Pergamon

Cement and Concrete Research 33 (2003) 63–71

CEMENT AND CONCRETE RESEARCH

Incorporation of V, Zn and Pb into the crystalline phases of Portland clinker

F.R.D. Andrade[a,*], V. Maringolo[b], Y. Kihara[a,b]

[a] *Departamento de Mineralogia e Geotectônica, Instituto de Geociências, Universidade de São Paulo, Rua do Lago, 562, 05508-900 São Paulo, SP, Brazil*

[b] *Divisão de Tecnologia, Associação Brasileira de Cimento Portland, São Paulo, Brazil*

Received 1 October 2001; accepted 8 July 2002

Abstract

Burning of industrial wastes in cement kilns has an increasing environmental importance, brought about by the incorporation of potentially hazardous elements into clinker crystalline phases and partial substitution of primary fuel and raw materials. In this study, experimental clinkers were synthesized, with the addition of V, Zn and Pb to a standard raw meal, from which a control clinker was obtained for comparison. The three metals were chosen as they are present in the alternative fuel petcoke (V) and in industrial wastes (Zn, Pb) commonly burned in cement kilns. Electron microprobe and scanning electron microscope analysis revealed the preferential partition of these metals among the clinker crystalline phases. It was observed that V has shown a preferential partition towards C_2S. Zn appears in higher amounts in periclase, and C_3S has higher Zn contents than C_2S. Pb concentrates in minute spherules and partitions toward C_3S in small amounts.

Keywords: Clinker; Vanadium; Zinc; Lead; Waste management

1. Introduction

Manufacturing of Portland cement plays an ever more important role in the management of hazardous wastes from different industrial sectors. Such wastes have substituted for fuels and raw materials, incorporating through clinker sintering their toxic components into the structure of clinker crystalline phases. Their subsequent stabilization in cement or mortar makes a significant environmental contribution. Partial substitution of industrial wastes for fossil fuels in cement kilns represents, therefore, an alternative source of energy, while meeting incineration standards and maintains the final product quality. Besides, this integrated activity offers additional revenues to the cement industry as the disposal of wastes normally receives a financial incentive.

The behavior of trace elements in the crystallization of clinker crystalline phases is a fundamental parameter for the evaluation of benefits and risks of burning hazardous wastes. The heavy metal and transition metal contents of industrial clinkers produced with burning of wastes are below the detection limit of conventional analytical methods. Experimental clinkers were obtained with the addition of V (as NH_4VO_3), Zn (as ZnO) and Pb (as $Pb(NO_3)_2$) to make the analysis of element distribution under the electronic microprobe and scanning electronic microscope possible. Incorporation of the three metals in crystalline phases was investigated by comparing the doped clinkers with a control one, made with the same raw meal.

The three metals (V, Zn, Pb) were chosen using the following criteria: (1) V is present in relatively large amounts in coal and petcoke, the major fuels currently utilised in Brazilian kilns; (2) Zn is present as a minor element in tires, which is a nonhazardous waste, extensively used as an alternative fuel in cement industry worldwide; (3) Pb commonly occurs as trace element in raw materials, fuels and industrial wastes and shows relatively higher volatility than other trace elements.

Worth noting is the magnesium contents, which are characteristically high in Brazilian clinkers. The cement plants, especially in southeastern Brazil, generally use MgO-rich Pre-Cambrian limestones. The clinkers of the

---

* Corresponding author.

E-mail address: dias@usp.br (F.R.D. Andrade).

PII: S0008-8846(02)00928-6

plant that supplied the raw mix for the test reportedly show periclase contents averaging 6%.

2. Materials and analytical methods

Experimental clinkers were produced at the Brazilian Portland Cement Association (ABCP) according to the following procedures. Four series of 270-g, 1-cm-diameter pellets were manufactured from industrial raw meal: a control one (without metal addition) and three series with addition of 1 wt.% of NH_4VO_3, ZnO and $Pb(NO_3)_2$. Addition of 1 wt.% of compounds of the three metals results in the following metal oxide contents: 1% $NH_4VO_3 = 0.78\%$ V_2O_5; 1% ZnO; 1% $Pb(NO_3)_2 = 0.67\%$ PbO. The mixtures were homogenized for 15 min in 54 ml water, corresponding to 20 wt.% of the raw meal. The pellets were left in an oven at 100 °C for 12 h and were calcined in a muffle furnace at 600 °C for 30 min from the time this temperature was reached. Finally, they were burned at 1450 °C for 15 min and were quenched, resulting in the experimental clinkers. Clinkers were kept in a moisture-free container until testing. Part of the pellets was used in polished sections for electron microprobe analysis and scanning electronic microscopy and part for X-ray fluorescence spectrometry. Modal mineral composition was not determined due to the high heterogeneity and porosity of experimental clinkers compared to industrial ones from rotary kiln. Table 1 presents the XRF data for the raw meal and clinkers, together with atomic absorption chemical data, which were used to check for the added element oxide content incorporated to clinker.

