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The effect of foreign ions on the reactivity of the $CaO–SiO_2–Al_2O_3–Fe_2O_3$ system
Part II: Cations

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Abstract

The subject of this paper is the effect of foreign cations on the reactivity of the $CaO–SiO_2–Al_2O_3–Fe_2O_3$ system. One reference mixture and eighteen modified mixtures, prepared by mixing the reference sample with 1% w/w of chemical grade MnO_2, CuO, V_2O_5, PbO, CdO, ZrO_2, Li_2O, MoO_3, Co_2O_3, NiO, WO_3, ZnO, Nb_2O_5, CrO_3, Ta_2O_5, TiO_2, BaO_2 and H_3BO_3 were studied. The effect on the reactivity is evaluated on the basis of the free lime content in samples sintered at 1200 and 1450 °C. At 1200 °C, the reactivity of the mixture is greatly increased in the presence of Cu and Li oxides. Based on their effect at 1450 °C, the added elements can be divided into three groups. W, Ta, Cu, Ti and Mo show the most positive effect, decreasing the free CaO (fCaO) content by 30–60%, compared with the pure sample. Cr and B cause an increase of fCaO content, while the rest of the elements exhibit a marginal positive effect. According to their volatility at 1450 °C, the added compounds can be subdivided into three groups of low (Ti^{4+}, Cu^{2+}, Mo^{6+}, W^{+6}, V^{5+}, Zn^{2+}, Zr^{4+}), moderate (Cr^{6+}, Co^{3+}, Ni^{2+}, Mn^{4+}) and high volatility (Cd^{2+}, Pb^{2+}). All burned samples, analyzed by means of X-ray diffraction, have a final mineralogical composition, which corresponds to the structure of a typical clinker. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: $CaO–SiO_2–Al_2O_3–Fe_2O_3$; Mineralizers; Cations; Free CaO; Volatility

1. Introduction

The significance of the $CaO–SiO_2–Al_2O_3–Fe_2O_3$ system in cement chemistry and the effect of foreign ions on its reactivity, during the thermal treatment, have been reviewed in Part I [1]. The role of minor components in Portland cement clinker, composed mainly by CaO, SiO_2, Al_2O_3 and Fe_2O_3, has been discussed and reviewed adequately [2–5].

Despite the extensive literature on the subject, the results are often contradictory, due to the variety of the materials and the techniques that have been applied. An attempt to summarize the existing literature is presented below. For convenience reasons, the cations are categorized according to the periodic table.

1.1. Cations of IA–IIA group

Small amounts of lithium oxide were reported to improve the reactivity of the raw mix, by lowering the temperature of the initial melt formation. However, if the concentration of Li_2O in the raw mix exceeds 1%, the combination of free lime is impaired and the conversion of C_2S to C_3S is inhibited [5,6].

Barium oxide has been found to decrease the clinkerization temperature, accelerate the relative reactions and stabilize β-C_2S [5,7,8]. The use of minerals and by-products, containing Ba, for the production of ordinary and belite clinkers, at lower temperature, has also been studied [9,10].

1.2. Cations of IVA group

The effect of Ti oxide is strongly depended on its concentration in the mixture. Moderate addition of Ti oxide promotes the decarbonation of the raw mix and accelerates the binding of lime. About 1% w/w of TiO_2 addition in the

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raw mix reduces the melt temperature by 50–100 °C and decreases the free lime content but above that limit, an increasing trend is observed [5,11]. The incorporation of Ti in the main clinker phases has also been studied [12–15].

Zirconium oxide does not change significantly the heating and cooling reactions of the cement raw mix, although it modifies the shape and size of calcium silicate crystals [16]. A noticeable colour change has been observed in OPC and alumino-belite clinkers, which contain small amounts of Zr compounds [16,17]. A retarding effect on the early hydration of cement has been observed in clinkers containing 1–1.5% ZrO_2 [18]. However, an increase of the early compressive strength has also been reported when smaller amount of ZrO_2 was added [5].

1.3. Cations of VA group

Vanadium ions are present as V_2O_5 in cement clinker. Odler et al. [19] reported that 1% V_2O_5 can significantly reduce the free lime in clinker, at 1200 °C. It decreases the melt viscosity, favours the formation of big alite crystals and stabilizes β-C_2S [2,5,20,21]. There is a disagreement whether it is concentrated preferentially in alite or in belite [5,22].

