SINTEF REPORT

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Effect of mineralizers in cement production

State of the art

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ABSTRACT

Available literature on mineralizers has been reviewed, in particular the effect of mineralizers on the combination of free lime from decomposition of limestone in the cement kiln.

Zinc and fluorides are classical good mineralizers and zinc may already be added to the kiln through the use of spent tyres as alternative fuel.

Chromium is an interesting mineralizer from a technical point of view that also promotes the strength evolution of the resulting cement. However, it is not recommended due to its potential negative impact on workers health (eczema) and on the environment during leaching from concrete products.

Cupper oxide (CuO) seems to have a very good effect as mineralizer at dosages of 1% of clinker mass, and at the same time cupper is a relative abundant element with a rather low potential impact on environment through leaching from concrete. It may also be added as cupper ore available in Norway, as the sulphides will be oxidised in the cement kiln to sulphates acting further as mineralizers. Thus, copper ore as mineralizer is proposed as an activity within COIN.

KEYWORDS	ENGLISH	NORWEGIAN
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Foreword

COIN - Concrete Innovation Centre - is one of presently 14 Centres for Research based Innovation (CRI), which is an initiative by the Research Council of Norway. The main objective for the CRIs is to enhance the capability of the business sector to innovate by focusing on long-term research based on forging close alliances between research-intensive enterprises and prominent research groups.

The vision of COIN is creation of more attractive concrete buildings and constructions. Attractiveness implies aesthetics, functionality, sustainability, energy efficiency, indoor climate, industrialized construction, improved work environment, and cost efficiency during the whole service life. The primary goal is to fulfill this vision by bringing the development a major leap forward by more fundamental understanding of the mechanisms in order to develop advanced materials, efficient construction techniques and new design concepts combined with more environmentally friendly material production.

The corporate partners are leading multinational companies in the cement and building industry and the aim of COIN is to increase their value creation and strengthen their research activities in Norway. Our over-all ambition is to establish COIN as the display window for concrete innovation in Europe.

About 25 researchers from SINTEF (host), the Norwegian University of Science and Technology - NTNU (research partner) and industry partners, 15 - 20 PhD-students, 5 - 10 MSc-students every year and a number of international guest researchers, work on presently 5 projects:

- Advanced cementing materials and admixtures
- Improved construction techniques
- Innovative construction concepts
- Operational service life design
- Energy efficiency and comfort of concrete structures

COIN has presently a budget of NOK 200 mill over 8 years (from 2007), and is financed by the Research Council of Norway (approx. 40 %), industrial partners (approx 45 %) and by SINTEF Building and Infrastructure and NTNU (in all approx 15 %). The present industrial partners are:

Aker Kværner Engineering and Technology, Borregaard LignoTech, maxitGroup, Norcem A.S, Norwegian Public Roads Administration, Rescon Mapei AS, Spenncon AS, Unicon AS and Veidekke ASA.

For more information, see www.sintef.no/coin

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1 Introduction

Mineralizers are compounds (mostly inorganic) which influence the process of reactions in the solid, liquid and solid liquid interface face during burning of cement clinker. The possible effects can be summarized in changes of the chemical, mineralogical, structural, textural, mechanical and physical properties. The effects of the mineralizers can often be regarded to specific elements in the compound added to the cement raw mix. Only small additions of selected elements, often referred to as foreign ions, can alter the properties of the melt extensively. The modified properties can easily be seen in terms of reactivity and burnability of the raw mix. Mineralizers can be added to the raw mix as pure compounds, constituents of wastes, alternatively fuels and secondary raw materials.

Extensive literature exists regarding this area of research. In spite of this, it is not easy to draw systematic conclusions with regard to the effect of specific elements due to the diversity in materials used and different techniques applied as recognized earlier (Kolovos et al. 2002). The overall driving force for using mineralizing agents is to improve and control the reactivity of the clinkering phases in order to increase the efficiency of the burning process. Compared to a normal Portland cement clinker, this often result in sufficient reaction combinations of the major clinkering oxides at lower temperatures which obviously is environmental beneficial. Over the past decades the cement production industry has put much effort in trying to reduce the burden on the environment, i.e. reduce the greenhouse gas emissions as well as more energy effective clinker production.

The world focus on the climate changes due to emission of CO_2 has also put a pressure on the different industry sectors that release CO_2 during production. Most of the CO_2 release, when producing cement, is regarded to the decarbonation of the limestone in cement raw feed ($\sim 60\%$). Reducing the release from this well known process can only be done by substitution of the limestone and chalk by other Ca sources in the cement raw mix. Since these types of rock are the only large scale Ca sources available for production of cement, replacement seem to be difficult. To deal with this issue, one way is to produce cement clinkers with changed chemical and physical properties (e.g. with the aid of mineralizers) which for example can be seen in changed hydration properties and final strength when refined and used as final cement. Another way to deal with the decarbonation issue (indirectly) is to produce cement clinker that is suitable for the production of blended cements (fly ash and slag). The latter gives a significant positive contribution to the environment as less cement clinker is used per kg (dilution) cement produced and the blended cements are today used world wide.

The other major source of the release during production of cement is the CO_2 emitted during the heating and burning ($\sim 30\text{-}40\%$) as a consequence of both, electric energy used for heating and the release when fossil carbon is used as fuel. It is quite common today to partly replace the conventional fuel with alternative fuels (waste organics, natural gas, etc.) in order to reduce the CO_2 emissions. Burning waste organics or hazardous waste is not only beneficial in reducing the emissions but it also solves a significant waste management problem. When using alternative fuels, mineralising effects can also be seen (e.g. decreased sintering temperatures, changed surface tension of the melt etc.) due to specific constituents in the waste. The principles of making cements with reduced CO_2 emission and/or less clinker content are thoroughly reviewed elsewhere[1].

Despite the effort that has been put into research and development regarding the environmental issues in cement production (improved burnability, blended cements, alternative fuels etc.), the

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[1] COIN/T1 Advanced cementing materials/State of the art report nr. 1: *"Principles of making cement with reduced CO_2 emission"* and State of the art report nr. 2: *"Making cements with less clinker content"*.

potential for further improvements is still believed to be significant. This is due to the fact that there are still chemical processes during clinkerization as well as in hydration that not yet are fully understood, which may be of significance. In addition, when facing parameters that affect the properties of the final cement at different stages in the production process (raw feed input, kiln parameters, grinding and blended properties), it makes the system even more complex. On the other hand, this also gives the opportunity to explore new reactions which lead to improved cementing properties. It is therefore obvious that mineralizers used for the above mentioned purposes in cement production is an important issue and still have great possibilities to improve the cement clinker reactions as well as the properties of the final cement.

This report will review this topic and give the current status in a concise way. Attention will be given to issues regarding mineralizers that have possibilities for improving both the clinker reactions and the cementing properties. Improvements that finally will relieve the environmental burden will be given priority.

2   Desirable effects of mineralizers

The effects of mineralizers have been explored during several decades. This literature survey is focused on the effects when the mineralizer is introduced by the cement raw mix prior to burning. Mineralizers can be active at several stages in the process. A useful picture of the burning process is given in Figure 1. The raw meal largely consists of ground limestone, clay and quarts. Some corrective (auxiliary) materials as iron oxide and bauxite (not shown) are also interground. Figure 1 shows in principle the main reactions/mechanisms as temperature increases including:

- Calcinations (decarbonation) of the limestone at 700-900 $^{\mathrm{o}}$C: $CaCO_3 => CaO + CO_2$,
- transformation of the quarts,
- calcium aluminates ($C_{12}A_7$), dicalcium silicate (belite = C_2S) and the ferrite phase [$C_2(A,F)$] formation from 700 $^{\mathrm{o}}$C,
- at 1300 $^{\mathrm{O}}$C the molten phase is starting to develop and formation of the tricalcium silicate (Alite = C_3S) is formed by the reaction combination: $C_2S + CaO => C_3S$.

After peak firing temperatures the melt is rapidly cooled. The cooling regime is important in order to keep undesirable clinker phase changes (C_3S decomposition, polymorphism of C_3S and C_2S) as low as possible.

