Mechanism and kinetics of binding of meat and bone meal ash into the Portland cement clinker

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Abstract

Meat and bone meal (MBM) is the alternative fuel with good calorific value used in cement production. The main problem with MBM combustion in a cement kiln is the high content of P_2O_5 , which incorporates in clinker phases, influencing phase composition of clinker and hence the quality of the cement. In cement industry, only limited amount of MBM is burned to prevent adverse effect. P_2O_5 has a significantly negative effect on the formation of the main clinker phase alite and it stabilizes belite by means of entering its structure. At 4.5 wt% P_2O_5 in the clinker, the alite formation is completely blocked. Research on kinetics of reactions between clinker and MBM proved reduction of negative reactions and minimization of migration of P_2O_5 into the clinker minerals using undispersed P_2O_5 carrier. The carrier in pellet form eliminates the negative effect of P_2O_5 on the formation of the alite. The research was conducted by means of XRD, optical and electron microscopy. Electron microanalysis showed that P_2O_5 migrated inside the clinker to a distance of less than 250 μm from the ash and clinker interface. Clinker was not influence outside this area. It is possible to prepare high quality cement from the clinker containing ash residues from MBM in an amount corresponding to up to 10 wt% P_2O_5 . The work was completed with preparation of cement with 7 wt% of P_2O_5 , which exhibited good technological properties. In addition, these cements significantly reduce the leachability of toxic elements.

Keywords Portland cement clinker · Meat and bone meal · Phosphorous pentoxide · Cement

1 Introduction

Meat and bone meal (MBM) is one of the alternative fuels used in cement production. It has good calorific value (16–20 GJ / t) and at the same time, a biodegradation occurs there as well as possible disposal of harmful substances at high temperatures in the cement kiln. In particular, the destruction of dead animals infected with various diseases, including the highly dangerous BSE (bovine spongiform encephalopathy), appears to be useful and effective [1, 2].

MBM is dosed in the cement kiln dispersed in a flow of air or fuel and its particles spontaneously burn. The

combustion residues, consisting of calcium phosphate (mainly hydroxylapatite— $Ca_5(PO_4)_3(OH)$) then react with clinker in its whole volume. P_2O_5 influences clinker melt properties [3], enters into the structure of clinker phases [4] and influences the phase composition of clinker [5–8] and thus the quality of the cement [7, 9].

In practice, the cement works combust only such amounts of MBM that negatively influence the clinker properties only to a small extent, i.e. only up to a safe maximum amount of 0.5, rarely up to 1 wt% P_2O_5 in clinker.

It was experimentally proven that P_2O_5 has negative effect on the nucleation of alite crystals, stabilizing C_2S . α - C_2S forms a continuous solid solution with C_3P above

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1,450 °C [10] with a miscibility gap at 1500 °C [11]. Negative effect of increased belite and free lime content at the expense of alite was observed from 0.7 wt% of P₂O₅. With the increasing content of P₂O₅, CaO does not completely react with belite to form alite even after 4 h burning at 1450 °C, which can be considered as equilibrium burning. Alite formation is completely blocked at 4.5 wt% of P₂O₅ in the clinker [8].

This paper explains the reaction kinetics of phenomenon at the clinker/MBM ash interface and suggests the possibility of multiply increase of the amount of co-incinerated MBM compared to the normal state. During that, clinker with residues of MBM ash are formed without a significant direct negative effect of P₂O₅ on the formation of the main clinker phase alite and from it prepared cement shows high-quality technological parameters.

2 Experimental

2.1 Materials

Raw meal from common cement raw materials was prepared for experimental work. The composition of the raw meal, its chemical composition and result of sieve analysis are shown in Tables 1 and 2. The phase composition of the equilibrium burned clinker from this raw meal (until CaO has completely reacted) determined by microscopy point-counting method (see Chap. 2.2) is shown in Table 3.

MBM ash was prepared by burning at 750 °C for 4 h. Chemical composition of this ash is shown in Table 4.

2.2 Methods

Reactions of ash particles in cement raw meal were simulated by two ways:

1. Sandwiches—compressed tablets 40 mm in diameter consisted of the layer of finished clinker or raw meal for clinker burning and the layer of MBM ash.
2. Tablets—tablets of different diameters pressed from MBM ash were homogenized with raw meal and larger tablets 40 mm in diameter were pressed from this mixture.

