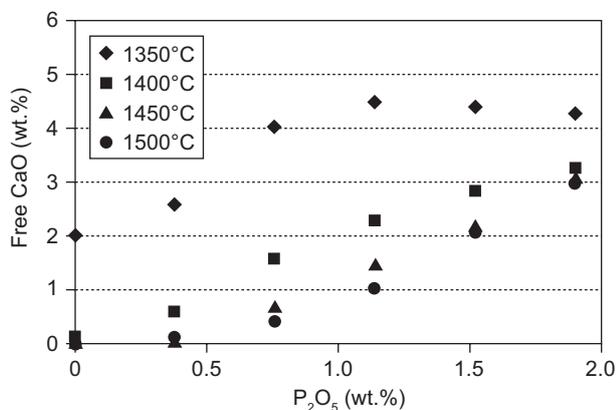


Figure 3. Influence of P₂O₅ upon the reactivity of cement raw meal at different burning temperatures - bone meal was considered as raw materials with consideration of CaO in bone ash.

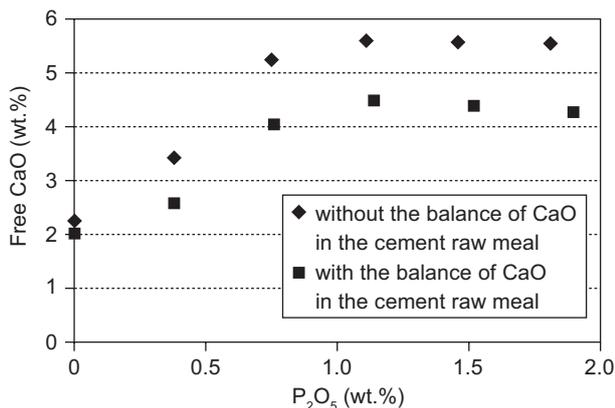


Figure 4. The comparison of free lime content dependences with addition of P₂O₅ in both series of samples at 1350 °C.

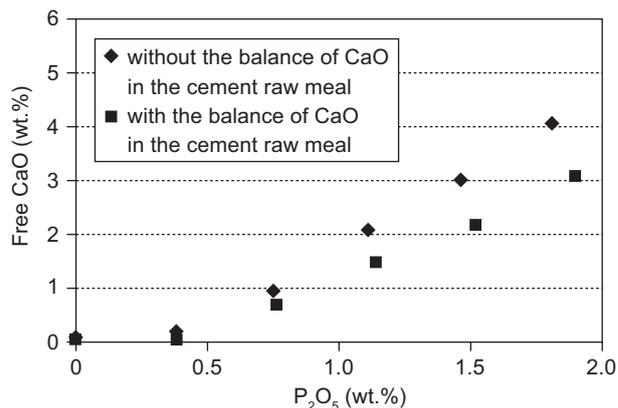


Figure 6. The comparison of free lime content dependences with addition of P₂O₅ in both series of samples at 1450 °C.

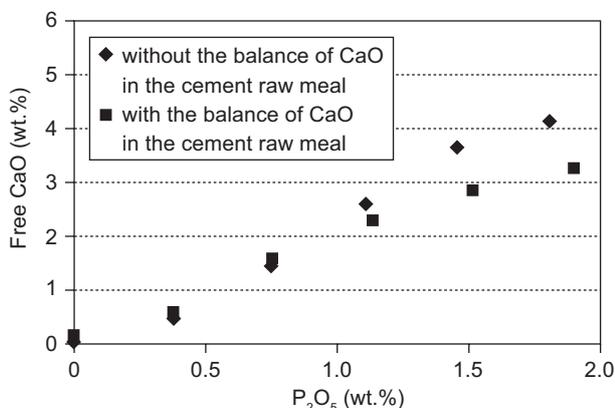


Figure 5. The comparison of free lime content dependences with addition of P₂O₅ in both series of samples at 1400 °C.