Mineralizers are reported to affect decarbonation, stabilize the hydraulic belite polymorphs (α- and β-forms), the formation of alite and properties of the melt. Substances that are affecting the latter are also called fluxes. Reaction temperatures are often decreased when applying mineralizer(s) which means increased burnability of the mix.
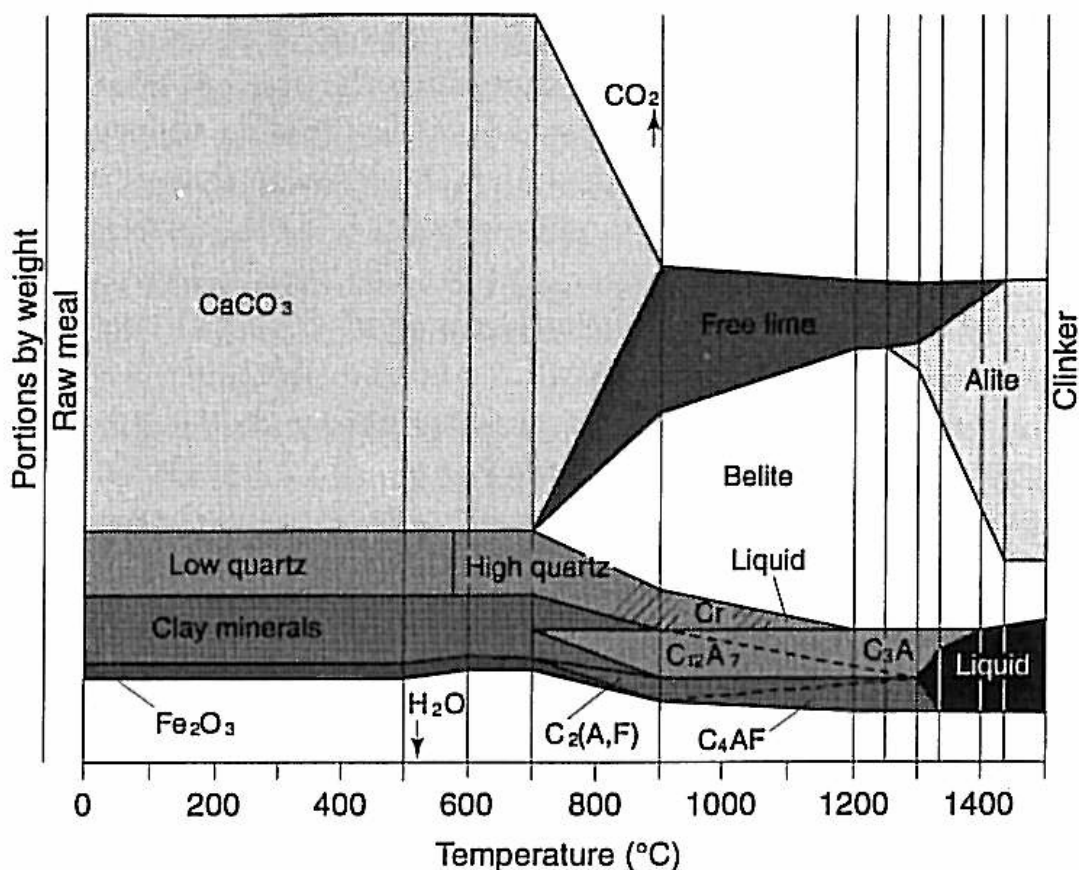
Figure 1 Reactions taking place in the burning of the raw meal to Portland clinker (Hewlett 1998).

In view of the main process given in Figure 1, the effects of adding a mineralizer to the cement raw mix can be the following:

- Decreasing burning temperature due to changes in the reactivity and burnability,
- acceleration of the clinkerization reactions (higher activity on the clinker minerals) at lower burning temperatures, e.g. fluorosilicates,
- alteration of surface tension (e.g. SO_4) and viscosity of the melt,
- formation of intermediate phases as well as more stable phases when approaching firing temperatures,
- controlling the polymorphism of clinker minerals,
- influencing properties of the produced cement (e.g. hydraulic activity and strength development).

An extensive literature review was carried out by Moir and Glasser (1992). They explored the effects of minor components in view of the periodic table of elements. In this review the elements were divided into the following groups:

- Alkalis
- Transition metals
- Halogens
- p-block elements

In the following sections these groups will form the basis for this report. In addition, a section concerning combined effects will be dealt with.

3 Effects of specific compounds or elements

3.1 Alkali and alkaline earth elements (Na, K, Li and Ba)

The overall clinker reactivity is increased by the presence of alkalis. Gies and Knöfel (1986) showed that when Na_2O was incorporated in C_3A, in the absence of SO_3, it resulted in reduced reactivity of this phase. However, they also explained the overall enhanced clinker reactivity by Na and K substitution into C_2S. With high sodium content in belite the burning temperature decreased approximately 100 ^{o}C and also good strength development was found.

Vonlampe and Seydel (1989) controlled the polymorphism of the belite phase in their attempts to develop active belite clinkers. By fast cooling and ~1.5% equivalent Na_2O, an ά-C_2S phase was identified and increased strength were measured compared to conventional β-C_2S clinkers. Also with lower alkali contents they found a C_2S polymorph (β*) with slight, but significant, different reflection angle which also showed increased strength development. The benefits of active belite cements are reduced energy consumption by clinker production at lower firing temperatures and hence also decreased NO_x emissions. It also allows the use of lower grade limestone. The lime saturation factor (LSF) lies typically in the range 75-80% (Hewlett 1998). Normal Portland clinkers contain (by weight) 15-30% C_2S and 50-70% of C_3S (Hewlett 1998) while (high) belite cement clinker contains more than 50% C_2S (Chatterjee 1996). Hence, production of such clinkers reduces the CaO consumption and less CO_2 is thus emitted during calcinations per kg clinker produced. Cement production at lower firing temperatures is also beneficial to the kiln material in terms of longer life time, which in turn obviously reduces the production costs.

When examining the effects of the primary alkalis (Na and K) it is important to take into consideration the important reactions with sulphates in the kiln. In Figure 2 the different sources of sulphur are shown and how the different forms react to form $CaSO_4$ and $(Na,K)_2SO_4$ in the cement kiln (Hewlett 1998). A part of the alkalis react most likely in a volatilisation-condensation cycle keeping in mind that the solid material flows through the kiln in opposite direction of the gas flow. The alkali oxides are volatilised and react with SO_3 to form the alkali sulphates as shown in Figure 2. $CaSO_4$ formed late in the burning zone decompose incongruently, thus leaving free CaO as the residue. Hence, the form of which Na and K are retained in the produced clinker (e.g. as sulphates or substitution in to the clinker minerals) are interdependent on the sulphur in the kiln system. This, in turn, directly affects the early hydration properties through the hydration of C_3A, in terms of available contents of the highly soluble alkali sulphates. Strunge et al. (1990) found that optimum clinker formulation existed in regard to LSF and they also found that K_2O increased the C_3A reactivity. Richartz (1986) found that the importance of alkali sulphates increased at higher alkali contents. He suggested 1% K_2O as a threshold and found that the presence of SO_3 reduced the formation of alkali solid solution in aluminates and thus decreased hydraulic activity. In a recent study (Morsli et al. 2007) 10 laboratory belite clinkers were synthesised with various amount of alkali (Na, K) carbonate and different SO_3 contents added as gypsum. They demonstrated the "activation" of the belite clinker by the effect of mineralizers (alkali and sulphate) and by the appropriate cooling rate. In this study the different polymorphs (α-C_2S α$_H$'-C_2S and β -C_2S) of C_2S, were identified and quantified. The alkalis promoted the formation of the highest temperature polymorphs (α and α$_H$'). It can also be seen that the α-C_2S did not form when K was added (up to 2.0 wt.% K_2O) together with only small amounts of Na (0.12 wt.% Na_2O).
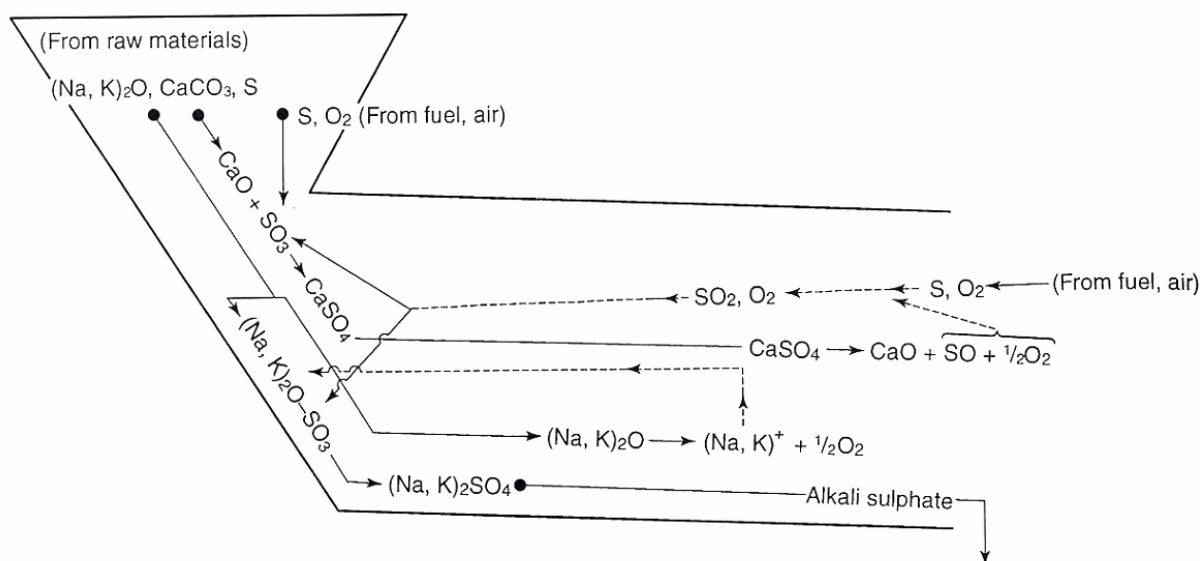
Figure 2 Overview of the alkali and sulphur cycle in the cement kiln (Hewlett 1998).

