

Influence of Using Meat and Bone Meal as an Alternative Fuel on Formation and Properties of Portland Cement Clinker

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1 Introduction

The industrial process of heating at high temperature in rotary kilns, which is essential in cement manufacture, creates favorable conditions to use wastes as alternative fuels. Careful controls of plant operations, composition of the waste and emissions are necessary in order to ensure a good quality of the final product (cement). Therefore, only certain types of waste can be considered as fossil substitute. The materials frequently used for this purpose are the following: meat and bone meal (MBM), solvents, used oils, waste tyres, sewage sludge, plastics, etc [1-3].

P₂O₅ occurs both in primary raw materials (limestone and shale) as apatite in certain parts of the world [4,5] and in industrial by-products, which may be used as secondary raw materials (slags from the metal extractive industries). The partial replacement of fossil fuel with MBM used as alternative fuel represents the source for an additional amount of P₂O₅ present in clinker. As concerns phosphorus inorganic compounds present in these materials, they would combine mainly with the silicates formed during clinkering [6,7].

It has been shown that a high level of phosphorus inhibits the alite formation. Halicz et al. [8] obtained synthetic clinkers prepared from oil shale containing up to 5 % wt. P₂O₅ as a secondary component. Although C₃S contents decreased considerably when the P₂O₅ amount increased, satisfactory C₃S contents were achieved by taking into account in the silica modulus formula the P₂O₅ concentration. Gutt [6] showed that the limit of inclusion of phosphate ions in alite solid solution is about 1.1 % wt. P₂O₅. High amounts of phosphate led to preferential formation of phosphatic dicalcium silicate solid solution. Diouri et al. [9] studied the effect of combination of manganese and phosphorus elements on the formation of solid solutions, by heterovalent substitution of corresponding ions in C₃S lattice. They observed that M3 polymorph of alite is formed at Mn and P inclusions less than 0.69 wt. % Mn₂O₃ and 0.62 wt. % P₂O₅. At

higher amounts of these oxides, the alite phase is not formed and solid solutions of C_2S phase along with $2CaO.MnO_2$ and CaO are obtained.

The Fe_2O_3 and P_2O_5 additions to a molar ratio $CaO/SiO_2 = 2$ mixture induce a reduction of the onset decarbonation temperature and stabilize β , α' , and α_L forms for amounts less than 9.50 % wt. Fe_2O_3 and 8.45 % wt. P_2O_5 [10]. The hydraulic activity evaluated by heat evolution was reported to be higher for β -phase than for α'_L -phase in the case of dicalcium silicate doped with phosphorus [11]. This effect was attributed to twin boundaries that appear in β form that behave like active centers for the reaction with water. On the contrary, the crystal fragments of α'_L -phase were nearly uniform with occasional line defects. As a result, the hydration rate of the β -phase was, during the early stage of the process, much higher than that of the α'_L -phase, leading to the higher cumulative heat evolution of the former phase.

The aim of the present work was to study:

- the phases in which phosphate can occur in Portland clinker and the polymorphic forms stabilized by its presence,
- the distribution of phosphorus between these phases in clinker,
- the effect of phosphorus presence on the hydration behaviour of clinker.

2 Materials and methods

In our experiments, MBM was transformed into ash by calcinations at $1000^\circ C$ and mix with an industrial raw meal in different proportions as presented in Table 1. The obtained mixes were clinkered at $1450^\circ C$ for 30 minutes.

Table 1. Percentage of MBM ash addition

Sample	% wt./wt. of ash
A0	0
A1	0.07
A2	0.14
A3	0.28
A4	0.57
A5	0.88

Laboratory clinkers were milled and then analysed for the oxide composition and free lime content. Furthermore, the calcium silicate phases were separated by dissolving the interstitial material with an

aqueous solution of KOH and sucrose (KOSH) at 95°C [12]. The KOSH residuum was analysed for the P₂O₅ content.

Four selected clinkers, denominated A0, A2, A3 and A5, were embedded in a low viscosity epoxy resin. The samples were ground with SiC paper and then polished, followed by coating with carbon as electrically conducting layer. Scanning electron microscope (SEM), LEO1530, equipped with an energy dispersive X-ray (EDX) analyser was used for backscattered electron imaging (BEI) and for X-ray microanalysis.

The milled clinkers were hydrated at a w/c = 0.4 and cured for 1, 7 and 28 days. Hydration was followed by means of XRD and nonevaporable water content.

3 Results and discussion

3.1 Clinker

The free lime content in the clinker is an indicator of the degree of burning. Apart from the concentration of the MBM ash in the raw mixtures, all conditions for the burning were constant. Accordingly, an increase in free lime means a decrease in the burnability due to the presence of P₂O₅ in the raw mixture at a specified concentration. In Fig. 1, the P₂O₅ content in the raw mixtures is plotted against the analysed content of free lime in the clinkers.

