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TITLE

Environmentally Sound Management of Hazardous and Industrial Wastes in Cement Kilns - Waste as Alternative Raw Materials

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ABSTRACT

A review of chemistry of cement production is given. The main focus is on the effects of different foreign elements, both when they are added deliberately as fluxing agents and mineralizers and when they are contaminants in raw meal and alternative raw materials. Many foreign elements, and in particular some heavy metals (e.g. Cu and Zn) can have a positive influence on the burnability of clinker. Most of the heavy metals are retained in the clinker and only a minor fraction is leached to the environment from concrete, even when it is recycled. The following emission limits from cement plants applies for Europe;

$(Cd + Tl) \leq 0.05$
$Hg \leq 0.05$
$(Sb + As + Pb + Cr + Co + Cu + Mn + Ni + V) \leq 0.5$

All values in mg/m^3 at temperature 273 K, pressure 101.3 kPa, 10 % oxygen, and dry gas.
The chemistry of cement hydration and reactivity of pozzolana along with cement definitions are also shortly reviewed. In terms of cement properties there are a few common foreign elements to be aware of when co-processing waste; chloride (Cl^-) content < 0.06 % (new Chinese regulation) to avoid initiation of corrosion of steel reinforcement in concrete, phosphorous oxide (P_2O_5) < 0.5 % in clinker to avoid destabilization of the main mineral C_3S, magnesium oxide (MgO) < 0.5 % to avoid detrimental expansion during concrete curing, zinc oxide (ZnO) < 1 % in clinker to avoid retardation of cement setting, hexavalent chromium (Cr^{6+}) is recommended to be < 2 ppm in water phase of fresh concrete to avoid contact eczema for workers and alkali content ($Na_2O_{equivalent}$) < 0.6 % if the cement is to used in concrete with alkali reactive aggregate. The latter value may be increased if the cement is blended with pozzolana.

KEYWORDS	ENGLISH	NORWEGIAN
GROUP 1	Materials Technology	Materialteknologi
GROUP 2	Concrete	Betong
SELECTED BY AUTHOR	Cement	Sement
	Heavy metals	Tungmetaller
	Emission	Utslipp

TABLE OF CONTENTS

1 INTRODUCTION

This report is a part of the Sino-Norwegian project “Environmentally Sound Management of Hazardous and Industrial Wastes in Cement Kilns” running from 2007 through 2009 (Karstensen and Justnes, 2007). The project comprises co-processing of waste in cement kilns and has two major advantages; the society gets rid of waste in a safe manner and the cement industry save energy if the waste has a calorific value (alternative fuel, AF) or save raw material (alternative raw material, AR) if the waste has a fraction that remains solid after burning. Sometimes it is difficult to distinguish the two since many wastes have a calorific value and a remaining solid component, and therefore co-processing of waste is often referred to as alternative fuel and raw material (AFR). Pure AF, such as spent oil, spent solvents (even chlorinated) and obsolete pesticides etc (Karstensen et al., 2006), is not a part of this report.

The Norwegian cement manufacturer Norcem, now a subsidiary of Heidelberg cement group, has been co-processing AFR for 25 years (Tokheim and Brevik, 2007) and it has also been common practice for quite a while in many other countries in Europe (e.g. Gäbel and Tillmann, 2005, Kääntee et al., 2004, and Mokrzycki et al., 2003), North America and Japan (Uchikawa and Hanehara, 1997) as well as emerging in other parts of the world (e.g. de Rougemont, 2003, and Maringolo et al., 2003). As an example, the goal of the Swedish cement producer Cementa, also a subsidiary of Heidelberg cement group, was to use 40 % AF in their production in 2003 (Gäbel and Tillmann, 2005).

Note that in addition to saving the environment from potential hazardous wastes and land fills, as well as saving fuel and raw material for cement industry, investment costs for building special incineration plants can also be saved since cement kilns is already there. Cement kilns are also very well suited for co-processing waste with a high temperature in the kiln, relatively long resident time and a basic melt perfect for destroying halogenated organic compounds (e.g. Karstensen, 2007) and capturing heavy metals. The entering points of AFR in a cement plant and the temperature profile in a cement kiln are reproduced in Fig. 1 from Mokrzycki and Uliasz-Bocheńczyk (2003).