Apart from Na and K small amounts of Li_2O has been reported to increase the reactivity of the raw mix (Bhatty 1995, Mathur et al. 1992). However, contents above 1% are inhibiting the free lime combination and thus the conversion of C_2S to C_3S. In the more recent study of Kolovos et al. (2002) the reactivity was measured in terms of the remaining free CaO (fCaO) at 1200 and 1450 $^{\circ}C$ by adding Li_2O among a number of other oxides (separately). Li_2O (and CuO) was found to have significant effect on the clinker reactivity at 1200 $^{\circ}C$. This was explained by the earlier decomposition of $CaCO_3$ as shown in their TGA measurements. At 1450 $^{\circ}C$ they only found marginal positive effects.

Barium has been reported to decrease the clinkering temperatures, accelerate reactions and stabilise β-C_2S (Bhatty 1995, Ghose et al. 1983, Katyal et al. 1999a). In Katyal et al. (1999a) the effect of $BaCO_3$ on pure C_3S was studied. Maximum conversion of C_2S to C_3S was found at 0.5% addition (expressed as BaO). Up to the miscibility level (1.8%) they suggested that BaO was present as solid solution with C_3S at 1450 $^{\circ}C$. Above this level C_3S was destabilised and disintegrated into C_2S and free CaO. In Kolovos et al. (2002) the addition of 1.0% BaO to their CaO-Al_2O_3-Fe_2O_3-SiO_2-phase system had small (but significant) effects on the reduction of the fCaO at 1200 and 1450 $^{\circ}C$. This illustrates the fact that there are several factors that are playing a role and make such comparisons difficult, including one or multi component system, differences in the heating and cooling regime, contamination of impurities from other phases etc. The complexity of the system further increases when moving from laboratory scale to the real cement kiln system where the level of foreign compounds is higher and different reaction cycles has to be considered due to the nature of the material stream and gas flows. However, it is emphasised that very often the same tendencies are found as in the barium case. Improved mineralizing effects are also often encountered when more than one active compound are considered (e.g. the use of by-products). Mullick et al. (1997) improved the burnability (decrease in fCaO) by the use of barite together with fluorspar and Rajczyk and Nocun-Wczelik (1992) used a barium containing by-product in the study of belite cements.

3.2 Transition metal oxides

The properties of the melt are indeed important for the formation and crystal growth of C_3S. Viscosity and surface tension are important parameters that have to be considered. Compounds that are changing the properties of the melt in such a way that more melt is formed are known as fluxing agents. Mineralizers are defined as substances, which through some mechanism(s), increase the rate of reactions between solid phases, in the molten state or at the solid-melt interface. Both groups of substances are often mentioned in the same context due to the close interconnections or the substances belong to both groups. Lowering the surface tension and the viscosity of the melt, normally formed at above 1340 $^{\circ}$C, will increase the diffusivity of the clinkering species. This, in turn, leads to increased rate of combination between C_2S and free CaO and thus enhanced C_3S formation. Distinguishing between fluxing and mineralizing effects will in this section not necessarily be pointed out.

Transition elements consist of the metals in Groups IB through VIIB (including Group III) in the periodic table. The elements that belong to this group which also have been reported in the literature are: Cd, Co, Cr, Cu, Fe, Mn, Mo, Nb, Ni, Ta, Ti, V, Zn, Zr and W. As early as in 1980 a relationship between the transition metals and the viscosity of the melt was established (Timashev 1980). Timashev showed that the melt viscosity decreased as the oxidation state increased (expressed as ionic charge to radius ratio) which also is equivalent with an increase in strength of the Me-O bond. This nice relationship is shown in Figure 3. The same author also found the same relation with the surface tension, though with a larger scattering.
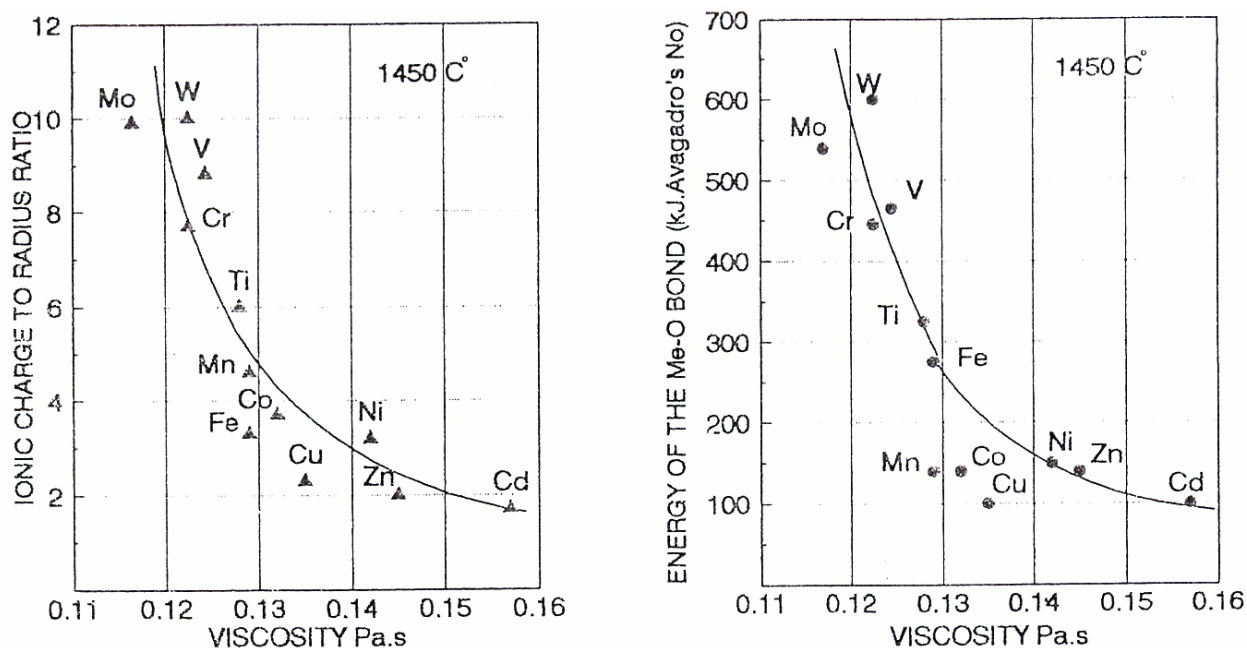

Figure 3 Effects of the ionic charge and the energy of the Me-O on the viscosity (Timashev 1980).