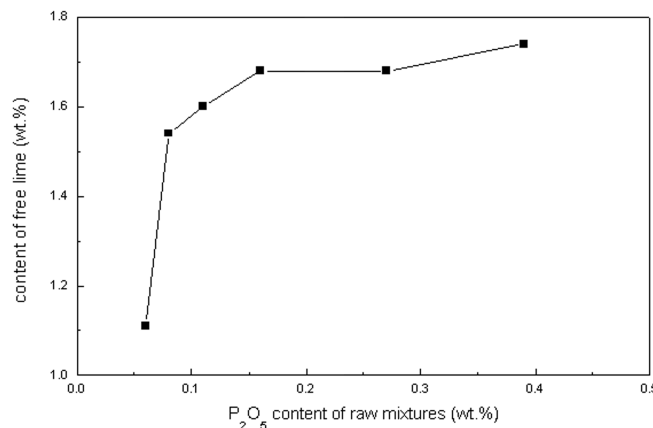


Fig. 1. Content of free lime in clinkers burned with MBM ash

The Portland clinker, obtained with MBM ash, shows a continuous increase of the free lime content depending on the amount of P_2O_5 present in the raw mixtures. An increase of free lime is observed starting from 0.06 up to a concentration of 0.16 % wt. P_2O_5 in the raw mixture. Between 0.16 and 0.39 % wt., the P_2O_5 addition to the raw meal has a smaller influence on the burnability.

The KOSH extraction separates mainly the silicate phases of clinker. The phase constitution of the obtained residue allows the differentiation between different polymorphic states of alite and belite crystals. The identified crystalline phases in the KOSH residue were semiquantitative estimated as can be observed in Table 2.

Table 2. Crystalline phases identified by X-ray diffraction in KOSH residue of clinker series A0-A5

Sample	C_3S	$\beta-C_2S$	$\alpha'-C_2S$	$\alpha-C_2S$	MgO
A0	+++	+	+	+	+
A1	+++	+	+	+	+
A2	+++	+	+	+	+
A3	+++	+	+	+	+
A4	+++	+	+	++	+
A5	+++	++	++	++	+

+++ = abundant; ++ = medium; + = little

The alite monoclinic polymorph was present in all clinker series. As can be observed in Table 2, the increasing amount of P_2O_5 in the raw mixtures leads to the stabilization of belite polymorphs in the following order $\beta \rightarrow \alpha' \rightarrow \alpha$. This result is in accordance with the reported effect of P_2O_5 [9,13].

According to the results of X-ray microanalysis, phosphorus is preferentially found in the silicate phases, especially in belite. In Fig. 2, the data for P_2O_5 concentrations in alite and belite are plotted against that in the clinker. The concentration in the belite is between two and three times higher than that in the alite. However, the total P_2O_5 content of the clinker is probably not the only factor that affects the concentration in the silicate phases.

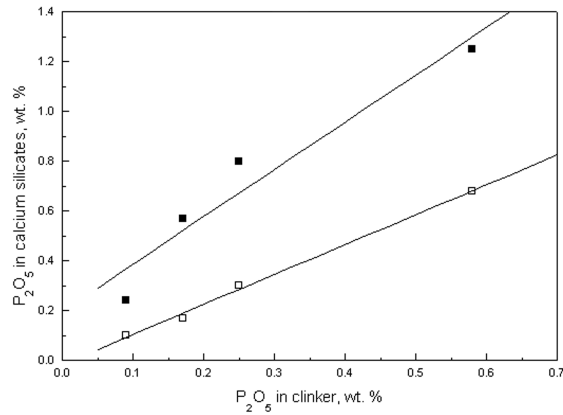


Fig. 2. Distribution of P₂O₅ between alite and belite.
Open squares, alite; filled squares, belite

The effect of defects introduced in crystalline structure by substitutions and solid solution plays a particular role on hydraulic activity [5, 11]. Substitution of P⁵⁺ for Si⁴⁺ in the tetrahedral sites, take place by the following mechanism $2\text{Si}^{4+} \leftrightarrow 2\text{P}^{5+} + \text{V}_{\text{Ca}}$ and the charge balance is achieved due to a Ca vacancy [9].

3.2 Clinker hydration

The hydration of the clinkers was observed by means of XRD for 1, 7 and 28 days. The XRD patterns indicated that hydration products were generated in different amounts depending on the MBM ash addition and hydration period. The differences observed were in the rate of disappearance of the silicate phases. The relative intensity of alite and belite peak at $2\theta=32.5^\circ$ was determined to provide a general view regarding silicate phase consuming during hydration process. The selected peak of silicates is not completely free for any interference with the calcium silicate hydrates peaks especially. The peaks of Ca(OH)₂ were not suitable to follow the hydration progress because of the preferred orientation of its hexagonal plates. Fig. 3 summarizes the results.

As can be observed in Fig. 3, within the measuring accuracy of this procedure, an abrupt decrease of alite and belite relative intensity is observed after 7 days of hydration, suggesting a higher reactivity of these phases. In addition, sample A5 at 28 days hydration presents peaks of C₃S and C₂S diminished respect to the ones of A0 under the same conditions.