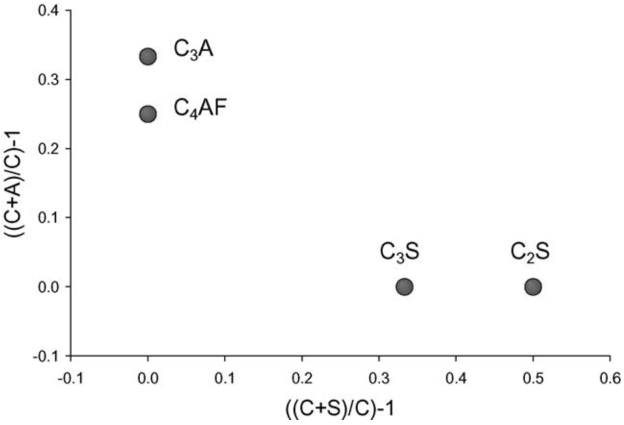

Fig. 1. Ideal composition of clinker crystalline phases with respect to the ratios $\{[(C+A)/C]-1\}$ versus $\{[(C+S)/C]-1\}$ in molecular proportions (C: CaO, A: Al_2O_3, S: SiO_2).

Table 1
Composition of raw mix and experimental clinkers by X-ray fluorescence

%	Raw mix	Clinker			
		Control	1% ZnO added	1% $Pb(NO_3)_2$ added ($PbO=0.67\%$)	1% NH_4VO_3 added ($V_2O_5=0.78\%$)
Loss on ignition	36.0	0.36	0.29	0.55	0.31
CaO	40.1	63.8	63.7	63.7	63.4
SiO_2	13.2	20.8	21.0	20.8	20.8
Al_2O_3	2.55	3.88	3.67	3.69	4.00
Fe_2O_3	2.12	3.33	3.34	3.32	3.32
SO_3	0.45	0.05	0.08	0.07	0.11
MgO	3.93	6.17	6.15	6.14	6.15
K_2O	0.59	0.34	0.43	0.39	0.45
TiO_2	0.18	0.30	0.30	0.29	0.29
Na_2O	0.12	0.14	0.16	0.15	0.16
SrO	0.13	0.20	0.21	0.20	0.20
P_2O_5	0.05	0.08	0.08	0.08	0.08
MnO	0.04	0.06	0.06	0.06	0.06
Total	99.5	99.5	99.5	99.5	99.3
Moduli					
FSC	96.8	98.0	97.6	98.2	97.4
MS	2.83	2.89	2.99	2.97	2.84
MA	1.20	1.16	1.10	1.11	1.21
Bogue					
Alite		70.6	70.6	71.5	68.6
Belite		6.47	6.95	5.81	7.80
C_3A		4.64	4.09	4.16	4.99
C_4AF		10.1	10.2	10.1	10.1
Free lime		3.80	4.33	4.01	4.38
ZnO	n.d.	28.3 ppm	1.36%	67.6 ppm	36.3 ppm
PbO	n.d.	n.d.	n.d.	0.39%	38.3 ppm
V_2O_5	n.d.	87.4 ppm	89.2 ppm	89.7 ppm	0.86%
Added metal retained in clinker (%)			86.6	37.1	69.9

Concentration of trace elements Zn, Pb and V was determined by atomic absorption.

Electron microprobe analyses were carried out in a JEOL 8600 equipment (Geosciences Institute, São Paulo University), using a current of 20 nA, a voltage of 15 kV and an electron beam diameter of 5 μm. The summation of most analyses is below 100%, which cannot be ascribed to the presence of water, because the analyzed phases are anhydrous. As peaks and backgrounds were carefully calibrated, discrepancies in CaO contents between the standard (wollastonite, 48.02% CaO) and clinker phases (up to 70% CaO) are assumed as a likely source of error.

Minute crystals (< 5 μm) of C_3A and C_4AF in the matrix of the clinker were not analyzed under the electron microprobe, because of difficulties in positioning the electron beam on individual crystals. The etching procedure, used to generate color contrast among clinker phases in polished sections, was not used to avoid roughness formation on the sample surface, prejudicial to probe analysis. Therefore, in several analyses, the electron beam reached more than one phase, and the result is a mixture not corresponding to the stoichiometric proportions of any of the four main clinker crystalline phases. Fig. 1 shows the stoichiometric compositions of pure ideal C_3S, C_2S, C_3A and C_4AF, with respect to the oxide ratios $\{[(CaO+Al_2O_3)/CaO]-1\}$ versus $\{[(CaO+SiO_2)/CaO]-1\}$ in molecular proportions. With this kind of diagram, it is possible to present the whole data set, including mixed analyses, which plot between the pure phases reached by the electron beam.

Backscattered electron (BSE) images and qualitative chemical analysis were acquired with a Zeiss DSM 962 scanning electron microscope (GFZ Potsdam, Germany) using the following analytical conditions: 20 kV–60 μA for V and Zn; and 25 kV–60 μA for Pb.

3. Results and discussion

3.1. Electron microprobe

The composition of C_3S and C_2S was determined under the electron microprobe, and selected analyses are given in Table 2. Matrix phases C_3A and C_4AF were not individually analyzed because of their small size but were, in some cases, marginally reached by the electron beam, resulting in mixed analyses. The whole set of microprobe data, including C_3S, C_2S and mixed analyses, is shown in Fig. 2. The diameter of the symbols is proportional to the molecular ratios of the metal oxides (V_2O_5, ZnO, PbO) in each analyzed spot. Fig. 2a shows the V partitions preferentially toward C_2S, with somewhat lower concentrations on and around C_3S. Fig. 2b and c reveals that Zn and Pb show the same trend, with the highest contents concentrated on and around C_3S.