Niobium and tantalum cations may be present as traces in the cement raw mix in the form of Nb_2O_5 and Ta_2O_5 oxides and are unlikely to impart any noticeable effect on the clinker formation. No remarkable changes were observed in the structure of clinkers containing up to 1% Nb_2O_5 [16]. Cement pastes made from those clinkers did not show any change in the setting or strength development [18].

1.4. Cations of VIA group

Chromium cations can exist in a number of oxidation states, the most stable, in clinker, being Cr^{3+} and Cr^{6+}. Cr and V are the only elements preferentially concentrated in belite, according to Hornain [22]. Cr was found to stabilise the β-C_2S form [20] and was used as additive in active belite cements [23]. Intakes of Cr, up to 0.5%, lower the content of free lime, while higher concentration and the addition of other metals cause an increase of free CaO [24,25]. Cr inhibits the reaction between belite and CaO to form alite but it is not clear whether it is caused by the destabilization of alite or the stabilization of belite [24,25].

Molybdenum is an effective reducer of the viscosity and the surface tension of the melt and therefore acts as a mineralizer [16]. Mo is mostly dissolved in the interstitial phase while very small amount is found in the silicate phases [26,27]. It was also found to improve the burnability of clinker [27]. It does not have any significant effect on the hydration of the cement [18].

Very little work has been reported on the effect of tungsten on clinker formation. It was noted that the addition of up to 1.5% WO_3 in the raw mix modifies the shape and size of the alite crystals and it was concluded that the dissolution of W^{6+} ions in the melt affects its properties [16].

1.5. Cations of VIIA group

Mn cations can occur in many oxidation states depending upon the burning conditions. MnO_2 increases the alite content in clinker but Mn^{4+} ions are more preferentially incorporated into the ferrite phase, reducing C_3A and increasing free lime [5]. A reaction mechanism to explain the mineralising effect of Mn on the formation of alite was proposed [28].

1.6. Cations of VIIIA group

Co^{3+} is found in traces in cement raw mix and is concentrated mainly in the ferrite phase by replacing the Fe^{3+} ions [5]. It was found to accelerate the formation of alite and reduce the free lime in both clinker and pure C_3S [29].

Nickel is preferentially concentrated in the ferrite phase, followed by alite, aluminate and belite [22]. Even high intakes of Ni have only marginal effects on the formation and hydration of clinker and its main compounds [24,25].

1.7. Cations of IB group

CuO acts both as mineralizer and flux. It decreases the melt temperature by at least 50 °C, even for 0.5% addition in the raw meal, and favours the combination of free lime even at 1100 °C [30]. CuO accelerates the C_3S formation whereas Cu_2O, under reducing conditions, inhibits it [5].

1.8. Cations of IIB group

The ZnO addition improves the burning behaviour of the raw mix and accelerates the clinker formation. ZnO is acting both as mineralizer and flux leading to higher activity and promoting the solid reactions as well as the formation of alite by increasing the amount of liquid phase [31–33]. The incorporation of ZnO in the aluminate phases has been thoroughly investigated by Bolio-Arceo and Glasser [34].

Although very little work was done for CdO, it was reported that it generally improves the burnability of the clinker by lowering the melt temperature [19].

1.9. Cations of IIIB group

Boron was reported to inhibit the formation of C_3S and affect the stability of the other major clinker phases [5]. An increase of the free lime, in the presence of B compounds, was also observed [35]. It must be noted that, although B compounds are not useful additions in regular clinkers, they might act as mineralizers in belite clinkers, since they stabilize β-C_2S and improve its reactivity [5].

1.10. Cations of IVA group

Lead compounds are quite volatile under sintering conditions but small amounts can still be retained in clinker. Pb oxide was found to lower the free lime content and improve the burnability of the raw mixture during the clinkering process [36]. The main effect of Pb in clinker seems to be the retardation of the hydration [5].

The incorporation of the foreign ions in the main clinker compounds has been the subject of many works. Most of the impurities are concentrated in aluminate and aluminoferrite compounds because their lattice contains holes and octahedral or tetrahedral positions, respectively, that are convenient for insertion and/or substitution of foreign ions. Calcium silicates are less capable of adopting impurities due to their dense structure. The only known exception is Cr and V that are preferentially concentrated in belite [22]. When quite large amounts of foreign elements were added in binary mixtures (usually $CaO-SiO_2$ or $CaO-Al_2O_3$), a variety of new compounds were identified. However, in quaternary samples, containing small amount of additions, the foreign elements are more likely to incorporate in the main phases of clinker, causing distortion of the crystal lattice, than to form new compounds.