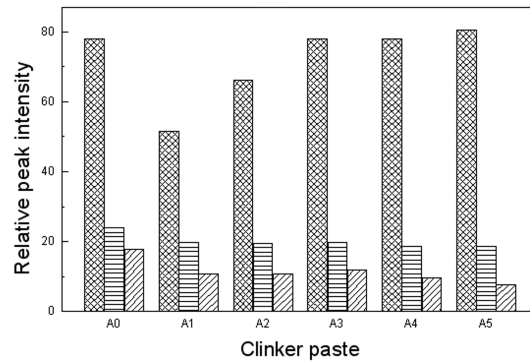


Figure 3. Relationship of the XRD peaks of calcium silicates for 1, 7 and 28 days of hydration
 1 day – cross hatching, 7 days – horizontally hatching, 28 days – diagonally hatching

The calculation of the degree of hydration (α) was made taking into account the amount of nonevaporable water, according to the following equation:

$$a = \frac{w_{nonev.w.}}{w_{max.nonev.w.}} \quad (1)$$

All weights in Eq. 1 are relative to the ignited clinker weight, g/g ignited clinker. $w_{nonev.w.}$ is the weight of nonevaporable water and $w_{max.nonev.w.}$ is the amount of nonevaporable water at complete hydration [14], when $\alpha=1$.

The values of degree of hydration presented in Table 3 represent the clinker fraction that has reacted after a specified time interval and are also indicators of the progress of hydration.

Table 3. Degrees of hydration (%) of clinkers for different curing times

Clinker	Curing time		
	1 day	7 days	28 days
A0	28,9	54,5	64,1
A1	31,0	58,2	66,9
A2	30,3	58,4	66,7
A3	29,6	58,5	65,8
A4	29,5	57,4	67,7
A5	27,5	57,2	69,4

As can be observed in Table 3, an increasing of the curing time from 7 to 28 days leads to an increasing of the degree of hydration with only 10%. Taking the A0 sample as comparative reference, for the A5 sample, it was observed an increase of the degree of hydration with 5% at 28 days. Because added clinker series showed almost the same particle size distribution, a high reactivity with water, is most probably due to introduction of defects with substitutions and solid solutions.

4 Conclusions

From the investigations carried out it may be concluded that:

- Introduction of phosphorus in the clinkering process resulted in higher free lime content, up to 2 % wt.
- The α belite phase was stabilized and no changes in alite polymorphism were observed with increasing P_2O_5 content
- The presence of P_2O_5 in alite and belite affects the hydration behaviour favourably, with higher degrees of hydration being observed with increasing amount of P_2O_5 .

References

- [1] H. Daldrup, B. Scheubel, Alternative fuels and their impact on refractory linings, *World Cement* 27 (3) (1996) 94-98
- [2] M. Trezza, A. Scian, Waste fuels: their effect on Portland cement clinker, *Cem Concr Res* 35 (3) (2005) 438-444
- [3] U. Kääntee, R. Zevenhoven, R. Backman, M. Hupa, Cement manufacturing using alternative fuels and the advantages of process modeling, *Fuel Processing Technology* 85 (2004) 293-301
- [4] R. Bucchi, Features on the role of minor compounds in cement clinker – Part I, *World Cement Technology*, 12 (6) (1981) 210-231
- [5] G. K. Moir, F. P. Glasser, Mineralisers, modifiers and activators in the clinkering process. Proc. 9th ICCI, New Delhi 1992, I, 125-152
- [6] W. Gutt, Manufacture of Portland cement from phosphate raw materials, Proc. 5th ICCI, Tokyo 1968, I, 93-105
- [7] R. W. Nurse, The effect of phosphate on the constitution and hardening of Portland cement, *J. Applied Chemistry* 2 (4) (1952) 708-716
- [8] L. Halicz, Y. Nathan, The influence of P_2O_5 on clinker reactions, *Cem Concr Res* 14 (1) (1984) 11-18
- [9] A. Diouri, A. Boukhari, Stable Ca_3SiO_5 solid solution containing manganese and phosphorus, *Cem Concr Res* 27 (8) (1997) 1203-1212

- [10] My. Y. Benarchid, A. Diouri, A. Boukhari, J. Aride, J. Rogez, R. Castanet, Elaboration and thermal study of iron-phosphorus-substituted dicalcium silicate phase, *Cem Concr Res* 34 (10) (2004) 1873-1879
- [11] K. Fukuda, H. Taguchi, Hydration of α'_L - and β -dicalcium silicates with identical concentration of phosphorus oxide, *Cem Concr Res* 29 (4) (1999) 503-506
- [12] W. A. Gutteridge, On the dissolution of the interstitial phases in Portland cement, *Cem Concr Res* 9 (5) (1979) 319-324
- [13] B. Matkovic, Dicalcium silicates doped with phosphates, Proc. 8th ICCG, Rio de Janeiro 1986, II, 276-281
- [14] O. M. Jensen, et al. Clinker mineral hydration at reduced relative humidities, *Cem Concr Res* 29 (9) (1999) 1505-1512