Table 2
Selected electron microprobe data for C_3S and C_2S of experimental clinkers

	C_3S				C_2S			
	Blank	V	Zn	Pb	Blank	V	Zn	Pb
CaO [%]	70.4	69.1	69.0	70.5	61.9	60.4	62.1	62.6
SrO	0.12	0.21	0.23	0.12	0.36	0.29	0.43	0.30
Na_2O	0.09	0.00	0.12	0.00	0.24	0.18	0.20	0.00
K_2O	0.12	0.42	0.21	0.16	0.99	1.02	0.99	0.92
SiO2	24.4	25.6	23.8	24.6	30.0	29.6	32.5	33.2
Al_2O_3	0.80	1.40	1.62	0.88	2.04	1.76	0.59	0.26
TiO_2	0.11	0.12	0.11	0.05	0.15	0.11	0.05	0.09
FeO	0.48	0.80	1.35	0.55	1.44	1.39	0.67	0.40
MgO	1.48	0.00	1.29	0.00	1.22	4.17	0.44	0.00
MnO	0.00	0.02	0.02	0.03	0.05	0.06	0.02	0.06
P_2O_5	0.04	0.02	0.06	0.02	0.05	0.03	0.01	0.05
V_2O_5	0.00	0.40	0.00	0.00	0.03	0.75	0.00	0.00
ZnO	0.00	0.00	0.66	0.00	0.00	0.00	0.19	0.00
PbO	0.02	0.00	0.00	0.33	0.03	0.00	0.00	0.11
Total	98.1	98.0	98.5	97.2	97.8	99.0	98.0	97.8
Cationic proportions	Calculated to 45(O)				Calculated to 16(O)			
Ca	26.3	25.7	25.9	26.7	7.89	7.57	7.88	7.93
Sr	0.02	0.04	0.05	0.03	0.02	0.02	0.03	0.02
Na	0.05	0.00	0.08	0.00	0.06	0.04	0.05	0.00
K	0.06	0.19	0.09	0.07	0.15	0.15	0.15	0.14
Si	8.54	8.89	8.33	8.71	3.57	3.46	3.85	3.92
Al	0.33	0.57	0.67	0.36	0.29	0.24	0.08	0.04
Ti	0.03	0.03	0.03	0.01	0.01	0.01	0.00	0.01
Fe	0.14	0.23	0.39	0.16	0.14	0.14	0.07	0.04
Mg	0.77	0.00	0.67	0.00	0.22	0.73	0.08	0.00
Mn	0.00	0.01	0.01	0.01	0.01	0.01	0.00	0.01
P	0.01	0.01	0.02	0.01	0.01	0.00	0.00	0.00
V	0.00	0.09	0.00	0.00	0.00	0.06	0.00	0.00
Zn	0.00	0.00	0.17	0.00	0.00	0.00	0.02	0.00
Pb	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00

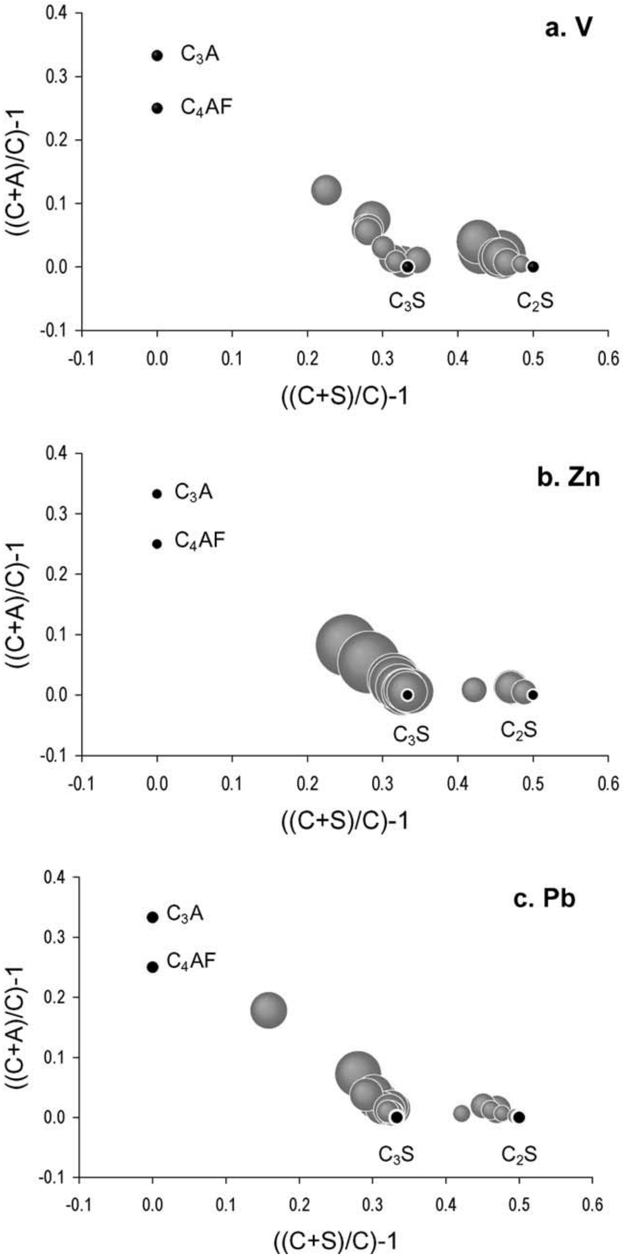

Fig. 2. Molecular proportion of V_2O_5, ZnO, PbO in clinker phases. The diameter of symbols refers to molecular proportion (%) of added metals: (a) V_2O_5 between 0.18% and 1.28% ($n=17$); (b) ZnO between 0.20% and 1.20% ($n=16$); PbO between 0.11% and 1.13% ($n=16$).