In the first part of the experiment, sandwiches with layer of ground clinker and layer of ground ash from MBM were prepared. Phase composition of ground clinker is shown in Table 3 and chemical composition of MBM ash is shown in Table 4. Sandwiches were burned at 1,450 °C, they were incoherenced and the layers were separated after burning.

Table 1 Composition and basic chemical parameters of experimental raw meal

Sign	Content of component in wt%			Basic chemical parameters		
RM-99	Limestone	Sand	Clay shale	LSF	SR	AR
	75.46	3.51	20.06	99	2.5	1.6

where: $LSF = \frac{100 \times CaO}{2.8 \times SiO_2 + 1.18 \times Al_2O_3 + 0.65 \times Fe_2O_3}$, $SR = \frac{SiO_2}{Al_2O_3 + Fe_2O_3}$, $AR = \frac{Al_2O_3}{Fe_2O_3}$

LSF, lime saturation factor

SR, silica ratio

AR, alumina ratio

Table 2 Granulometric analysis of raw meal RM-99

Sign	Rest in wt% on sieves with openings in mm				
RM-99	0.045	0.063	0.090	0.125	0.200
	27.2	18.1	8.4	2.9	0.3

Table 3 Phase composition of equilibrium burned clinker from raw meal RM-99 in wt%

Sign	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
C-99	71.0	13.7	10.0	5.7

Table 4 Chemical composition of MBM ash

Component	Content in wt%
SiO ₂	1.77
TiO ₂	< 0.01
Al ₂ O ₃	0.48
Fe ₂ O ₃	0.67
P ₂ O ₅	37.02
MnO	0.022
MgO	1.49
CaO	47.11
Na ₂ O	4.18
K ₂ O	2.63
SO ₃	0.56
Cl-	2.60
LOI	7.11
Ash content	21.25

Therefore, in the next part of the experiment, the tablets consisted of MBM ash with diameter of 20 mm were pressed and homogenized with ground clinker C-99 and then pressed to the form of larger tablet 40 mm in diameter. Burning were done at programmable super kanthal furnace at 1450 °C for 1, 2 and 4 h. Other samples were prepared by the same way—tablet of MBM ash in tablet from raw meal RM-99. Burning were done at 1,450 °C for 0, 30, 60 and 90 min. Incoherence of the tablet was noticeable after burning and pulling of the samples from the furnace and the inner tablet, which was initially formed from MBM ash fell out from the finally clinker tablet.

After that, pellets from MBM ash, 5 mm in diameter were prepared on pelletizing plate. These pellets were mixed with the raw meal RM-99 and tablets of 40 mm in diameter were pressed from this mixture. Estimated content of P₂O₅ in clinker was 5 wt% (91 wt% RM + 9 wt% MBM ash). The burning of large amount of clinker for cement preparation was carried out at 1450 °C with an isothermal dwell for 2 h. Sample identification—C-5P-T.

Subsequently, experimental burnings with raw MBM were performed. Firstly, solid pellets from MBM in the small pelletizing machine MGL 200 were made (see Fig. 1).

Fig. 1 Preparation of pellets from MBM in the granulator line MGL 200

These pellets were mixed with the raw meal RM-99 and the mixture was burned to clinker. The ratio between RM and MBM contents was chosen, that the total content of P₂O₅ was similar to the previous case. The burning of larger amount of clinker for cement preparation was carried out in the same way at 1450 °C with isothermal dwell for 2 h. Sample identification—C-5P-MBM.

Phase composition of experimental clinker samples was analyzed by optical microscopy and X-ray diffraction.

Burned clinkers were crushed below 1 mm. Polished sections were prepared from the 0.045–1 mm size fraction. Quantitative phase composition of prepared clinkers was determined by point-counting method in polished sections [12]. For perfect differentiation of individual phases, the surface of polished section was etched in vapor of acetic acid [13]. Quantitative phase composition is expressed in vol. % and for calculation of wt% the following densities of clinker minerals were used: C₃S—3.15; C₂S—3.28; C₃A—3.03; C₄AF—3.77; free CaO—3.35 and C₃P alkali—3.07 g cm⁻³.