When exploring the mineralising effects of the transition metals it is very useful to recall which principle clinker phases the different metals are expected to incorporate in. The study of Hornain (1971) is referred to in journal articles as well as in text books. In this study it was found that the main concentrations of the first series transition metals were found in the ferrite phase (C_4AF), as shown in Figure 4. The exceptions were Cr and V (vanadium) which also concentrate in C_2S and C_3S.
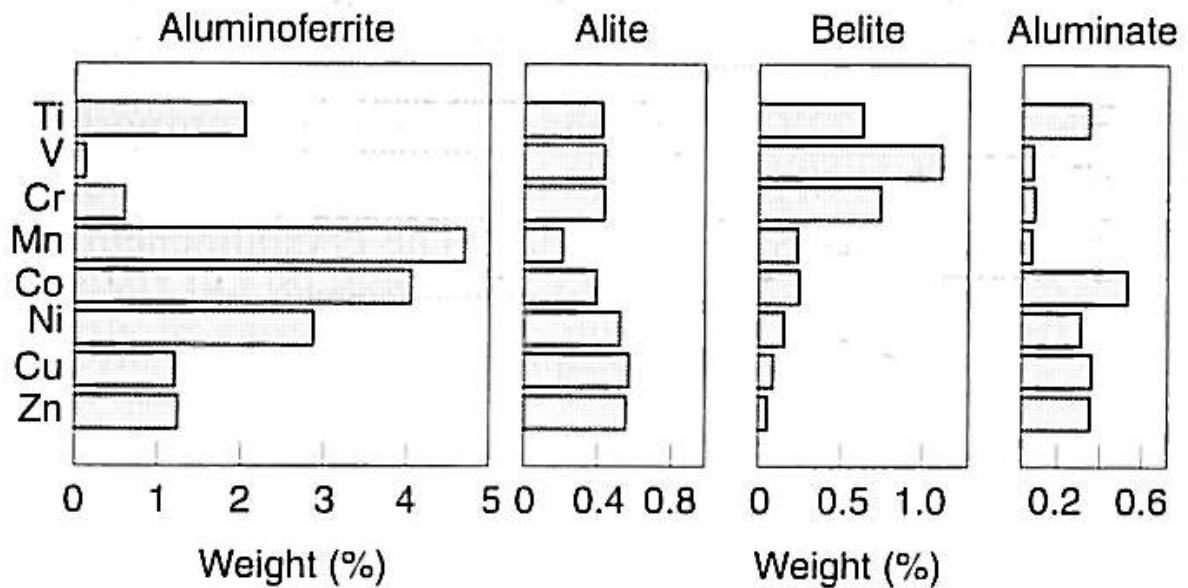
Figure 4 Distribution of some transition elements in the principle clinker phases (Hornain 1971).

3.2.1 Ti, V, Cr and Mn

Titanium (Ti) promotes decarbonation, decrease the melt temperature and the free lime content. It is strongly dependent of concentration (Bhatty 1995, Katyal et al. 1999b). Vanadium (V) is present in the clinker as the oxide (V_2O_5) and V is reported to decrease the melt temperature, favour formation of big alite crystals and stabilize β-C_2S (Moir and Glasser 1992). Considerable efforts have been used in order to stabilize β-C_2S phase. Of the transitions metals, only Cr^{6+}, V^{5+} and Mn^{7+} seems to have this property according to Xiuji and Shizang (1986). Of these elements, in turn, only chromium (Cr) had the ability to increase the C_2S activity according to Moir and Glasser (1992).

The oxidation state of chromium (i.e. Cr^{3+}, Cr^{4+}, Cr^{5+} or Cr^{6+}) is of health concern as Cr^{6+} is well known to give negative effects when it is brought in contact with human skin (cause eczema). The actual oxidation state of Cr in the clinker is dependent on the burning conditions. Under oxidising burning conditions the Cr (IV-VI) forms will dominate. Feng and Yan (1990) found that Cr^{4+} and Cr^{5+} were present in C_2S as distorted Si tetrahedra under oxidising conditions. However, when brought in contact with water they normally disproportionate to yield only Cr^{3+} and Cr^{6+} (Hewlett 1998). In the cement clinker Cr (also V) most likely substitute for Si. It has been reported that levels above 0.5% stabilise C_2S in such a way that C_3S formation was reduced. However, cements usually contain less than 0.02% Cr (total). In a recent national study (Petkovic et al. 2004) an upper limit of 0.011 % Cr (III +VI) in crushed concrete, used for road base applications, was proposed in the national road authority guidelines (Petkovic et al. 2006). This acceptance limit was risk based and it was assumed that no more than 50% Cr^{6+} was present. Taking the latter into account and the fact that normal cement contents in concrete are 300-400 kg/m³, the proposed acceptance limits for Cr will cover most of the cements used today (translates to about 0.07% Cr in cement). The acceptance limit, however, indicate that increased Cr levels in the cement could be of environmental concern when the material is recycled and used in the described scenario.

Stephan et al. (1999a) prepared C_3S in laboratory contaminated with different concentration levels of Cr^{3+}, Ni^{2+} and Zn^{2+} added as oxides. It was found that the fCaO decreased with additions of Cr up to 0.5 % and this positive effect disappeared above this level. In the following up study (Stephan et al. 1999b), pure C_3A and C_4AF were prepared with the same metals at the same elevated concentrations levels. They found no change in the modification of these phases. When metal concentration was as high as 5 %, significant amounts of fCaO could be detected in the C_3A. This indicated the increased defect concentration of the crystal lattice of C_3A. In contrast, addition of these metals did not affect the C_4AF (ferrite) in terms of increased fCaO. It is recalled that the general formula of this phase is $C_2(A_xF_{1-x})$ and when x = 0.5 we have the brownmillerite (C_4AF) phase. I an actual clinker, the ferrite phase can constitute solid solutions for a range of x-values (0 - 0.7). This is the reason why many elements are accumulated in the ferrite phase. It is also worth mentioning that Cr^{6+} was identified by XRD as $C_4Al_6O_{12}CrO_4$, both as a separate phase and in solid solution with C_4AF.

Manganese (Mn), as many of the transition elements, can occur in different oxidation states. Xiuji and Shizang (1986) reported that Mn^{4+} was not able to stabilise β-C_2S in contrast to the higher valence species. Under normal burning conditions Mn is distributed in the clinker as Mn^{2+} and Mn^{3+} species. The redox (reducing or oxidising) conditions are decisive for the presence of the valence state. It is notable that if reducing conditions prevail (less oxygen in the kiln, reducing agents in the raw meal etc.), Mn^{2+} seem to substitute with Ca. Under oxidising conditions (oxygen rich kiln atmosphere), Mn^{4+} are mostly concentrated in the ferrite phase (Hewlett 1998). Puertas et al. (1988) also demonstrated the importance of the valence state in their study of manganese solid solution formation in C_3S and C_2S. It was shown that Mn^{4+} under oxidising conditions substituted for Si^{4+} and Mn^{2+} under corresponding reducing conditions substituted for Ca^{2+} in C_3S. The substitution limits were found to be 0.72 and 2.54 % for Mn^{4+} and Mn^{2+}, respectively, and are nicely confirming the selectivity.

3.2.2 Co, Cu, Ni and Zn

Co (Cobalt) is to a large extent concentrated in the ferrite phase, see Figure 4. According to Bhatty (1995) the mechanism is substitution of Co^{3+} with Fe^{3+}. Early studies (Odler and Abdul-Maula 1980 part I-II) showed that Co to some extent enhance the combination of C_3S and reduce the fCaO at 1200 ^{o}C. This effect increased at 1300 ^{o}C. If we look at Cu in the same studies, significant reduction in fCaO at both temperatures were measured. In fact Cu acted both as mineralizer and a flux. Kakali et al. (1996) studied the effect of CuO addition to a cement raw meal. They found that the fCaO was reduced, indeed in the temperature region 1000-1300 ^{o}C. Moreover, the sintering temperature was lowered. In the recent study of Kolovos et al. (2002), they basically confirmed the positive effect of CuO (at 1200 and 1450 ^{o}C) among the elements most encountered in the field of mineralizers. Figure 5 gives a nice overview of some of the results and illustrates the effect of CuO. In Kolovos et al. (2002) CuO and ZnO were added separately to the raw mix of industrial origin and positive effects were indeed found for both elements. Hou et al. (2007) confirmed the mineralizing effect of CuO for a special prepared high C_3S cement clinker (73%). With the addition of 1% CuO a remarkable effect in the burnability (fCaO) was found in the temperature region 1200-1450 ^{o}C. This proves that Cu is applicable to different clinker types (high C_2S and high C_3S).
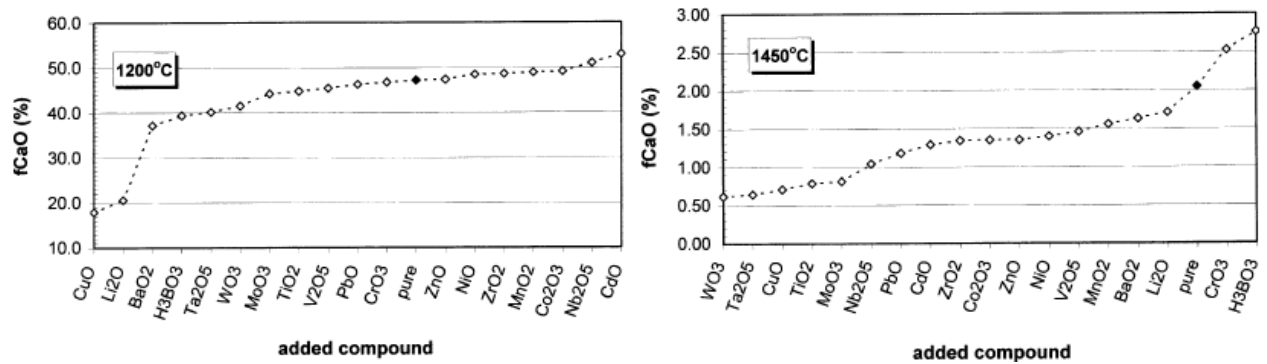
Figure 5 Effect of different elements on the burnability (fCaO) at 1200 and 1450 °C (Kolovos et al. 2002).