The high temperature of the thermal treatment increases the mobility of the elements and may cause extensive volatilisation. In general, Pb and Cd show a high volatility while the rest of the elements are more stable at the sintering temperature [37–40]. In some cases, the volatility of the elements varies depending on the conditions at the burning zone [41].

Despite the extensive literature, it is difficult to draw any comparative results concerning the effect of foreign ions on the reactivity of cement raw meal, since a great variety of materials and techniques have been applied. In the present paper, the effect of selected cations on the reactivity of the $CaO-SiO_2-Al_2O_3-Fe_2O_3$ system is studied. The volatility of the added compounds and the modifications of the structure of the sintered samples are also discussed.

2. Experimental

One reference mixture, composed of chemical grade $CaCO_3$, SiO_2, Al_2O_3 and Fe_2O_3 and having a composition very close to this of a typical cement raw meal, was prepared. Quartz and aluminum oxide were ground to a particle size < 90 μm and then were intensively mixed with Fe_2O_3 and precipitated $CaCO_3$ in a laboratory swing mill for 1 h. Homogeneity was ascertained by measuring the loss of ignition (LOI) in three individual samples of the mixture. The results indicated that LOI values were very close to the estimated one (34.99%), certifying a good homogeneity of the raw mix. Table 1 shows the chemical and the mineral composition (according to Bogue) of the reference mixture, after it was sintered at 1450 °C.

Table 1
Chemical and mineral composition of the reference mixture after thermal treatment at 1450 °C

Clinker chemical composition		Clinker mineral composition (according to Bogue)	
Oxide	Wt. (%)	Mineralogical constituent	Wt. (%)
CaO	68.08	C_3S	65.0
SiO_2	22.81	C_2S	15.0
Al_2O_3	5.84	C_3A	10.0
Fe_2O_3	3.27	C_4AF	10.0

Eighteen modified mixtures were prepared by mixing the reference sample with 1% w/w of chemical grade MnO_2, CuO, V_2O_5, PbO, CdO, ZrO_2, Li_2O, MoO_3, Co_2O_3, NiO, WO_3, ZnO, Nb_2O_5, CrO_3, Ta_2O_5, TiO_2, BaO_2 and H_3BO_3. The studied elements were introduced in the form of oxides, in order to avoid the effect of foreign anions on the reactivity of the mixture. B was added in the form of H_3BO_3. When necessary, the added compounds were ground in order to have, approximately, the same fineness with the reference sample. Very fine compounds (e.g., ZnO) were sieved, prior to mixing, in order to avoid agglomeration. The homogeneity was ascertained by dosing the added element, in some indicative samples.

All the samples were pressed to form pellets, then sintered at 1200 and 1450 °C for 30 min in an electrical furnace and cooled rapidly in air. The sintered pellets were ground and analysed by the ethylene glycol method in order to estimate the free CaO (fCaO) content. The samples were, also, examined using a Siemens D-5000 X-ray diffractometer, with nickel-filtered Cu $K\alpha_1$ radiation ($\lambda = 1.5405$ Å), for the identification of the mineralogical phases formed during sintering.

The content of the added compounds in the samples, sintered at 1450 °C, was determined, using atomic absorption spectroscopy.

3. Results and discussion

The free lime content in the samples was measured after thermal treatment at 1200 and 1450 °C, in order to evaluate the effect of the additives on the solid state reactions and on the reactions in the presence of the melt, respectively. Figs. 1 and 2 show the free lime content in the samples, at both temperatures, in relation to the added compound.

3.1. Effect of the added oxides at 1200 °C

As it was expected, most of the added compounds have only marginal effect on the reactivity of the raw mix, at 1200 °C. However, the addition of CuO and Li_2O causes a remarkable decrease of the fCaO (Fig. 1).