Qualitative determination of phases in clinker was analysed by powder X-ray diffraction of the clinkers with a Bruker D8 Advance diffractometer with variable slits and a position sensitive detector. The diffractometer was operated at 40 kV and 30 mA, using Ni-filtered CuKα of λ = 1,541,718 Å, recording 6–80° in 0.02° 2θ increments with 188 s counting time per step and total scan time of 1 h 5 m 59 s.

Electron microprobe CAMECA SX100 was used for the analysis of clinker phases and concentration changes of selected elements on the clinker – MBM ash interface. The analytical conditions were: accelerating voltage 15 kV, beam current 20 nA and spot size 2 μm. The standards used for internal calibration were natural

standards—wollastonite (Ca, Si), barite (S), orthoclase (K, Al), andradite (Fe), jadeite (Na), rhodonite (Mn), pyrope (Mg), hydroxylapatite (P), and synthetic TiO (Ti); all elements were analyzed on their K α lines. The lower limits of detection varied between ~0.01 wt% (e.g. for P, S, Si, Al, Ca) and ~0.02 wt% (e.g. Ca, K, Mn, Fe). The acquired counts, corrected for background, were recalculated to oxides using the PAP correction procedure included in the CAMECA PeakSight automation program. The EMPA results in wt% oxides were recast into composition formulae in atoms per formula unit (apfu).

Specific weight of cements was determined by the pycnometer method and specific surface by the Lee-Nurse permeability method according to the British standard B. S. 12:1958. Clinkers with the addition of gypsum were ground to approximately same surface area in a laboratory ball mill.

According to the standard EN 196–1, mortar prisms were prepared from the cements and the development of compressive strength was tested after 2, 7, 28 and 90 days of hydration. Normal consistency, soundness, start and time of the setting were determined according to EN 196–3. Hydration heat of cements after 7 days of hydration was determined by dissolution method according to EN 196–8.

Fly ash containing elevated levels of toxic elements was used to monitoring the immobilization of toxic elements. Fly ash was mixed in 1: 1 ratio with cement C-5P-MBM and as well as the reference cement CEM I 52.5 N. The test prisms prepared from these mortars were after demolding placed in humid environment (temperature 20 °C, relative humidity 90%). After 28 days of hydration the test bodies were ground to 1–10 mm and this material was leached according to EN 12,457–4. The decanted leachates were filtered through a 0.45 μ m pore filter. The leachates were analyzed by ICP-MS (Agilent).

3 Results and discussion

3.1 Sandwich experiments

Sandwich experiments revealed, that most of the MBM ash layer is separated from the clinker layer. A thin reaction rim composed of belite grains is formed in place, where the two layers remain connected (see Fig. 2). The width of the reaction rim and the belite grains increase with the burning time (see Table 5).

Sandwich interfaces were studied by electron microanalysis. The results showed that diffusion in the solid state occurred only in the immediate vicinity of its own interface, more precisely to a distance of about 500 μ m from it. Diffusion occurred in both directions, as evidenced, for

Fig. 2 Microstructure of the sandwich cross Sect. (1,450 °C, 2 h), from left to right – layer of clinker formed by blue crystals of alite and brown grains of belite, brown grains of belitic reaction rim (in the middle), light gray right part is formed by burned MBM ash (reflected light, etched by acetic acid vapor)

Table 5 Approximate width of reaction belitic rim and average size of belitic grains in rim

Burning time [h]	1	2	4
Width of layer [μ m]	75	110	140
Size of belite grains [μ m]	20	40	50

example, by increased concentrations of Al₂O₃ and alkalis, typical for the phosphate zone in the clinker zone at the interface. In substance, only Si is diffused from the clinker layer into the layer formed by the melting and recrystallization of the MBM ash.

The joint occurrence of some oxides (Al₂O₃, K₂O, Na₂O) is evidenced by the very similar concentration curves of these oxides. The depth of the zone, where the main phases of the two parts of the sandwich were influenced is 300–500 μ m. Point analysis in the immediate vicinity of the interface are analysis of the solid solution C₂S–C₃P, at a distance of > 200 μ m from the interface, the second phase fraction already decreases below 5%. The concentration profiles at the clinker-MBM ash interface are shown in Figs. 3 and 4.