Karstensen (2007) gave a compressed introduction to the different kilns and processes as follows; Depending on how the raw material is handled before being fed to the kiln, basically four different types of rotary kiln processes can be distinguished: the dry, semi-dry, semi-wet and wet processes. In the dry process the feed material enters the kiln in a dry, powdered form. The kiln systems comprise a tower of heat exchange cyclones in which the dry raw material feed is preheated (‘‘suspension preheater kiln’’) by the rotary kiln’s hot exit gases prior to entering the kiln. The calcination process can almost be completed before the raw material enters the kiln if part of the fuel is added in a secondary combustion chamber, the precalciner. In the wet process, the feed material is ground with water and the resulting slurry, typically containing 30–40 % water, is fed directly into the upper end of the inclined kiln. In the semi-dry or semi-wet processes water is either added to the ground dry feed material or removed from the slurry, e.g., by filter presses, resulting in a feed material containing about 15–20 % moisture. Pellets of feed material are loaded onto a travelling grate where they are preheated by the rotary kiln’s hot exit gases. By the time the feed material reaches the kiln entrance, the water has evaporated and calcination has begun. Preheater kilns usually have four cyclone stages with a capacity of approximately 4,000 tons of clinker per day. A considerable capacity increase can be obtained with a second combustion device located between the rotary kiln and the preheater section, the precalciner, were up to 60 % of the total fuel of the kiln system can be burnt. Modern preheater/precalciner kiln systems with 5–6-staged cyclone preheaters are considered to constitute best available techniques

(BAT). Such a configuration will use 2,900–3,200 MJ of energy per ton of clinker and can have a production capacity up to 10,000 tons of clinker per day (Environment Agency, 2001; IPPC, 2001). The primary fuels used in the cement industry are coal, petcoke, heavy oil and – to a lesser extent – natural gas. The average exhaust-gas volume is 2,300 Nm^3/ton of clinker. Dust, or fine particulates, is collected and controlled in air pollution control devices (APCD) like electrostatic precipitators (ESP) and/or bag filters (fabric filters).

The Chinese cement production was 1,065 billion ton in 2005 accounting for approximately 50 % of the world production (Karstensen, 2006). 60 % was produced by vertical shaft kilns, making them the dominating production technology in China (approximately 4,000 vertical shaft kilns existed in 2005). Vertical shaft kilns are refractory-lined, vertical cylinders with diameters of 2–3 m and heights of 8–10 m. They are fed from the top with a mix of dry ground raw material and fuel called black meal, consisting of approximately 13 % of coal or coke and produce usually less than 300 tons of clinker per day. A sketch of a vertical shaft kiln is shown in Fig. 2. Note that shaft kilns are NOT suitable for co-processing organic waste as dioxins etc may be formed and escape without destruction when entering at the top. Already burnt ashes or slags may, however, be used as AR in vertical shaft kilns and can for instance be added as part of the raw meal. Shaft kilns are currently shut down many places in China and replaced by more modern and energy effective rotary kiln plants.

In the cement clinker making process it is necessary to maintain material temperatures of up to 1450°C in order to obtain the required sintering reactions. In addition, the clinker needs to be burned under oxidising conditions; typically 2–4 % excess oxygen is required in the combustion gases. A modern rotary cement kiln has many inherent features, which makes it ideal for hazardous waste treatment; such as high temperatures, long residence time, surplus oxygen during and after combustion, good turbulence and mixing conditions, thermal inertia, counter currently dry scrubbing of the exit gas by alkaline raw material, fixation of the traces of heavy metals in the clinker structure, no generation of by-products such as slag, ashes or liquid residues and complete recovery of energy and raw material components in the waste (Chadbourne, 1997).

For some readers the chemistry of clinker making and cement hydration may not be well known and since it is of importance for the discussion of incorporation of foreign elements and how it will effect clinker formation and cement hydration, a relative brief introduction is given here as Chapter 3. For those who would like to have a more in depth understanding, there is a number of good books on the topic that can be recommended (e.g. Bensted and Barnes, 2002, Bhatty et al., 2004, Hewlett, 1998, Locher, 2006, an Taylor, 1997) However, readers experienced in the chemistry of cement may skip this chapter.