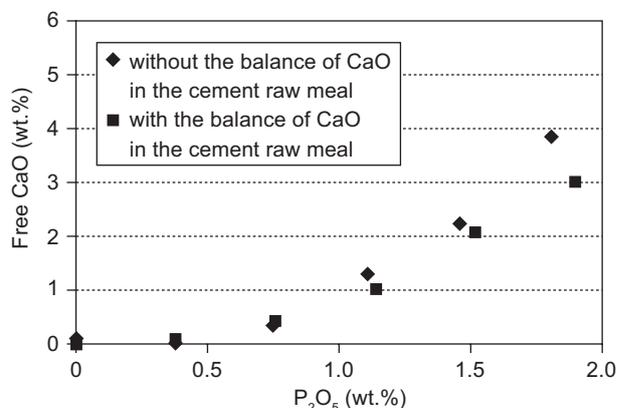


Figure 7. The comparison of free lime content dependences with addition of P₂O₅ in both series of samples at 1500 °C.

The Tables 5 and 6 show calculated values of burnability index according to formula (3) for individual series of samples. The low values of burnability index reveal good burnability. The samples with good burnability are with BI value lower and equal to 60.

The dependence of burnability index with P₂O₅ content for both series of samples shows that the border value of BI = 60 is reached by addition 1.42 wt.% P₂O₅ in the first series of samples (without CaO account balance in the raw mixture) while in the second series (with CaO account balance in the raw mixture) is reached by addition 1.61 wt.% P₂O₅. It means that although the increasing content of P₂O₅ negatively influences clinker burnability, the CaO account balance in the raw mixture partially inhibits this negative influence.

Chemical microanalysis results

The samples with different content of P₂O₅ from both series were analyzed with Electron Probe Micro Analyzer (EPMA JEOL JXA-840A, EDS parameters-

Table 5. The burnability index values in the first series of samples.

Ash of bone meal (wt.%)	P ₂ O ₅ (wt.%)	BI
0	0	7.92
0.99	0.38	12.35
1.96	0.75	24.38
2.91	1.11	42.30
3.85	1.46	60.65
4.76	1.81	96.28

Table 6. The burnability index values in the second series of samples.

Ash of bone meal (wt.%)	P ₂ O ₅ (wt.%)	BI
0	0	7.25
1	0.38	10.09
2	0.76	22.31
3	1.14	35.06
4	1.52	54.06
5	1.9	79.76

15KV, Takeoff Angle 40.0°) to detect P₂O₅ content in calcium silicates. The line analysis with detected oxide composition in each point in the line was done. Each sample was analyzed in five different areas with five lines in each one. The analysis of the sample with maximum content of P₂O₅ from the 1st series is shown in the Figure 9. The grains of calcium silicates were identified according to the SiO₂ content in analyzed points. The content of P₂O₅ in this area of the sample varies from 3.30 to 4.46 wt.% for C₂S and from 1.81 to 2.06 wt.% for C₃S.

The Figure 10 presents the microstructure of the sample with maximum content of P₂O₅ in the 2nd series. The P₂O₅ content in calcium silicates of this sample varies from 3.31 to 5.47 for C₂S and from 1.84 to 3.75 for C₃S. The free lime in this sample is presented by points 17 and 18 where the content of CaO reached the maximum. Higher Al₂O₃ and Fe₂O₃ content in the points located in the section between calcium silicates grains showed that C₃A and C₄AF form interstitial phase.

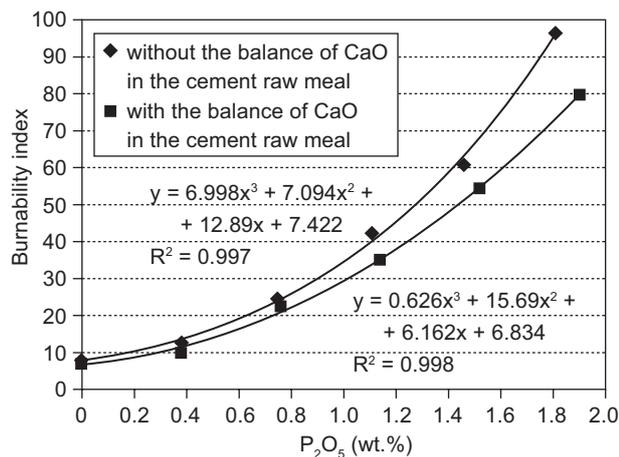


Figure 8. Changes of burnability index with variation of P₂O₅ content for both series of samples.