As follows from the concentration profiles of Si and P (Fig. 3), the diffusion of Si towards the ash layer from the MBM is much more significant than the diffusion of P towards the clinker, where the concentration decreases to zero already at a distance of less than 250 μ m. The diffusion of Si into the MBM ash layer is most significant to a depth of about 350 μ m, gradually decreasing from this distance, while at a distance of 1.25 mm, about 10% of the atoms of P are replaced by atoms of Si.

Fig. 3 Concentration profiles of Si and P through clinker (left) / MBM ash (right) interface, burning at 1,450 °C, 2 h (a.p.f.u.—atoms per formula unit)

Fig. 4 Concentration profiles of Al, K, Na and Mg through clinker (left) / MBM ash (right) interface, burning at 1,450 °C, 2 h (a.p.f.u.—atoms per formula unit)

Correlation coefficients were calculated from the values of individual cations from C_2S-C_3P analysis. It follows that there is a very strong correlation between phosphorus and sodium ($r=0.983$), the positive correlation between K and P is also significant ($r=0.763$), beside between P and C is significantly negative correlation ($r=-0.988$, and -0.827 , respectively).

3.2 Experiments with tablets

The newly formed clinker with residues after MBM ash tablets was analyzed by X-ray diffraction and electron microprobe to determinates qualitative phase composition. It was found that the residues are not formed by apatite, but by alkaline calcium phosphate, which with its diffraction spectrum is closest to mineral nagelschmidtite ($Ca_3(PO_4)_2 \cdot 2(\alpha-Ca_2SiO_4)$). Apatite is represented here only in a small amount and belite in the orthorhombic modification α' doped with P_2O_5 occurs here.

Microstructure of the newly formed clinker with tablets of burned MBM ash interface is shown in Fig. 5. There is not a clearly visible reaction rim as in the case of a sandwich prepared from a clinker (see Fig. 2).

The electron microanalysis of phosphate residues revealed that they are formed by the oval grains of $Ca \pm Na$, K phosphate with a small proportion of Si, which are bounded by a boundary material, which has a composition corresponding to ferrite, rarely aluminate. It has been found that the composition of the predominant phase of these residues is very variable, both in the cationic and in the anionic part. K_2O (1.7–12.6%), Na_2O (1.1–6.0%), CaO (39–60%), P_2O_5 (10.6–32.0%) and SiO_2 (1.3–16.4%) have the largest variance. Statistical analysis of ratios (Na + K):

Ca and P: Si showed that there is a relatively strong positive correlation between them ($r=0.73$). It means, alkali is bound to the phosphate component in silicophosphates, not to the silicate. According to X-ray diffraction analysis, these phases correspond by the structure closest to nagelschmidtite $Ca_3(PO_4)_2 \cdot 2(\alpha-Ca_2SiO_4)$, which is a mineral formed in nature by high temperature (contact) metamorphosis of phosphorus-rich sediments and has also been described from slags. The amount of alkali, especially potassium, is too high to be neglected by comparing to the theoretical composition of nagelschmidtite, and the fact that the stoichiometric ratio of P: Si is 1: 1 in the theoretical formula of nagelschmidtite found in only 4 of 27 analysis. Thus, it will be rather one of the phosphates described in [14], in which, at position A of compounds of the A_2XO_4 type, Ca and Na occur. For example, $Ca_5Na_2(PO_4)_4$ with a structure close to nagelschmidtite was synthesized by these authors, but they also mention the existence of a much wider range of Ca: Na—from $Ca_{4.8}Na_{2.4}(PO_4)_4$ to $Ca_{5.2}Na_{1.6}(PO_4)_4$. Due to the approximation of the ionic radii of sodium and potassium, the existence of phases in which potassium, together with calcium, would also emerge is certainly not excluded.

The analyses show that the Na_2O content varies between 3.0 and 10.4% in the phases that are darker in the backscattered electrons, the K_2O content varies between 1.5 and 4.3%. After conversion to atomic quotients, (Na + K) / Ca ratio ranges from 0.1 to 0.5, most often about 0.17, which would correspond to the empirical formula $Ca_6(Na, K)[(PO_4)_{3.5}]$. In the lighter phases, the alkali contents are low and correspond to carbonate hydroxyapatite. Si content is low in both phase types, silicophosphate is rarely found with them.