The cationic proportions of C_3S and C_2S were calculated based on 45 oxygens for C_3S (unit cell, $9Ca_3SiO_5$) and 16 oxygens for C_2S (unit cell, $4Ca_2SiO_4$), as proposed by Hornain in 1971. Ideal C_3S and C_2S have octahedral sites occupied by Ca^{2+} and tetrahedral sites occupied by Si^{4+}.

Analyzed elements were ordered according to their charge and ionic radius, and plots were done to test the possibilities of solid solution of V, Zn, Pb and other analyzed elements in the structure of C_3S and C_2S.

Although the cationic proportions of V, Zn and Pb in C_3S are quite low, several tentative conclusions may be drawn based on the microprobe data (Fig. 3).

- Among the added metals, Zn is more easily incorporated in C_3S, followed by V and Pb, while Pb has the best negative correlation with Ca, indicating its preference for the octahedral site (Fig. 3a). A good negative correlation was found between Ca and alkalis for the octahedral site (Fig. 3b).
- Mg enters C_3S only in the sample doped with Zn, and not in those with Pb and V (Fig. 3c). Hence, a plot of Ca^{2+} versus all cations that are likely to occupy the octahedral site shows two trends (Fig. 3d), given the preferential concentration of Mg in Zn-doped C_3S.
- In the tetrahedral site, Si is in part replaced by Ti and Al (Fig. 3e). The negative correlation is slightly worse if Fe^{3+} is added to Ti and Al (Fig. 3f), suggesting a possible preference of Fe for the octahedral site.

Therefore, with exception of Ti and Al, all other cations seem to have a preference for the octahedral site. Some problems with site occupancy may be due to the presence of cations in defects in the crystalline structure.

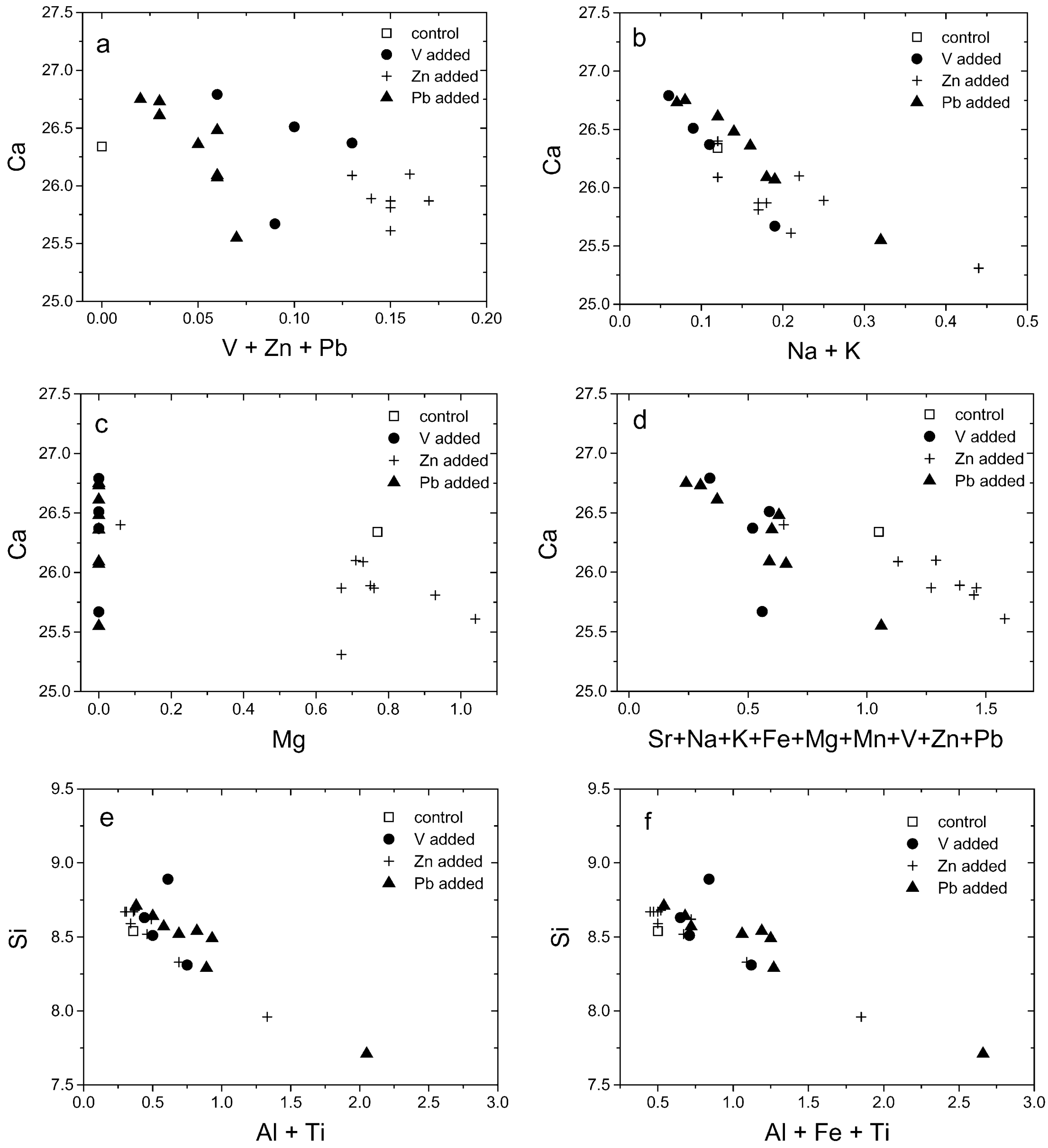

Fig. 3. Cationic correlation for C_3S, using cation units in the formula based on 45(O).