The intervals of P₂O₅ content in C₂S and C₃S for both series of samples are shown in the Figures 11 and 12. The P₂O₅ content in both phases increases with the content of P₂O₅ in the clinker.

The Figures 11 and 12 documented that P₂O₅ content in C₂S is higher than that in C₃S. The content of P₂O₅ in C₂S and C₃S in the 2nd series is higher than in the 1st series. This is due to the fact that CaO present in the calcium phosphate is bounded and less reactive than CaO from limestone decomposition. CaO from limestone reacts preferentially. Because of the decreased addition of limestone, CaO from calcium phosphate is required to react with SiO₂. This CaO and also P₂O₅ from calcium phosphate enters the reaction to form C₂S with more P₂O₅ in its structure.

The maximum level of P₂O₅ in both calcium silicates was also presented in the thesis of S. Punkte [30]. In his work, (NH₄)₂HPO₄ was used as the source of P₂O₅. In comparison to the results achieved in this paper the maximum level of P₂O₅ in both calcium silicates presented in the work [30] was lower than that displayed in the Figures 11 and 12.

CONCLUSION

The burnability of the clinker is negatively influenced by increasing amount of P₂O₅. The burnability index (BI) expresses the influence of P₂O₅ addition upon the reactivity of cement raw meal. The good burnability is reached when the value of BI is lower than 60. This border value (BI = 60) was reached at 1.42 wt.% P₂O₅ addition in the first series of samples while this limit reached 1.61 wt.% P₂O₅ in the second one. It follows that if the CaO content from the ash of bone meal will count in the total balance of CaO in the raw mixture, better burnability will be achieved. There through the negative influence of P₂O₅ upon the burnability of the clinker can

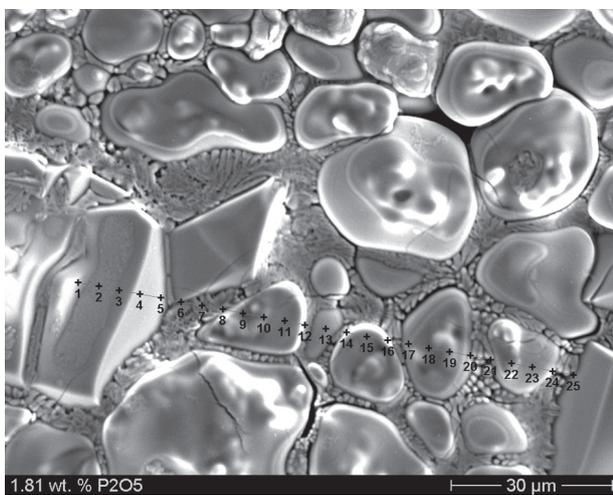


Figure 9. Microstructure of the sample with 1.81 wt.% P₂O₅ (1st series).

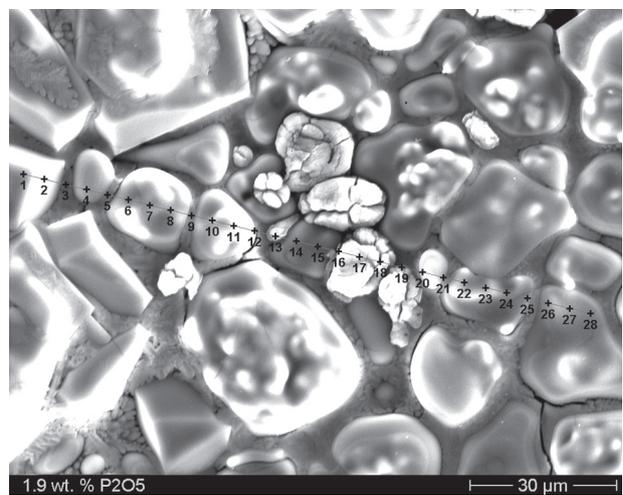


Figure 10. Microstructure of the sample with 1.90 wt.% P₂O₅ (2nd series).