The mineralizing effect of nickel (Ni) is reported to be marginal as concluded in Stephan et al. (1999a-b) where the effects of NiO on the formation of C_3S, C_3A and C_4AF where studied. It can be seen that Ni preferentially concentrates in the C_4AF phase (Figure 4) and that Ni has some effect on the burnability at normal firing temperature only (Figure 5). Stephan et al. (1999a) did report that increased liberation of heat was measured during hydration of C_4AF.

The last element of interests in the first series transition metals in the periodic table is zinc (Zn). Odler and Schmidt (1980) stated that the clinker could contain up to 0.5 % Zn without having negative effects of the cement properties. Moreover, Odler and Abdul-Maula (1980) found that 1 % ZnO promoted the combination of free lime at 1300 °C whereas smaller effects were measured at 1200 °C in agreement with the trend shown in Figure 5. Kakali and Parissakis (1995) found that addition of ZnO to the raw mix in the range of 2-4%, decreased the clinkerization temperature by 100-150 °C. At *normal* temperatures (1450 °C), this leads to increased melt formation and ZnO is thus also behaving as a flux. They concluded that the addition of ZnO not only affected the melt, but also promoted the combination of free lime and therefore influenced the sintering reactions. They also found that clinker contents of ZnO above 3% did not increase the burnability. This is, however, not the solubility limit for Zn in clinker. In another study (Murat and Sorrentino 1996), 10% of $ZnCl_2$ (among other metal salts) were added to the raw mix and approximately 50 % of this in turn was found to be taken up in the clinker phases. They also confirmed that alite crystals increases with increasing amount of Zn and high amounts will eventually retard the setting of the cement.

Bolio-Arceo and Glasser (1998) studied the CaO-ZnO-Al_2O_3 (C-Z-A) and CaO-ZnO-Fe_2O_3 (C-Z-F) system and identified $C_6Z_3A_2$ and C_3ZA_2 phases. They concluded that the former coexisted with C_3S, C_2S and the clinker liquid phase. In their subsequent publication (Bolio-Arceo and Glasser 2000) they added 1.5% ZnO to an industrial raw meal. It was emphasised that in the presence of a melt (realistic conditions), Zn solid solution in alite and belite probably were low (~ 0.1%). Instead, co-crystallisation of $C_6Z_3A_2$ together with C_3A, ferrite and secondary belite occurred upon cooling. The setting time for the mineralised clinker was measured to be the same as for reference sample and improved strength was reported.

3.2.3 Second and third transition elements

The elements encountered in the field of mineralizers in these groups, are usually zirconium (Zr), niobium (Nb), molybdenum (Mo), cadmium (Cd) and tungsten (W). These elements are, however, considerable less often encountered in the literature compared to the first series transition metals. Up to the year of the comprehensive review of Moir and Glasser (1992) only a few studies where available. Positive effects, however, of the addition of Mo and W have been found. In Figure 3 we

can see that Mo and W are significantly affecting the viscosity of the melt which in turn increase the diffusion of the reactants in the melt. Kakali et al. (1990) also concluded that viscosity decreased with the addition of these elements (as oxides). Moreover, in the recent study of Kolovos et al. (2002) the fCaO was found to significantly be reduced when adding these elements (1 %), see Figure 5. This is in accordance with the earlier studies showing increased diffusion in the melt causes increased consumption of free lime.

The effects of using Nb and Zr are in general not expected to have large mineralising effect and not many studies exist. The mineralizing effect of up to 1% addition of Nb_2O_5 was found to be negligible (Kakali et al. 1990). Moreover, no effect was observed on the strength development for cement paste with such addition of Nb_2O_5. It is noteworthy to mention that in the more recent study, see Figure 5, it can be seen that addition of 1% Nb_2O_5 did reduce the f(CaO) significantly at 1450 ^{o}C and that an adverse effect was observed, however, at 1200 ^{o}C.

The literature concerning the mineralizing effect of Zr is scarce. Bhatty (1995) reported that increased early strength for small additions of ZrO_2, whereas Kakali et al. (1989) found reduced early strength with 1-1.5% additions. In general, addition of ZrO_2 to the raw mix is not believed to have large impact on the heating and cooling reactions (Kolovos et al. 2002). In Figure 5 we can see that ZrO_2 showed the same negative behaviour as for Nb_2O_5 at 1200 ^{o}C. At 1450 ^{o}C even smaller positive effect was observed compared to Nb_2O_5.

In relation to cement burning, Cd is along with Pb the most volatile constituent of the transition metals under consideration. In the systematic study of Kolovos et al. (2002) they concluded for both elements that < 20 % of the added quantity was retained in the clinker. Although the literature is scarce, addition of CdO to the raw meal is believed to increase the burnability by lowering the melt temperature (Odler and Abdul-Maula 1980b). In Figure 5, this is confirmed only to a certain extent. The fact that cadmium is a carcinogenic metal significantly reduces the use of such a mineralizer.

3.3 Halogens: F, Cl, Br and I

The halogens (F, Cl, Br and I) are mainly introduced by the fuel (coal) and also to some extent through the raw materials. Marine clay for example is often containing chlorides. The halogens volatilise as alkali halides in the burning zone and condense in the cooler region (heat exchanger) where they form low melting point mixtures. They also cause deposits which limits the total input of halogens in the feedstock. The halogens are highly reactive and this can be explained from their basic chemical nature. Their locations in the periodic table of elements tell us that they are close to fulfil the octet rule. This means that they are strong oxidising agents and therefore tend to have strong complexation abilities. These features are strongest for F^- and tend to decrease as we move downwards this main element group. This in turn explains the number of reactions that halogens are involved in.

During burning, the alkali halides create a volatile cycle in the kiln which leads to accumulation of halides in the clinker and the kiln dust. This results in max tolerable input contents of chlorides of 0.03% and 0.04% for preheater and precalciner kilns respectively. Chlorides are also restricted to a level in the finished cement that not causes reinforcement corrosion. This means that it is not much *"concentration space"* left to play with chloride additions for cements used in concrete with reinforcement. Mineralising effect has been reported (Odler and Abdul-Maula 1980) and levels of 0.5-1.5% $CaCl_2$ were actually found to reduce the reaction combination. In the production of low alkali clinker, $CaCl_2$ has also been added in order to aid the volatilisation of the alkalis. Alinite cements are clinkered at temperatures below 1200 ^{o}C and received much interest in the early1980. In this clinker $Ca_{11}(Si_{0.75}Al_{0.25})_4O_{18}Cl$ (alinite) is formed instead of C_3S (alite). Eventually, alinite

cements with acceptable early strength development have also been reported (Moir and Glasser 1992). When combining $CaCl_2$ with $CaSO_4$ several new phases were developed and C_3S was reported to form at 1200 ^oC (Chen and Fang 1989, Damao and Daxi 1985).