The addition of 1% CuO in the raw meal, caused a decrease of fCaO by approximately 60%, showing the better result among the other doping agents. In fact, CuO

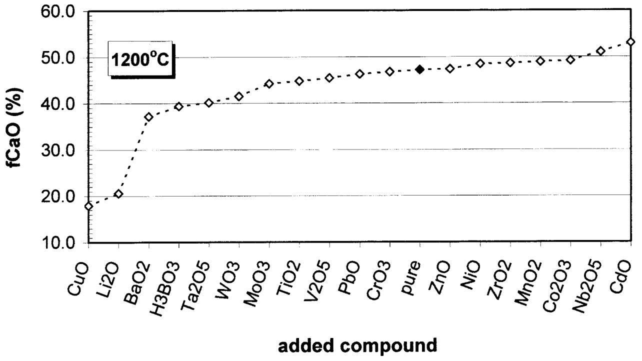

Fig. 1. fCaO content in samples at 1200 °C in relation to the added compound.

was reported to be an efficient mineralizer and flux, its action beginning already at 1100 °C [19,29,30]. The action of CuO seems to be related to the acceleration of the reactions among the four main oxides, rather than the decomposition of calcium carbonate. The dark color of this sample, even at 1100 °C, indicates a high degree of combination of the main constituents and especially of Fe_2O_3. This color change is observed above 1300 °C, in the other samples. This low temperature effect of CuO on the reactivity of the $CaO-SiO_2-Al_2O_3-Fe_2O_3$ system seems to be unique and needs further investigation.

Li_2O, on the other hand, is found to affect the decomposition of calcium carbonate. The TGA measurement of the sample containing Li_2O recorded a two step decomposition of calcium carbonate, starting at lower temperature than in pure sample. Saraswat et al. have also observed the same effect, as well as an accelerated formation of belite in samples containing Li_2CO_3. They have attributed these effects to the formation of higher reactive CaO [42].

3.2. *Effect of the added oxides at 1450 °C*

Based on their effect at 1450 °C, the added elements can be divided into three groups (Fig. 2). W, Ta, Cu, Ti and Mo show the most positive effect, decreasing the fCaO content by 30–60%, compared with the pure sample. Cr and B cause an increase of fCaO content, while the rest of the elements exhibit a marginal positive effect.

The most important reaction in this temperature range, is the formation of alite ($3CaO\cdot SiO_2$) that can proceed only in the presence of the melt. The main stages of the reaction are the dissolution of the CaO and belite and the diffusion of Ca^{2+}, O^{2-} and SiO_4^{4-} to the points where precipitation and growth of alite crystals take place. The mobility (diffusion coefficients) of the different ionic species is strictly related to the structure and physical/chemical properties of the melt and especially the viscosity and the surface tension. The reduction of the viscosity accelerates the diffusion of the reactants while high values of the surface tension improve the wetability of the grains and facilitate their rearrangement and combination. Both cases result to the promotion of the clinkering reactions and the accelerated the consumption of the free lime.

Most of the foreign ions, present in the raw mix, are dissolved in the melt and affect its properties. In previous works, quaternary mixtures, having the typical composition of the liquid phase, were studied and the correlation between the electronic configuration of the added ions (ionic radius, electronegativity, field intensity) and their effect on the properties of the melt was well established [2,3]. However, it is not clear whether any changes of the melt properties can be reflected on the overall reactivity of the $CaO-SiO_2-Al_2O_3-Fe_2O_3$ mixture.

According to Timashev's classic work, the higher the energy of the Me–O bond or the higher the ionic potential of the ion, the greater the reduction of the viscosity [2]. The positive effect of W, Mo, Ta and Ti ions is fully explained by this statement, since they possess the higher energy bond and ionic potential among the studied ions. V and Cr were expected to have similar effect but it was not confirmed by our measurements. According to Hornain, these two elements are the only ones that are preferentially concentrated in belite and not in the calcium aluminate compounds of clinker and therefore they cannot extensively affect the properties of the melt [22]. CuO was found to be an effective mineralizer at 1450 °C, but in a lesser extend, compared with 1200 °C.

The negative effect of Cr and B ions can be attributed to their effect on the alite formation reaction. These ions were found to inhibit this reaction but it is not clear whether this is caused by the stabilization of the β-C_2S or the destabilization of C_3S [24,25].