Table 7. Oxide composition in the sample with 1.81 wt. % P₂O₅ (1st series).

Point	MgO (wt.%)	Al ₂ O ₃ (wt.%)	SiO ₂ (wt.%)	P ₂ O ₅ (wt.%)	CaO (wt.%)	Fe ₂ O ₃ (wt.%)	CaO/SiO ₂
1	1.0115	1.2634	24.8423	2.0080	70.8748	0.0091	2.85
2	1.9396	6.3495	18.2903	1.9538	66.4084	5.0584	3.63
3	0.8026	1.0974	23.8351	2.0596	72.2053	0.0093	3.03
4	0.7806	1.4562	23.8772	1.8122	70.7074	1.3664	2.96
5	1.1371	2.1209	23.7661	1.8691	71.1068	0.0091	2.99
6	2.9967	6.1203	16.6609	1.7768	68.6628	3.7824	4.12
7	2.9765	16.8401	4.2851	0.6115	60.9289	14.3580	14.22
8	2.9717	19.7880	7.0873	0.9219	57.6936	11.5374	8.14
9	0.5961	1.2910	26.7760	3.3011	68.0358	0.0105	2.54
10	0.0027	1.5971	29.0666	3.3027	64.1447	1.8889	2.21
11	0.0027	1.8533	27.5041	4.3790	66.2635	0.0099	2.41
12	2.5794	13.9776	13.0614	0.7806	55.3526	14.2483	4.24
13	0.7720	2.3185	27.9619	3.8804	63.3437	1.7236	2.27
14	1.4027	6.2313	19.9635	2.6197	62.5140	7.2688	3.13
15	0.0028	1.9644	28.0204	3.7633	66.2519	0.0102	2.36
16	1.1242	3.5652	26.6029	4.4242	61.5604	2.7230	2.31
17	0.0026	2.0527	28.0128	4.0031	65.9314	0.0106	2.35
18	0.0022	1.6261	25.2980	3.0426	68.6852	1.3481	2.72
19	0.5019	1.9340	27.4181	4.4603	64.6608	1.0249	2.36
20	2.0226	9.0396	19.2346	2.2541	58.9242	8.5249	3.06
21	1.0445	4.5180	18.7880	2.6125	68.0564	4.9807	3.62
22	0.7493	1.6260	28.5384	3.7619	65.3244	0.0108	2.29
23	1.0019	1.5762	28.4066	3.6863	63.7840	1.5450	2.25
24	1.0206	4.6767	21.8797	2.8618	65.6947	3.8665	3.00
25	0.0022	2.1512	15.3665	1.0864	81.3959	0.0113	5.30

Table 8. Oxide composition in the sample with 1.90 wt. % P₂O₅ (2nd series).