Cationic site occupation for C_2S (Fig. 4) shows less clear correlations than for C_3S, nevertheless, the following may be proposed:

- For the three metals added to the experimental clinkers, only V is accepted to some extent in the C_2S structure, as substitute for Ca (Fig. 4a).
- A slightly negative correlation between Ca and alkalis indicates the intake of Na + K in the octahedral site (Fig. 4b).
- Different to what is observed for C_3S, Mg substitutes for Ca preferentially in the V-doped C_2S, and not in those with Pb and Zn (Fig. 4c).
- The plot of Ca versus all cations that may occur in octahedral coordination shows that the subtitutions in this site are of a more complex nature than in C_3S (Fig. 4d).
- Regarding the tetrahedral site, Ti and Al are clearly substituting for Si (Fig. 4e). Similarly to C_3S, the negative correlation is slightly worse if Fe^{3+} is considered together to Ti and Al (Fig. 4f), suggesting a preference of Fe for the octahedral site.

3.2. Scanning electron microscope

Backscattered electron images and qualitative chemical analyses by energy dispersive spectra (EDS) confirmed that

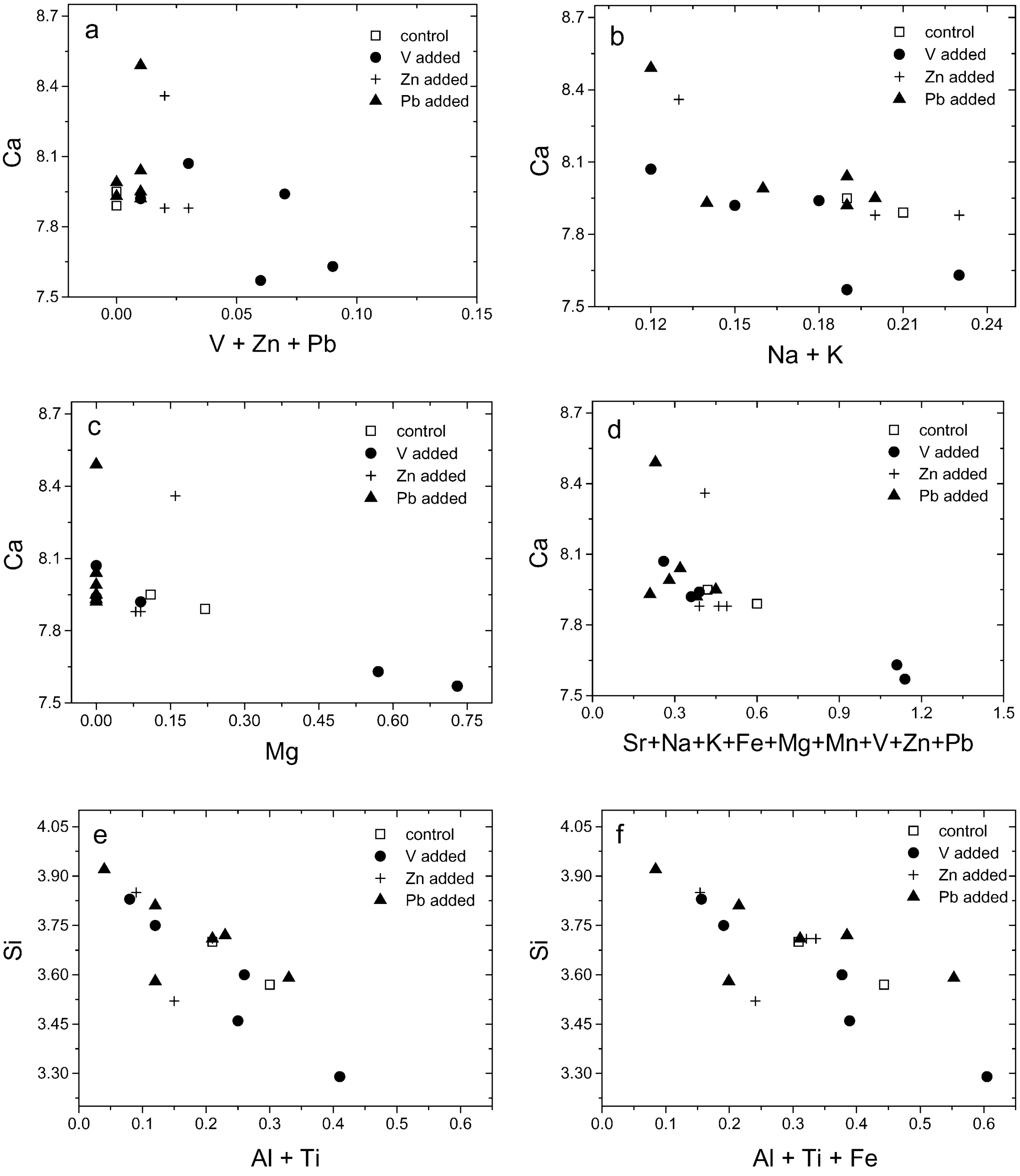

Fig. 4. Cationic correlation for C_2S, using cation units in the formula based on 16(O).

V is incorporated in C_2S, although its EDS peaks are observable only in analyses of relatively large areas of single crystals (Fig. 5), and are not high enough to produce well-defined compositional profiles. The tendency is consistent with the microprobe data (Fig. 2a).