The effect of the added ions to the reactivity of the mixture, at 1450 °C, was evaluated on the basis of their electronic configuration. Fig. 3 presents the fCaO ratio (ratio of fCaO content in modified samples to the fCaO content in the reference sample) and the atomic radii of the added ions, in relation to their atomic number. Fig. 4 presents the fCaO ratio and the electronegativity (according to Pauling) of the added elements, in relation to their atomic number. As it is shown, the changes of the free lime content closely follows

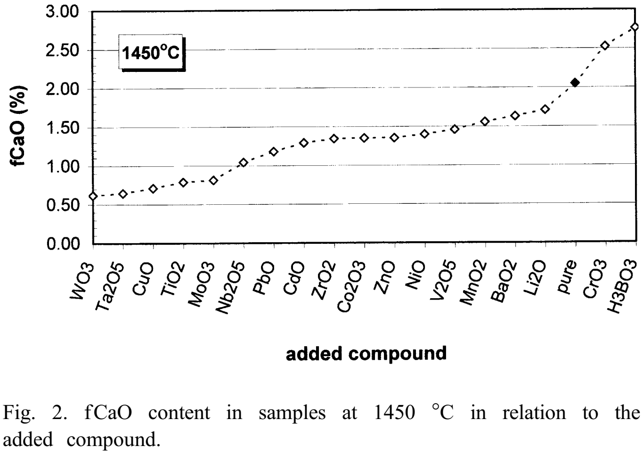

Fig. 2. fCaO content in samples at 1450 °C in relation to the added compound.

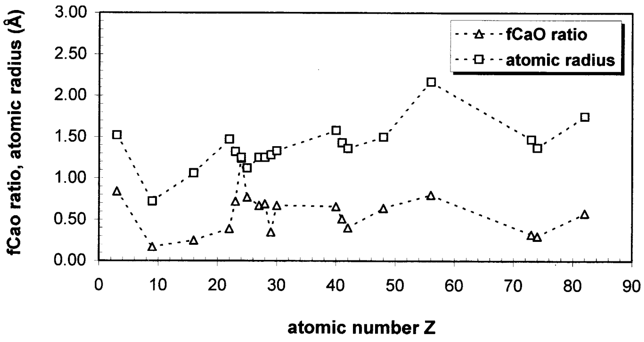

Fig. 3. fCaO ratio at 1450 °C and atomic radii of the added ions in relation to their atomic number.

the periodicity of the atomic radii and the electronegativity of the added elements. The presence of ions, having decreased size or increased electronegativity, favors the combination of the free lime and therefore improves the reactivity of the mixture. The only deviation of this simple rule concerns the elements Cr, V, Mn and Cu. Cr and V are preferentially concentrated in belite and they are not expected to affect extensively the properties of the melt. The sintered sample containing Mn oxide did not have a uniform color, although the homogeneity of the starting mixture was found to be satisfactory. This may be due to the coexistence of different oxidation states of Mn ion in the sample. In this case, the effect of Mn ions becomes more complex and it can not be easily correlated with the atomic size or the electronegativity. As it has been previously mentioned, the effect of Cu is unique and needs further investigation.

Our work confirms that the overall reactivity of the mixture can be correlated with the electron configuration of the added ions, in the same way as the properties of the melt. The addition of small amount of selected compounds can alter extensively the properties of the melt and these modifications of the melt properties are reflected on the reactivity and burnability of the raw mix, which is very important in the case of the cement production. These compounds in the raw mixture can be introduced as constituents of wastes, alternative fuels or secondary raw materials [43,44]. It must be noted, however, that when several elements are jointly present in the mixture, the reactivity is not additively changed and any secondary material that is expected to have a positive effect on the reactivity must be individually investigated. In any case, the use of small additions of selected compounds in order to improve the reactivity of the $CaO-SiO_2-Al_2O_3-Fe_2O_3$ mixture may be a promising way to reduce the financial and the environmental cost in cement production.

Our measurements, concerning the volatility of the added elements showed that these elements can be divided into three groups:

High volatile elements: Cd^{2+}, Pb^{2+} (<20% remained in sample)
Moderate volatile elements: Cr^{6+}, Co^{3+}, Ni^{2+}, Mn^{4+}
Low volatile elements: Ti^{4+}, Cu^{2+}, Mo^{6+}, W^{6+}, V^{5+}, Zn^{2+}, Zr^{4+} (almost 100% remained in sample)

It was not possible to measure the content of Li, Ba, Nb, Ta and B but other researchers found that most of the Ba, Nb and Ta remain in the sintered samples [37,40], while Li_2O was found to be relatively nonvolatile at elevated temperature [5].