The mineralising effect of fluoride is well known. Fluoride is a strong complexation agent and its reactions in clinker are complex. Fluoride is also a fluxing agent as the viscosity and surface tension of the melt is reduced. The mineralizing mechanisms in relation to C_3S formation is discussed below. Generally, the substitution of F^- for O^{2-} in C_3S demand charge compensation in terms of vacancies or interstitials (defects) to preserve the charge balance. These mechanisms occur only to a limited extent. In stead, a double substitution with Al^{3+} for Si^{4+} and of F^- for O^{2-} occurs in order to fulfil the electroneutrality principle in the crystal (Glasser and Marr 1980, Shame and Glasser 1987). This leads to extensive solid solution formation and this is well illustrated in Figure 6. It clearly shows that the thermodynamic stability of C_3S relative to C_2S has increased. The lower stability limit was obtained at a temperature below 1100 ^oC compared to a normal limit at 1250 ^oC. Moreover, addition of fluoride seems to stabilise the rhombohedral (R) form of C_3S to ambient temperature. The substituted C_3S showed excellent strength development. Other fluorosilicates are reported as $Ca_{6-0.5x}Si_2O_{10-x}F_x$ where substitution of F^- with O^{2-} occurs followed by defect formation (Ca vacancies) in order to maintain the electroneutrality.

Reaction of fluoride with aluminates is also commonly encountered as it reacts strongly with $C_{12}A_7$ thus forming $C_{11}A_7 \cdot CaF_2$ solid solutions. Fluoraluminates tends to increase the early strength development and forms the basis for some rapid hardening clinkers. It should be noted that $C_{11}A_7 \cdot CaF_2$ is not encountered in normal fluoride mineralized clinkers as it appears at F levels above 0.5 %, at firing temperatures lower than 1320 ^oC or with lower cooling rate than in conventional clinker production.
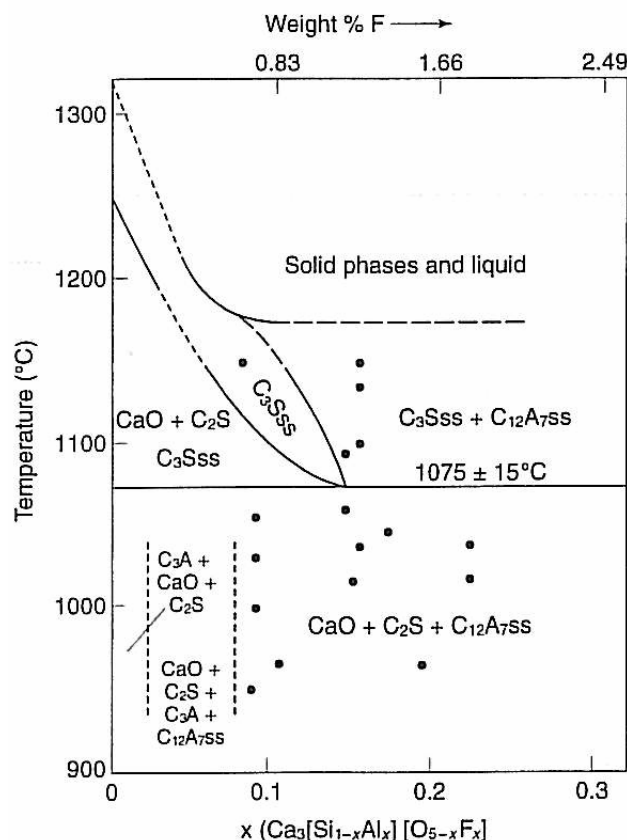

Figure 6 C_3S stabilised by addition of fluoride. Extensive formation of solid solution (ss) and theoretical C_3Sss is stable as low as 1075 ^oC when x = 0.15 (Glasser and Marr 1980).

If x = 0.15 (15 mol%) in Figure 6 the stoichiometric content of F in the $Ca_3[Si_{1-x}Al_x][O_{10-x}F_x]$ (C_3Sss) is 1.25 %. This is somewhat theoretical and assumes pure single phase alite. In a real clinker system we account for 60% C_3S and the fact that C_3Sss will not be a pure single phase, the corresponding F content in clinker is more close to 0.5 wt.%. Fluoride used in pure C_3S will decrease the reactivity towards water. In a real clinker system, however, contribution from alkalis, alumina and sulphate can in an optimised way actually increase the hydraulic activity. It was found by Moir (1983) that ~ 0.2% F in clinker was the optimum concentration for optimum early strength. This is somewhat in the same area, although lower, as the concentration needed for C_3Sss to be stable as low as below 1100 ^{o}C, see Figure 6.

This brings us to the fact that fluoride in combination with sulphates is a far more effective mineralizer than fluoride alone (Moir and Glasser 1992). The $CaSO_4$-CaF_2-Ca_2SiO_5 is explained in Giminez-Molina et al. (1991) and the apatite like structure fluorellestadite, $3C_2S·3CaSO_4·CaF_2$, was recognised up to the incongruent melting point at around 1240 ^{o}C. It was recommended to avoid the composition that favoured fluorellestadite due to its inertness. Borgenholm et al (1995) reported increased stability of the rhombohedral form of C_3S by combined mineralising effect from fluorine (fluorite) and sulphur (desulphurisation gypsum and high sulphur petcoke). The mineralised clinker achieved increased early strength development. By addition of 15-20% ESP (electrostatic precipitator) dust with the ground clinker, the hydration was further accelerated. No loss of strength was reported for addition of ESP up to 20%.

Recent studies (Emanuelson et al. 2003a, Emanuelson et al. 2003b) investigated F and SO_4 mineralized industrial clinkers. They concluded that it was the overall production process and the raw mix composition that determined the polymorphs of alite (C_3S) rather than the addition of mineralizers. This proves the complexity of assessing specific mineralising effects. Moreover, rhomboedral as well as monoclinic alite was identified in the two different clinkers tested.

3.4 P-Block elements

The most encountered elements in this group are sulphur (S) and phosphorus (P) and to a lesser extent also boron (B), lead (Pb) and antimony (Sb). The latter will be dealt with in a later section concerning secondary raw materials. Sulphur participates in the alkali sulphate cycle in the cement kiln as explained in section 3.1. Moreover, in a previous mentioned study (Emanuelson et al. 2003b), the mineralising mechanism on the silicates is a double substitution: $3Si^{4+} <=> S^{6+} + 2Al^{3+}$. In general, sulphur addition to raw mix is limited due to build-ups in the preheater and in the kiln. In addition, too high sulphur content in the final cement is not desirable. Adding gypsum to the raw meal as a mineralizer is therefore rare for the burning of normal Portland clinker. Raina and Janakiraman (1998) tested both gypsum and CaF_2 separately and in combination. They had a problem with too high free CaO in the finished clinker and additions of these mineralizers showed promising results. The best effect was obtained with the combination of 1% of each compound. The least effect was obtained by gypsum alone (0.5-1%) but significant improvement in the reduction of fCaO was still achieved. The compressive strength was improved in all of the measurements in the period of 3-28 days, even when only CaF_2 was used. Probably the strength gained during the first day of hydration was lower for the F mineralised clinker compared to the ordinary clinker. Emanuelson et al. (2003a) showed that the accumulated reaction heat of the clinker mineralised with CaF_2 was higher after hydration for half a day as shown in Figure 7.
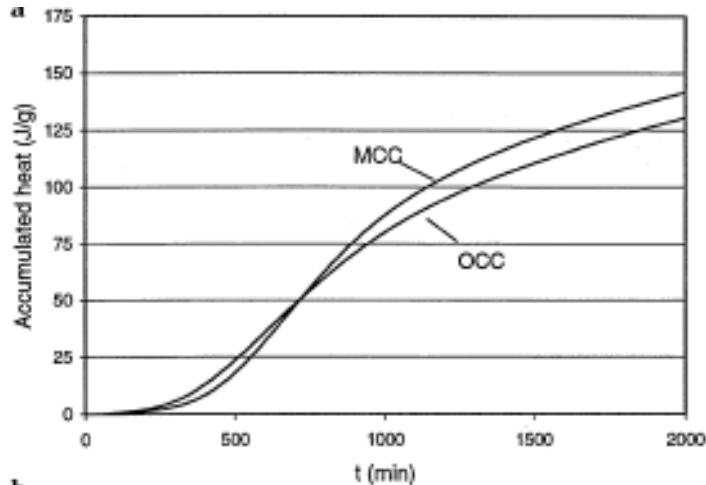
Figure 7 Accumulated heat of reaction for hydration of ordinary cement clinker (OCC) and CaF_2 mineralised cement clinker (MCC) (Emanuelson et al. 2003a).