In regard to Zn, the highest contents were found in periclase (MgO) disseminated as small cubic crystals all over the clinker, as shown in the compositional profile x–x' in Fig. 6. Additionally, a relatively high concentration of Zn was observed in C_3S, confirming the microprobe data (Fig. 3).

Pb concentrates in minute spherical crystals (< 1 μm in diameter), frequently situated on the borders of C_3S crystals. In backscattered images, Pb-rich spherules appear in a gray tone lighter than that of C_3S (Fig. 7). The qualitative chemical composition of the spherules (Fig. 7) reveals the presence of Pb, but it is overall similar to that of its host phase, C_3S, given the small size of the spherules that leads to interference from the surroundings.

4. Concluding remarks

The presence of trace elements in raw materials of Portland clinker influences the kinetic of reactions in the kiln, the viscosity of the liquid phase, the crystallization of the different phases and their phase equilibria, as well as the development of microtextures [1]. Diffusion and substitution of trace elements among the major components of crystalline structures is a function of cell parameters, ionic radius and charge. Temperature plays a decisive role in these processes, as crystalline structures are more accommodating of foreign ions at higher temperatures. Sudden cooling after high-temperature crystallization precludes transformation to lower-temperature polymorphs and exsolution phenomena to occur, freezing the clinker phases in a state of high metastability. MgO in raw mix provides Mg^{2+} to the system, which can substitute for Ca^{2+} in alite crystal lattice, thus increasing the content availability of Ca to react with belite and form more alite. Incorporation of Mg in the main

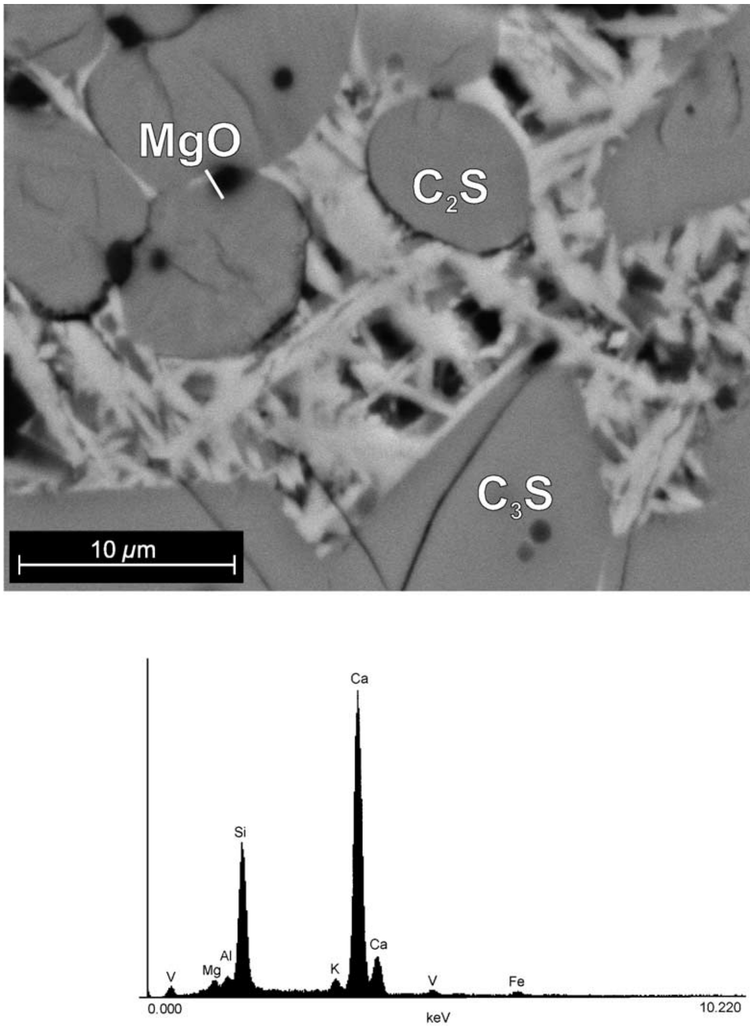

Fig. 5. BSE image of clinker with addition of V, showing C_3S, C_2S and interstitial C_3A, C_4AF and MgO. The EDS refers to C_2S, the only phase where V was detectable.