2 OBJECTIVE

The objective of this report is to give an overview of waste co-processing in cement kilns that gives a solid component after burning, which will end up in the cement clinker and in this respect may be considered as alternative raw (AR) material.

The second objective is to describe how this solid component may influence the formation and composition of cement clinker and the performance of cement, including binding and leaching of heavy metals or other elements posing potential hazards to the environment.

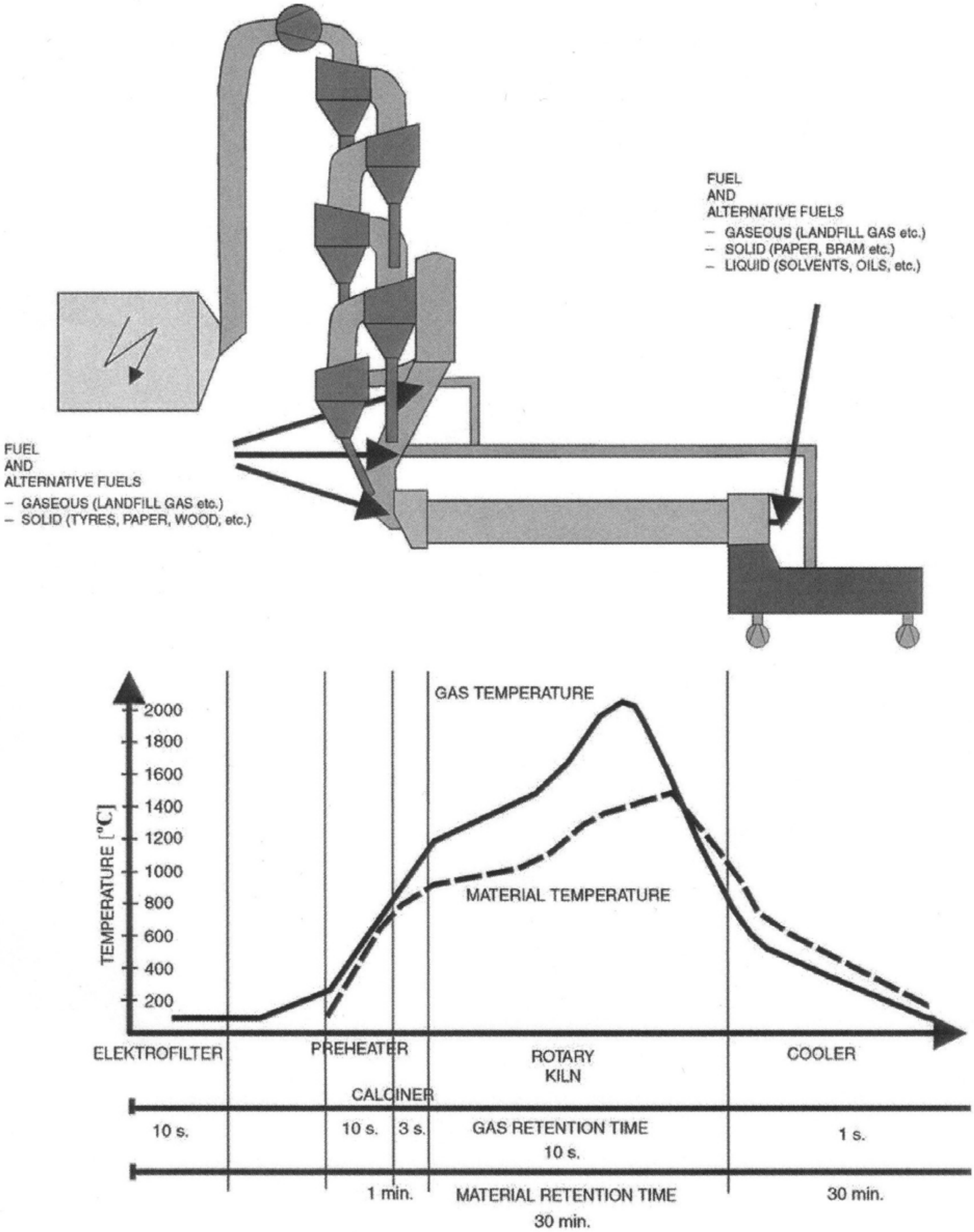


Fig. 1 Diagram showing entrance points of AFR in the cement plant as well as temperature profile and retention time of gas and solids (Mokrzycki and Uliasz-Bocheńczyk, 2003).