As it is obvious, the content of the added elements is not constant in all burnt samples, since each element has a different volatility. However, we have chosen to have a constant percentage of added oxides in the raw meal for two reasons: (i) it is more convenient to control the composition of the raw mix than the composition of the clinker and (ii) even the elements with increased volatility and small retention in clinker may considerably affect the reactions that take place before their removal from the mixture.

Our results concerning the volatility are in general agreement with previous publications concerning the volatility of minor elements during the sintering of cement raw mix. Minor deviations are mainly due to the variety of the starting materials and the burning conditions. It must be noted that the thermal treatment of the samples was performed as a batch operation in a laboratory electrical furnace. In industrial practice, the evaporation of heavy metals depends on the composition of the raw meal, burning conditions and atmosphere (oxidizing or reducing) during the burning process. The high temperatures during the burning process, together with the usual operating conditions in the rotary kiln system, "mobilize" the trace elements contained in the materials used. In many cases, the presence of alkalies or chlorine in industrial raw meals, increases the volatility of certain elements that form volatile chlorides or alkali salts which participate in the so-called alkali cycle. Especially in the case of Pb, the emissions are raised to a noticeable extent when chloride is present in the raw meal due to extended formation of lead chloride.

The XRD studies, conducted in samples that were burned at both 1200 °C and 1450 °C, showed that the diffraction patterns correspond to a structure of a typical clinker, obtained at the above temperatures. The dominant phases

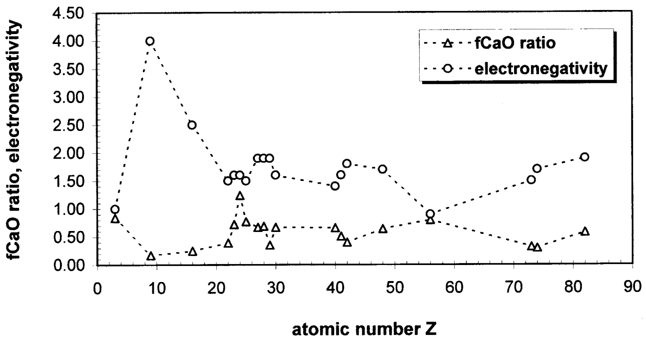

Fig. 4. fCaO ratio at 1450 °C and electronegativity (according to Pauling) of the added elements in relation to their atomic number.

(alite, belite, calciumaluminate and calciumaluminoferrite) were well crystallized, giving peaks at the common 2θ values. There are some modifications in the XRD pattern of the doped samples that may be indications concerning the formation of new phases but, due to the complexity of the pattern and the small amount of the added oxides, it was not possible to identify any of them. Further investigation is required in order to identify completely any new compounds that may be formed with the incorporation of the added ions and the temperature limits for the formation and decomposition of relative intermediate phases.

The incorporation of minor elements in clinker and their effect on the raw mix sintering and the structure of the clinker minerals are a complex physicochemical phenomenon. In the present work, it is shown that (i) there is a correlation of the effect of introduced cations and their electronic configuration and (ii) the well-known effect of minor compounds on the formation and the properties of the melt can be reflected on the overall reactivity of the cement raw mix. Further experiments concerning the effect of varying content of added compounds on the reactivity of the mixture, the volatility of the elements at intermediate temperatures and the structure of the clinker minerals are in progress.

4. Conclusions

From the present study the following conclusions can be drawn, concerning the effect of selected cations on the reactivity of the $CaO-SiO_2-Al_2O_3-Fe_2O_3$ system:

- The effect of foreign cations on the reactivity of the $CaO-SiO_2-Al_2O_3-Fe_2O_3$ system, at high temperature, is directly related to the electronic configuration of these ions.
- At 1200 °C, the reactivity of the mixture is greatly increased in the presence of Cu and Li oxides. Based on their effect at 1450 °C, the added elements can be divided into three groups. W, Ta, Cu, Ti and Mo show the most positive effect, decreasing the fCaO content by 30–60%, compared with the pure sample. Cr and B cause an increase of fCaO content, while the rest of the elements exhibit a marginal positive effect.
- Based on their volatility at 1450 °C, the added elements can be divided into three groups of low (Ti^{4+}, Cu^{2+}, Mo^{6+}, W^{6+}, V^{5+}, Zn^{2+}, Zr^{4+}), moderate (Cr^{6+}, Co^{3+}, Ni^{2+}, Mn^{4+}) and high volatility (Cd^{2+}, Pb^{2+}).

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