Analyses of alite and belite in clinkers with residues of MBM ashes show very low average contents of P_2O_5 (about 0.1% in alite, 0.3–0.6% in belite) in contrast with belite in clinkers with finely dispersed P_2O_5 carrier, where content of P_2O_5 is normally higher than 6.0% with a total content of 4.5 wt% P_2O_5 in clinker [8].

Fig. 5 Microstructure on the MBM ash / clinker interface in clinker C-5P-T (1450 °C, 2 h), bright blue drops near interface in burned MBM ash are grains of C_{free} (reflected light, etched by acetic acid vapor)

3.3 Cement preparation and their parameters

Quantitative phase composition of clinker burned using MBM ash pellets and raw MBM determined by microscopy is shown in Tables 6 and 7. Chemical composition of both clinkers is presented in Table 8.

The results in Tables 6 and 7 showed that P_2O_5 , which is released from ash inclusions, partially affects the phase composition of the surrounding clinker (see difference in columns 2 and 3 in the tables). However, with a content of about 6.5 (resp. 7) wt% P_2O_5 in clinker is its influence acceptable.

Table 6 Quantitative phase composition of clinker C-5P-T in wt%

Phase	C-5P-T	C-5P-T ^a	C-99 ^x
C ₃ S	53.2	64.1	71.6
C ₂ S	13.3	15.9	10.8
C ₃ A	5.8	6.9	12.4
C ₄ AF	10.3	12.4	4.4
C _{free}	0.5	0.7	0.8
C _{free} II	0.2	–	–
M _{free} II	0.1	–	–
C ₃ P alk	16.6	–	–

where C_{free} II—free CaO from MBM ash

M_{free} II—free periclase from MBM ash

^aphase composition of clinker without phases from MBM ash

C-99^x—clinker burned at the same conditions from reference meal RM-99

Table 7 Quantitative phase composition of clinker C-5P-MBM in wt% (explanations see Table 6)

Phase	C-5P-MBM	C-5P-MBM*	C-99 ^x
C ₃ S	55.0	67.1	71.6
C ₂ S	10.7	13.1	10.8
C ₃ A	7.9	9.7	12.4
C ₄ AF	6.8	8.2	4.4
C _{free}	1.6	1.9	0.8
C _{free} II	0.4	–	–
M _{free} II	0.2	–	–
C ₃ P alk	17.4	–	–

Table 8 Chemical composition of clinkers C-5P-T and C-5P-MBM in wt%

Phase	C-5P-T	C-5P-MBM
SiO ₂	19.45	18.13
TiO ₂	0.24	0.26
Al ₂ O ₃	4.22	4.40
Fe ₂ O ₃	3.06	2.93
P ₂ O ₅	6.45	7.09
MnO	0.064	0.076
MgO	1.05	1.28
CaO	63.42	63.38
Na ₂ O	0.75	0.90
K ₂ O	0.79	0.59
SO ₃	0.08	0.35
LOI	0.34	0.41
Total	99.91	99.80

The basic characteristics of cements prepared from clinkers whose phase composition is shown in Tables 6 and 7 are shown in Table 9. Cements prepared from clinkers with residues of MBM ash with the same content

Table 9 Specific weight [kg/m³] and specific surface [m²/kg] of prepared cements

Parameter	CEM-5P-T	CEM-5P-MBM	CEM-99
Specific weight	3122	3127	3132
Specific surface	358	354	366

Table 10 Compressive strength [MPa] of prepared cements according to EN 196–1

Cement	2 days	7 days	28 days	90 days
CEM-5P-T	18.4	39.0	57.9	63.3
CEM-5P-MBM	21.7	37.6	60.5	65.0
CEM-99	20.0	50.4	67.4	69.3

Table 11 Determination of setting development, normal consistency and soundness according to EN 196–1

Cement	Normal consistency [%]	Start of setting [h: min]	Setting time [h: min]	Soundness [mm]
CEM-5P-T	25.3	2:20	3:30	0.7
CEM-5P-MBM	27.0	5:20	6:10	1.7
CEM-99	26.0	5:00	5:50	0.3

Table 12 Hydration heat of cement after 7 days of hydration according to EN 196–8

Cement	Hydration heat [kJ/kg]
CEM-5P-T	292
CEM-5P-MBM	337
CEM-99	368

of solidification regulator and with approximately the same specific surface have high-quality technological properties. The results are compared with the reference cement (CEM-99) and shown in Tables 10, 11, 12. The results show that the clinker parameters with MBM ash residues are of high quality and comparable to the reference cement.