Phosphorus (P) as mineralizer is relevant in relation to the use of alternative raw materials due to its presence in different industrial by products (see section 5) and also from burning animal and bone meal as alternative fuel. However, an early study (Gutt 1968) on the CaO-SiO_2-P_2O_5 showed a stabilisation effect of C_2S on the expense of C_3S formation. The mechanism is C_2S solid solution with C_3P ($3CaOP_2O_5$) with increasing phosphorus content.

In the more recent study of Kolovos et al. (2001) the effect of adding different anions to the raw mix was studied at 1200 and 1450 ^{o}C. They found that the chemical form (speciation) of the mineralizer added did not affect the fCaO content determined for sulphur and fluorine as can be seen in Figure 8. For phosphorus, however, the chemical form largely affected the burnability of the mix. The addition of 1% $Ca_3(PO_4)_2$ caused even higher fCaO at both temperatures compared to the reference. In contrast, a large reduction was determined by the addition of 1% $CaHPO_4$. This was unexpected as the PO_4^{3-} actually is unstable at the temperatures in consideration. It was also claimed in this study that PO_4^{3-} contents above 0.75% cause negative effects. It should be emphasised that 1% of $Ca_3(PO_4)_2$ and $CaHPO_4$ are equivalent to 0.6% and 0.7% PO_4^{3-} respectively, i.e. well below this limit.
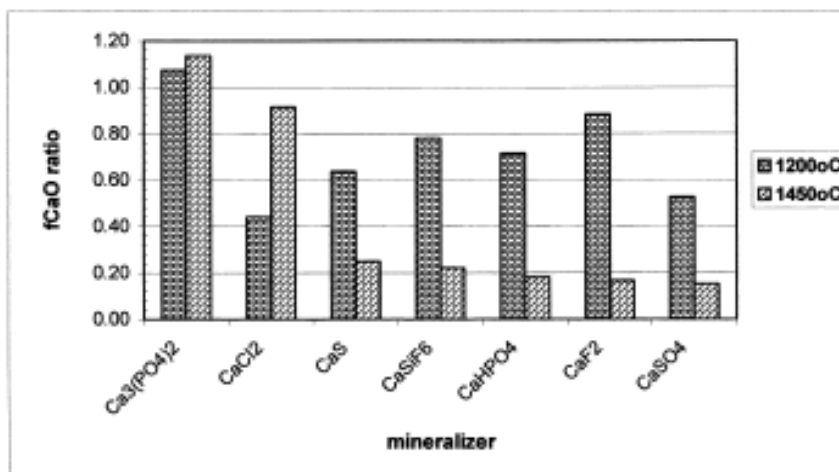

Figure 8 The fCaO ratio of mineralised samples relative to the reference sample (Kolovos et al. 2001).

Boron may be present in the raw materials and may very well act as a mineralizer as well as a fluxing agent. However, the overall effect on C_3S is negative since boron stabilise C_2S. According to Kolovos et al. (2002) it still is debateable, concerning the C_3S formation, whether boron stabilises C_2S or destabilise C_3S. However, earlier studies (Moir and Glasser 1992) pointed out that B_2O_3 was not found to be present as C_3S solid solution and the decomposition (destabilisation) was the likely explanation, i.e. $C_3S => C_2S + CaO$.

Concerning the boron mineralising effect on C_2S, extensive solid solution formation was found (Moir and Glasser 1992). The general formula is $Ca_{2-0.5x}[SiO_4]_{1-x}[BO_3]_x$ and the mechanism was proposed to be substitution of borate for silicate with formation of Ca vacancies. It was found that with increasing boron additions (x ~ 0.3) α-like C_2S polymorphs were formed. In view of these findings it seems that boron might be used in production of belite clinkers. The effect of 1% H_3BO_3 addition can be seen in Figure 5. The determined fCaO (free CaO) at 1200 ^{o}C was largely reduced whereas a significant negative effect was found at 1450 ^{o}C. This is in good agreement with our overall picture; enhancement of the belite phase and inhibition of the alite phase.

4 Auxiliary raw materials

Auxiliary materials are often called corrective materials and are added to the raw mix. Such materials are used if the primary raw materials (limestone, chalk and clay) do not have the appropriate chemical composition that favours the formation of the primary clinker phases. The following materials are in widespread use (Moir and Glasser 1992):

- o iron oxide (1-4%)
- o Silica sand (1-10 %)
- o Bauxite (1-4 %)
- o BFS (5-30 %)
- o Fly ash (1-15 %)

The addition of corrective raw materials is always accompanied with the introduction of foreign elements. Provided that the chemical composition (minor and trace level) is known, the effects of such additions can in principle to some extent be predicted on the basis of the studies that already are available (see section 3). If combined effects are present, however, correct predictions are quite difficult to achieve as pointed out earlier.

Iron oxide contains metals like As, Cd, Cr and Tl in such concentrations that they hardly gives any mineralising effect. Bauxite is a heterogeneous aluminium ore material. It normally consists of aluminium minerals (gibbsite, bohemite and diaspore), iron oxides (goethite and hematite), clay mineral (kaolinite) and 2-8 wt.% of TiO_2 (anatase). The latter might be of significance as TiO_2 is known to increase the burnability of the mix by reducing the fCaO. However, the mineralising effect is strongly concentration related. If bauxite with 8 % TiO_2 is added to the raw mix, the real concentration will be ~ 0.4% provided 10% addition to the raw mix. Obviously, the TiO_2 will be higher in the production of calcium aluminate cements (CAC). It might be of significance as Ti also is incorporated in the aluminate phases, see Figure 4.

Blast furnace slag (BFS) is a byproduct from the iron making industry. In the context of using slag as auxiliary materials (and not interground with finished clinker) the contents of MgO (5-15%), SO_3 (~ 1-5%) and TiO_2 (< 4%) would have to be considered. In addition, foreign metals are also present and possible mineralising effects are determined by the slag addition level. In Didamony et al. (2002a) 0-10% of slag was tested in laboratory. They found increased burnability in terms of fCaO. They concluded that 5% BFS had better mineralising effect than the addition of 1% CaF_2,

as the latter also was tested in the same study. The same authors also tested cement kiln dust under the same conditions (Didamony et al. 2002b) and significant mineralising effects were found at 10% addition. The effects were regarded to the levels of alkalis and SO_3 in the kiln dust.

The same principles for judging potential mineralising effects are applicable for fly ash as an auxiliary material. Moreover, mineralising effects may also be achieved when conventional fuels are partly replaced by alternative fuels (AF) such as different organic waste, used tyres, saw dust etc. The potential mineralising effects need to be judged in the same way as explained above. In some cases the effects are difficult to systemise due to the heterogeneity of the AF. In addition, the fact that the AF matrices are highly organic in most cases (organic solvents, tyres etc.) must be taken into account. It is referred to Karstensen (2006) for a thorough overview of the use of AF in cement production.

5 Combined effects from Waste materials used as mineralizers added to the raw mix

Some additions to the raw mix have only minor mineralising effects but is however important as a waste management option. In addition, it might have increased mineralizing effect when combined with other compounds. Several studies have recently been carried out regarding this topic.

Kolovos (2006) studied the addition of waste ammunition material (WAM) which had high contents of Cu, Pb, Sn and Zn. The cement raw mix samples were prepared in such a way that all elements were present except for the unspiked reference sample. In Figure 9 it can be seen that the burnability increases with increasing WAM addition. In addition, the M3 sample showed the highest increase in the burnability. This sample also contained far more Cu and Zn than M1 and M2 and confirms again the positive effect of especially Cu. The term burnability capacity (BC) is used in Figure 9 and it is referred to as the fCaO determined at temperatures in the region of 1100-1450 ^{o}. The DTA analyses upon heating of the raw mix samples indicated no influence on the decarbonation mechanism (700-900 ^{o}C) by the addition of WAM. However, the melt temperature was decreased in the samples with WAM thus indicating that the reactions in the melt were affected and that the WAM constituents were dissolved in the melt. The melt formation shifted to lower temperatures with addition of WAM.