Point	MgO (wt.%)	Al ₂ O ₃ (wt.%)	SiO ₂ (wt.%)	P ₂ O ₅ (wt.%)	CaO (wt.%)	Fe ₂ O ₃ (wt.%)	CaO/SiO ₂
1	1.4418	1.5533	24.0031	2.0215	70.5424	0.4377	2.94
2	0.7690	1.8889	24.2283	1.8448	70.4947	0.7743	2.91
3	1.3144	8.3188	8.8607	0.6256	65.8354	15.0451	7.43
4	0.5832	2.2949	24.8890	3.7539	67.2851	1.1939	2.70
5	1.3256	8.2478	17.2930	2.5644	64.2277	6.3416	3.71
6	0.0014	1.4329	23.2421	3.4172	70.4354	1.4725	3.03
7	0.0015	2.1060	27.4101	4.1487	65.6096	0.7255	2.39
8	0.4881	2.1073	28.2191	4.8682	63.5878	0.7295	2.25
9	2.0070	10.1303	18.4363	2.0602	59.2326	8.1336	3.21
10	0.5530	2.2070	27.0738	3.3141	65.7099	1.1421	2.43
11	0.0017	2.3007	30.2455	3.5867	62.9609	0.9063	2.08
12	2.2147	10.0619	19.8325	2.3787	58.4852	7.0269	2.95
13	0.8213	3.6260	6.6204	0.4882	85.5545	2.8895	12.92
14	0.5535	1.2761	22.7928	3.2650	70.8460	1.2666	3.11
15	0.0014	1.5032	22.6936	3.5057	70.8277	1.4698	3.12
16	0.3543	1.8066	11.3730	1.9428	82.0047	2.5185	7.21
17	1.1840	0.7156	0.0017	0.0017	98.1004	0.0036	56880.75
18	1.6298	0.9823	0.7197	0.0017	95.7896	0.8785	133.10
19	1.5454	8.4478	4.1092	0.3943	75.6499	9.8533	18.41
20	0.5597	1.2238	10.6545	1.2588	82.0000	4.3032	7.70
21	1.1848	5.3703	18.3013	2.7470	67.8097	4.5869	3.71
22	0.5254	2.0909	26.7109	5.2672	63.8063	1.5993	2.39
23	0.4497	1.5958	26.6847	5.4693	64.7546	1.0459	2.43
24	0.0015	1.8837	25.3506	4.5180	66.8232	1.4245	2.64
25	0.4501	3.0572	24.0267	3.6780	66.4145	2.3736	2.76
26	0.8985	1.4473	25.5098	3.5679	67.5000	1.0764	2.65
27	0.0016	1.6955	28.8685	4.4074	63.8365	1.1921	2.21
28	0.6821	1.8492	27.4157	4.7208	64.2073	1.1249	2.34

be partially inhibit. The results from EPMA show that the formation of alite isn't totally blocked neither the maximum selected addition of P_2O_5 . Phosphorus enters calcium silicates (C_2S , C_3S), preferentially C_2S and its content is higher in the case of C_2S than in C_3S in analyzed samples. As the CaO from the bone meal ash was considered in the calculation of total CaO in the mixture, calcium silicates contained more P_2O_5 in the structure.

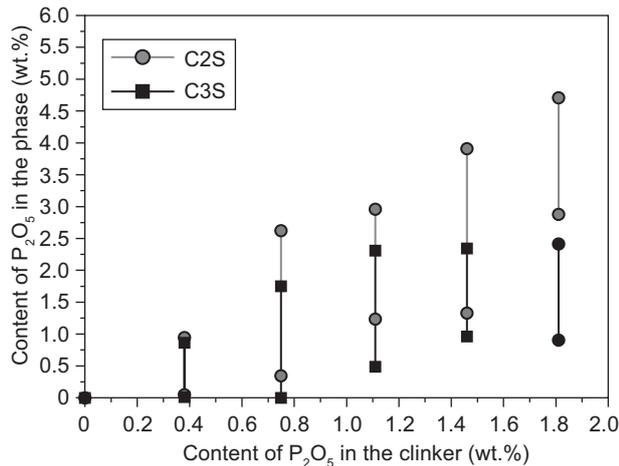


Figure 11. Content of P_2O_5 in C_2S and C_3S phase for the 1st series of samples.

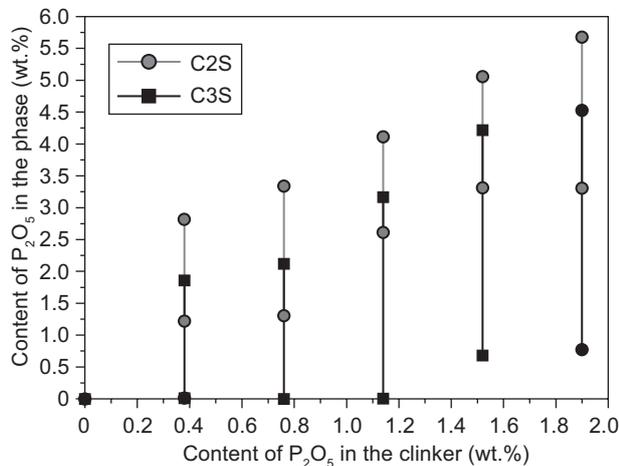


Figure 12. Content of P_2O_5 in C_2S and C_3S phase for the 2nd series of samples.

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