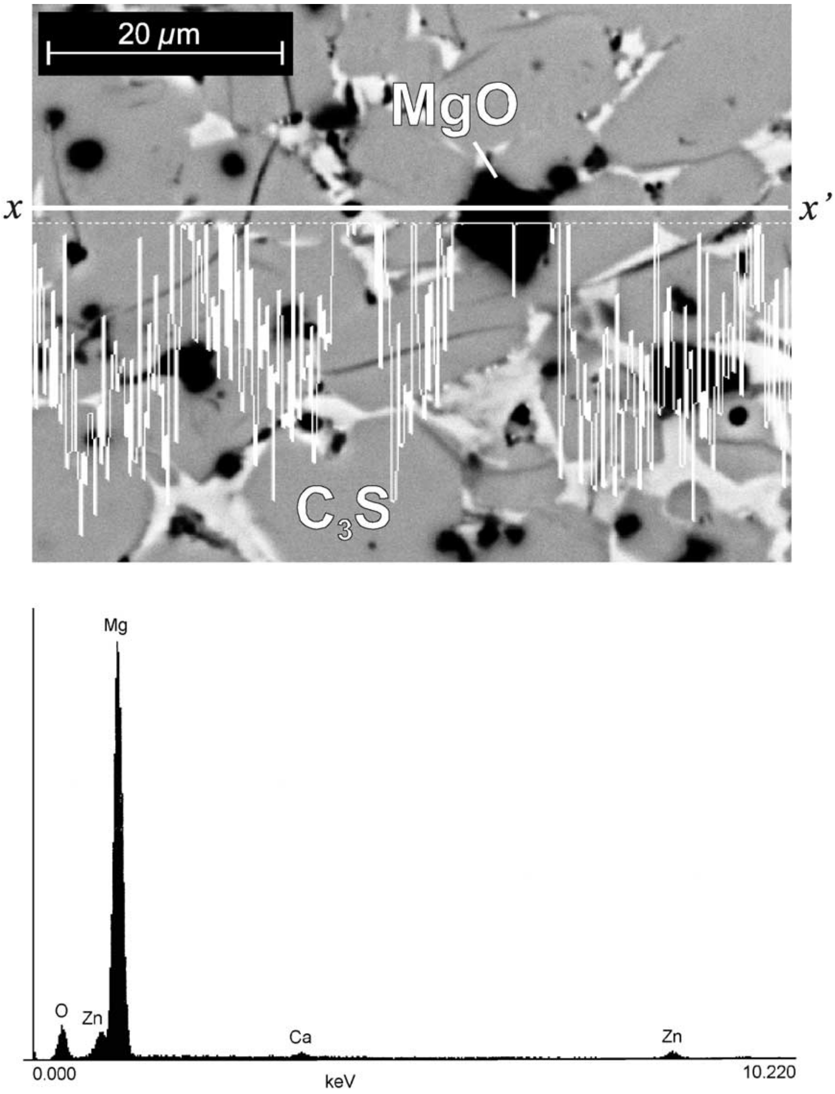

Fig. 6. BSE image of clinker with addition of Zn, showing relative Zn contents along the profile $x-x'$. The EDS refers to a MgO crystal.

clinker components can reach as much as 2 wt.%; higher contents then crystallize as periclase.

The presence of transition metals as solid solutions in clinker phases increases the density of lattice defects, which would theoretically cause an improvement in the reactivity of the cement [2]. However, the effects of Cr, Ni and Zn on the burnability of meals and on the reactivity of the major clinker phases are increased only if the metal content is significantly higher (2.5–5 wt.%) than in the ordinary Portland cement [3–6].

The transition metals have an influence on the grindability of Portland clinker. Zn and V, the latter to a minor degree, increase the melt content in the kiln, reducing the porosity of the clinker and, consequently, reducing the grindability [7].

It is known that C_3A and C_4AF are the clinker phases with the highest capacity to accommodate substitutions in their crystalline structure [8,9]. Unfortunately, the small size of these matrix phases precluded proper analysis under the electron microprobe, and microprobe data were obtained for C_3S and C_2S only.

V, Zn and Pb are shown to behave differently among the crystalline phases of the Portland clinker. It was observed that Pb concentrates in minute spherules (Fig. 7) but also goes into C_3S in small amounts (Fig. 2c). Microprobe data show that Zn appears in higher amounts in C_3S than in C_2S (Fig. 6), although qualitative chemical analysis (Fig. 6) also revealed the presence of Zn peaks in periclase (MgO). The element V has shown a preferential partition towards C_2S (Fig. 2), confirming previous data from the literature.

The incorporation of the three added metals in the experimental clinker is 86.6% for Zn, 69.9% for Pb and 37.1% for Pb (Table 1), confirming the high volatility of the latter.

Experiments to assess incorporation of Pb in clinker came to widely different results, from 25% [10], 72–96% [11] up to 97% [12] or even 100% Pb [13]. Discrepancies in incorporation rates of Pb are in part due to the addition of Pb