During the research of hydration and durability of P-enriched cements was found a very important property of these cements. It is their ability to increase the immobilization of toxic elements. This phenomenon was observed both with cements containing MBM ash residues, and with cements with phosphorus incorporated in clinker silicates. The leachability of hazardous elements added to the mortars from these cements has substantially decreased both in elements forming cations and in anions-forming hazardous elements [15].

Table 13 Comparison of leachabilities of hazardous elements

Element	Element content in eluate [μg/l]		Leachability of mortar from cement with 7% P ₂ O ₅ compared to the leachability of mortar made of CEM I 52.5 N [%]
	CEM I 52.5 N	CEM-5P-MBM	
As	7.59	0.97	13
Cr	262.8	97.2	37
Cu	1.27	0.37	29
Pb	3400	350	10
Zn	650	210	32
Mn	261.5	9.1	3
Sb	1.30	0.28	22
V	1.50	0.51	34

Table 13 demonstrates an example of the immobilization ability of the cement C-5P-MBM from clinker containing 7 wt% P₂O₅ in form of residues from MBM ash.

Analogues of apatite, in which a part of calcium or phosphate ions has been replaced by other ions are over the range of pH these phases can encounter in materials based on Portland cement or in their immediate vicinity in outdoor applications (pH 6–12), are insoluble. It was evidenced that in aqueous environment (e.g. in soil solution) occurs in the presence of apatite ion exchange, by which cations of metals like Pb, Zn, Co or Cd substitute Ca²⁺ ions in the structure of apatite [16, 17]. Similar exchange is known to happen with the phosphate anion, which can be replaced by arsenate, selenate, chromate or vanadate ions [18–20].

4 Conclusions

From the results it is clear that the reaction between the ash particles from the MBM and the surrounding clinker (or raw meal for clinker burning) is slow and does not have a significant impact on the phase composition as in the case of the scattered P₂O₅ carrier.

During the reaction, narrow belitic rim is formed at the interface of clinker-ash on the clinker side. In this rim, belitic grains increase due to recrystallization. When using raw meal, this belitic line is not so clearly formed and also alite crystals occur there. A higher concentration of CaO close to the interface of both components is noticeable.

Also, electron microanalysis showed a slight reaction and migration of elements at the interface of MBM ash and clinker. It was found that the Si diffusion into the layer of MBM ash is much more significant than the phosphorus diffusion into the clinker, where its content is almost zero already at a distance of less than 250 μm.

By analyzing the ash residues in the clinker, it was found that the mineral produced by burning is rentgenographically the closest to nagelschmidite

(Ca₃(PO₄)₂·2(α-Ca₂SiO₄)). However, electron microanalysis has shown that the mineral has a variable composition, especially a low SiO₂ and a high alkali content. It is therefore rather an alkaline calcium phosphate with a structure close to nagelschmidite.

Because the migration of P₂O₅ to clinker is negligible, its entry into clinker silicates is also negligible. Thus, there is only a slight manifestation of the negative effect of P₂O₅ on clinker formation, i.e. decreasing the alite content and the increase of belite content. With total analytically determined content of 6.5–7 wt% P₂O₅ in the clinker decreased the alite content by only 6–10 wt%. In the case of using the scattered P₂O₅ carrier in the clinker already at 4.5 wt% P₂O₅ completely blocks alite formation and produces a purely belitic clinker with a high free CaO content that does not enter into reaction.

These conclusions revealed the possibility of a significant multiple increase of the co-incinerated MBM in the cement rotary kiln compared to the current state. In practice, the MBM must be firstly modified by compacting, for example, by the pelletizing or granulating method or biomass fuel production machines. So produced compacted pellets can be dosed either directly into the raw meal, or into any part of the rotary kiln, possibly also into the main burner. MBM pellets will gradually burn out, utilizing their energy potential for clinker burning, and the resulting ash residues remain in the form of inert alkaline calcium phosphate residues in clinker granules.