This study is a nice example of how the findings in earlier systematic studies on mineralizers, (based on addition of pure compounds, e.g. salts, oxides etc.), also is applicable when waste is used as a secondary raw material.
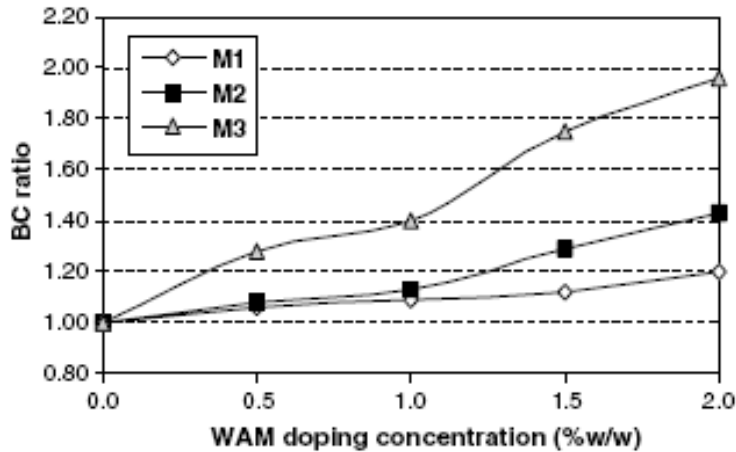
Figure 9 Burnability Capacity (BC) ratio for the three different mix samples (M1-M3) as function of the WAM doping concentrations (0-2%) (Kolovos 2006).

In Kacimi et al. (2006) the by-product phosphogypsum (PG) from the fertiliser industry was used as a mineralizer. It mainly contains gypsum with smaller amounts ($\sim$ 3%) of sodium fluorosilicate (Na_2SiF_6), alkalis (1-2%) and P_2O_5 ($\sim$1%). In general, the composition is indeed favourable for clinker mineralization. The amount of PG added to the raw mix was 0-10%. Important results are shown in Figure 10 and the reduction of fCaO can easily be seen as the PG addition increases. In the same figure the formation of C_3S at lower temperatures is quite significant. The authors found SO_3-C_3S solid solutions and substitution of Ca in the alite phase by Mg, Na and F. The former mechanism may stabilise the C_3S from decomposition whereas the latter increase the hydraulic reactivity. The SO_3 incorporation in C_2S is higher than in alite. This is probably the reason why the β-C_2S is preserved at ambient temperature although fluoride is present. The latter may enhance the transformation of β-C_2S to γ-C_2S during cooling at 500 ^{o}C. The overall amount of amorphous phases was found to decrease and increased porosity was therefore determined which in turn increase the grindability.
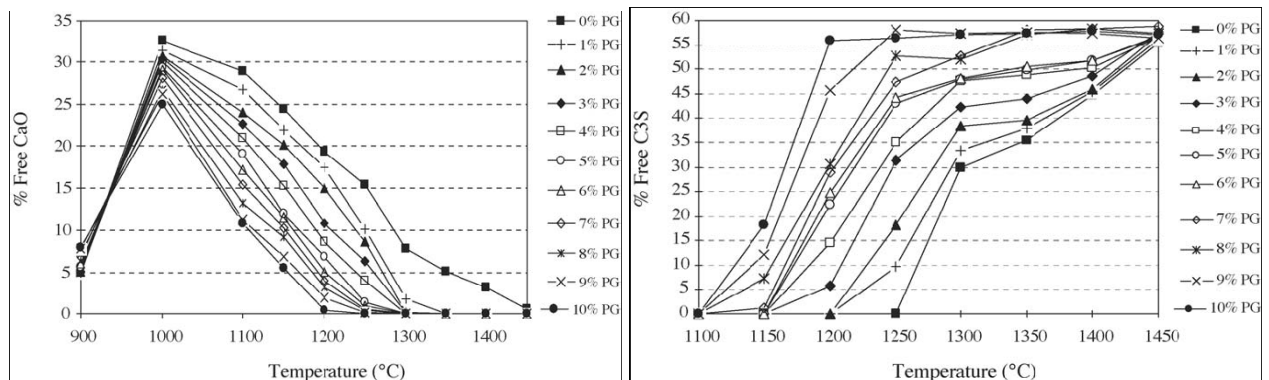

Figure 10: Free CaO contents (left diagram) and C_3S formation (right diagram) as function of temperature and different quantities of phosphogypsum additions (Kacimi et al. 2006).

Other by-products from different industries have been tried recently with fair improvements of the burnability. Medina et al. (2006) used copper slag as a raw material in the cement raw mix and achieved improved burnability. In another study (Kakali et al. 2005) 0-2% wolframite-stibnite ore

was used as a secondary raw material in order to introduce W, Sb and S to the raw feed. The decarbonation and the belite formation was not influenced indicating the dissolution in the molten phase as also found in the study of waste ammunition material (Kolovos 2006) although different constituents in charge. Significant reduction in fCaO was achieved from 0.5% addition of the ore material. Helmy (2003) studied the mineralizing effects of adding as high as 15% phosphogypsum, granulated pig iron slag and cement kiln dust to the raw mix. The iron slag was found to be the most suitable mineralizer.

In Katsioti et al. (2006), 10% jarosite-alunite precipitate ($2M[Fe_2Al(SO_4)_2(OH)_6]$, M = Na or K) was used in production of sulfoaluminate clinker. This precipitate originates from a hydro metallurgic process which treats low-grade nickel oxide ore. Due to the high level of mineral addition, the purpose of this study was more like to maintain the original properties of the final cement which they also succeeded in. Increased content of C_4AF and $C_4A_3\hat{S}$ was determined in the clinker. In another study (Shih et al. 2005) heavy metal containing sludge from the electro plating and surface finishing industry was used. As much as 15% of this inorganic waste in the raw mix was tested with promising results. They also concluded that if the heavy metal concentration exceeded 1.5% (roughly 15% sludge addition) in the raw mix, clinker phase formation was negatively affected. Espinosa and Tenorio (2000) found that up to 2% addition of galvanic sludge from the chromium electroplating process did not change the formation temperatures on C_2S, C_3S and the melt.

Trezza and Scian (2000) studied the effect of adding small amounts (< 0.04%) of ash to the raw mix. The ash was prepared separately by burning several fractions of used oil from cars at 1000 °C. The results showed no influence on the fCaO content probably due to the small amounts added. It was believed that the addition influenced the crystallinity and increased early strength evolution was found. In addition, a small tendency of increased grindability was also determined. This study is important in relation to burning of organic waste in cement production, both as a waste management option and as alternative fuel with mineralizing effects.

6 Future research

Among the mineralizers reviewed, CuO seems the most interesting transition metal oxide to pursuit both due to its abundance and to its relatively low potential for environmental negative impact. It may probably also be added as cupper ore where the sulphides will be oxidized to sulphates in the kiln, where they also will contribute to the general mineralization.
Although chromium is also an interesting mineralizer from a technical point of view, it is not recommended to pursuit due to its potential impact on workers health and the environment.

Zinc and fluorides are classical good mineralizers and could also be subjects for investigation, but it is recommended to focus on copper if an activity on mineralizers is to be launched in COIN.

In relation to potential environmental impact from construction products and materials, this issue is largely focused by the European Commission (EC) today through the mandate M/366[2]. When considering addition of inorganic mineralizers (CuO, ZnO, F, etc.) the status of the ongoing European work has to be considered. One specific action, in this relation, is to consider the recommended limit values for crushed concrete developed in the national project Gjenbruksprosjektet (Petkovic et al. 2006). Comparison with such values will immediately give

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[2] M/366 EN: Development of horizontal standardised assessment methods for harmonised approaches relating to dangerous substances under the Construction Product Directive - Emission to indoor air, soil, surface water and ground water

an indication of the acceptable concentration levels of specific substances in the concrete which in turn are easily recalculated to concentration levels in the produced cement clinker.

7 Conclusions

Available literature on mineralizers has been reviewed, in particular on the effect of mineralizers on the combination of free lime from decomposition of limestone in the cement kiln.

Zinc and fluorides are classical good mineralizers and zinc may already be added to the kiln through the use of spent tyres as alternative fuel.

Chromium is an interesting mineralizer from a technical point of view that also promotes the strength evolution of the resulting cement. However, it is not recommended due to its potential negative impact on workers health (eczema) and one environment during leaching from concrete products.

Cupper oxide (CuO) seems to have a very good effect as mineralizer at dosages of 1% of clinker mass, and at the same time cupper is a relative abundant element with a rather low potential impact on environment through leaching from concrete. It may also be added as cupper ore available in Norway as the sulphides will be oxidised in the cement kiln to sulphates acting further as mineralizers. Thus, copper ore as mineralizer is proposed as an activity within COIN.

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