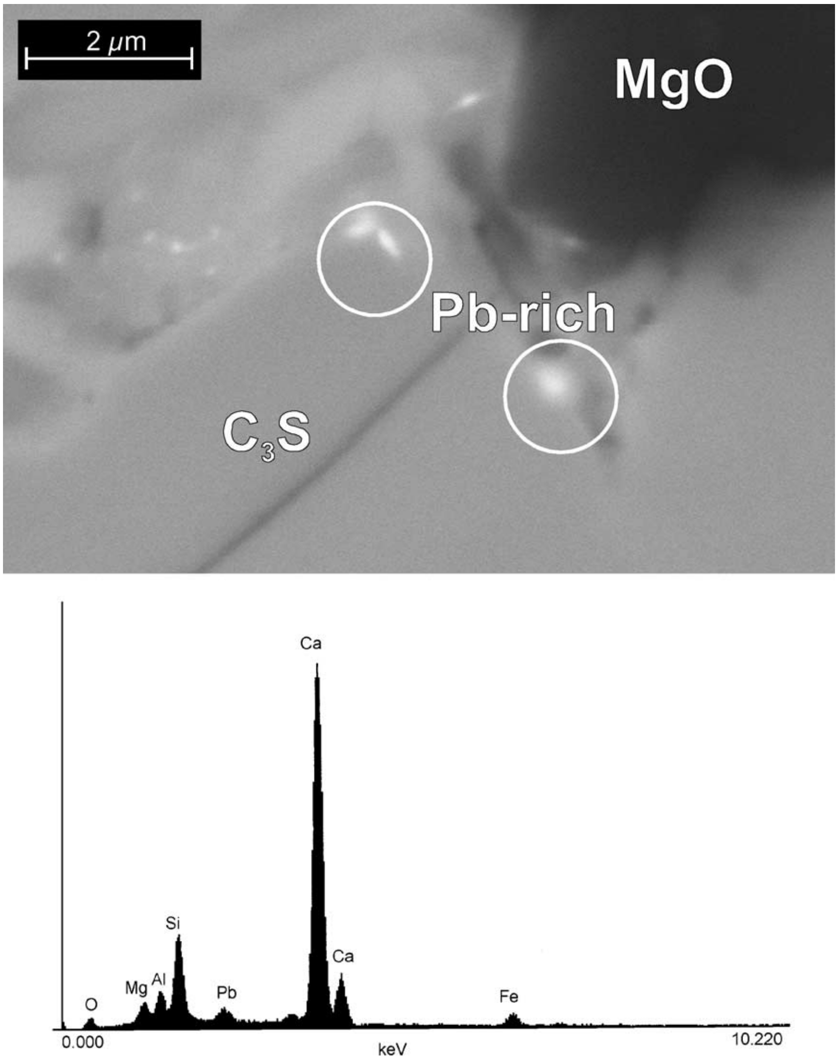

Fig. 7. BSE image of clinker with addition of Pb, which is concentrated on the light spherules surrounding C_3S (circles) and surrounded by MgO and C_4AF. EDS of the Pb-rich spherules.

in different compounds. It is known that Pb is substantially lost by volatilization at 750 °C, particularly in the presence of chlorine, as a very low degree of Pb fixation was observed in phases of a clinker with addition of $PbCl_2$ [14].

The recognition that V, Zn and Pb are retained in crystal structures of clinker phases, mostly as solid solutions, is a favourable environmental aspect. The Pb-rich spherules represent an exception, as they seem to be associated with a different phase, which may be ascribed to the abnormally high Pb content of the synthesized clinker. Leaching experiments performed on cements made from these V-, Zn- and Pb-added clinkers revealed a low mobility of the metals incorporated in the clinker phases [15].

Acknowledgements

The authors would like to thank Dr. S.R.F. Vlach and M. Mansueto (electron microprobe, Universidade de São Paulo, Brazil) and U. Glentz (scanning electron microscope, GFZ Potsdam, Germany). N. Varzacacou are acknowledged for the help in clinker synthesis. The final version of this paper was greatly improved by comments from two anonymous referees.

References

[1] Y.M. Butt, V.V. Timashev, The mechanism of clinker formation processes and the modification of its structure, In: Int. Congr. Chem. Cem. 6, Moscow, September 1974. Proceedings of the International Congress of Cement Chemistry, Moscow, vol. 1, 1976, pp. 64–102 (Scientific Institute of Cement Chemistry).

[2] G.K. Moir, F.P. Glasser, Mineralizer, modifiers and activators in the clinkering process, In: Int. Congr. Chem. Cem. 9, Delhi, September 1992. Proceedings of the International Congress of Cement Chemistry, Delhi, vol. 1, 1992, pp. 125–152 (International Cement Microscopy Association).

[3] D. Stephan, R. Mallmann, D. Knöfel, R. Härdtl, High intakes of Cr, Ni

and Zn in clinker: Part II. Influence on the hydration properties, Cem. Concr. Res. 29 (1999) 1959–1967.

[4] D. Stephan, H. Maleki, D. Knöfel, B. Eber, R. Härdtl, Influence of Cr, Ni and Zn on the properties of pure clinker phases: Part II. C_3A and C_4AF, Cem. Concr. Res. 29 (1999) 651–657.

[5] D. Stephan, R. Mallmann, D. Knöfel, R. Härdtl, High intakes of Cr, Ni and Zn in clinker: Part I. Influence on burning process and formation of phases, Cem. Concr. Res. 29 (1999) 1949–1957.

[6] D. Stephan, R. Mallmann, D. Knöfel, R. Härdtl, High intakes of Cr, Ni and Zn in clinker: Part I. Influence on hydration properties, Cem. Concr. Res. 29 (1999) 1959–1967.

[7] S. Tsivilis, G. Kakali, A study on the grindability of portland cement clinker containing transition metal oxides, Cem. Concr. Res. 27 (5) (1997) 673–678.

[8] H. Hornain, Sur la répartition des éléments de transition et leur influence sur quelques propriétés du clinker et du ciment, Rev. Mater. Constr. 671–672 (1971) 203–218.

[9] H.F.W. Taylor, Cement Chemistry, 2nd ed., Academic Press, New York, 1998.

[10] S. Sprung, W. Rechenberg, The reactions of lead and zinc in the burning of cement clinker, Zem.-Kalk-Gips 5 (1994) 258–263.

[11] F.W. Locher, Development of environmental protection in the industry, Zem.-Kalk-Gips 3 (1989) 120–127.

[12] W. Gerger, Experience with specialized control techniques when using secondary materials, Zem.-Kalk-Gips 10 (1994) 582–585.

[13] G. Kirchner, Behavior of heavy-metals during cement clinker burning, Zem.-Kalk-Gips 39 (10) (1986) 555–557.

[14] M. Murat, F. Sorrentino, Effect of large intakes of Cd, Pb, Cr, Zn to cement raw meal on the mineralogical composition of clinker, In: Int. Congr. Cem. Microscopy, 18, Houston, 1996. Proceedings of the International Congress of Cement Chemistry, Houston,1996, pp. 272–283 (National Council for Cement and Building Materials).

[15] V. Maringolo, Clínquer coprocessado: produto de tecnologia integrada para sustentabilidade e competividade da indústria de cimento, Unpublished PhD Thesis, Universidade de São Paulo, 2001, 177 pp.