Cements prepared from clinkers with MBM ash residues showed good technological parameters. In addition, the apatite structure contained in these cements causes immobilization of a variety of toxic elements.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

- Scheuer A (2003) Verwertung von Sekundärstoffen in der Zementindustrie. *Cem Int* 1:48–66
- Conesa JA, Fullana A, Font R (2003) Thermal decomposition of meat and bone meal. *J Anal Appl Pyrolysis* 70:619–630
- Timašev VV, Osokin AP (1982) Physico-chemical bases of the structure formation and properties of clinker. *Cement* 9:4–6 (in Russian)
- Ifka T, Palou M, Baráček J, Šoukal F, Boháč M (2014) Evaluation of P_2O_5 distribution inside the main clinker minerals by the application of EMPA method. *Cem Concr Res* 59:147–154
- Goetz-Neunhoeffer F, Neubauer J (1998) Effects of raw meal substitution by sewage sludge on OPC clinker studies by Rietveld analysis. In: Proceedings of 20th international conference on cement microscopy, Guadalajara, Mexico, 130–138
- Pech M, Douillet G (2002) Operational experience in co-incineration of animal meal in cement kilns. In: Proceedings of 5th international VDZ-Congress, Düsseldorf, 352–356
- Puntke S (2004) Auswirkungen des Phosphateintrages in Drehofenanlagen der Zementindustrie auf Klinkermineralogie und Zementeigenschaften, Dissertation. Clausthal University of Technology
- Staněk T, Sulovský P (2009) The influence of phosphorous pentoxide on the phase composition and formation of Portland clinker. *Mater Charact* 60:749–755
- Lieber W (1974) The influence of phosphates on the hydration of Portland cement. In: Proceedings of 6th ICCI, Moscow, 110, 3–13 September 1974, supplementary paper, section 2–6
- Nurse RW, Welch JH, Gutt W (1959) High-temperature phase equilibria in the system dicalcium silicate–tricalcium phosphate. *J Chem Soc* 34:1077–1083
- Gutt W (1963) High-temperature phase equilibria in the system $2CaO \cdot SiO_2 - 3CaO \cdot P_2O_5 - CaO$. *Nature* 197:142–143
- Chromý S (1978) Accuracy and precision of microscopic qualitative phase analysis of Portland clinker. *Silikáty* 22:215–226 (in Czech)
- Chromý S (1974) Anfärben des freiem CaO und Silikate in anschliffen von Portlandklinker. *Zement-Kalk-Gips* 27:79–84
- Celotti G, Landi E (2003) A misunderstood member of the nagelschmidtite family unveiled: structure of $Ca_5Na_2(PO_4)_4$ from X-ray powder diffraction data. *J Eur Ceram Soc* 23:851–858
- Staněk T, Sulovský P (2015) Mechanism of immobilization of toxic elements in special binders. *Adv Mater Res* 1124:3–9
- Ioannidis TA, Zouboulis AI (2006) Detoxification of a highly toxic lead-loaded industrial solid waste by stabilization using apatites. *J Hazard Mater* 97:173–191
- Gómez del Río J, Sanchez P, Morando PJ, Cicerone DS (2006) Retention of Cd, Zn and Co on hydroxyapatite filters. *Chemosphere* 64:1015–1020
- Vega ED, Pedregosa JC, Narda GE (1999) Interaction of oxovanadium(IV) with crystalline calcium hydroxyapatite: surface mechanism with no structural modification. *J Phys Chem Solids* 60:759–766
- Duc M, Lefevre G, Fedoroff M, Jeanjean J, Rouchaud JC, Monteil-Rivera F, Dumonceau J, Milonjic S (2003) Sorption of selenium anionic species on apatites and iron oxides from aqueous solutions. *J Environ Radioact* 70:61–72
- Vega ED, Pedregosa JC, Narda GE (2009) Adsorption of oxovanadium (IV) from aqueous solutions by nanoparticulated hydroxyapatite, thermodynamic and kinetic study. *J Argent Chem Soc* 97:1–12

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