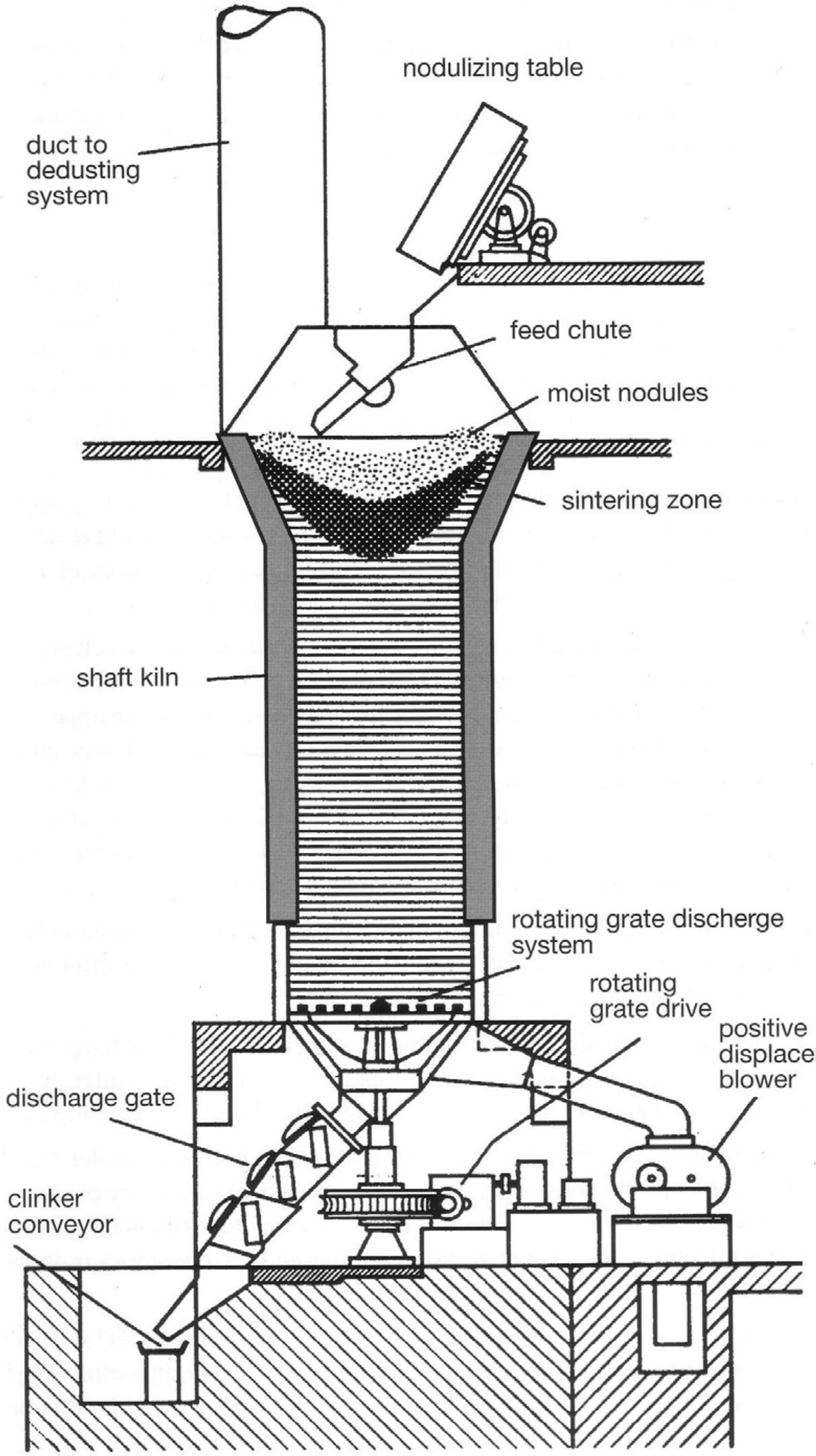


Fig. 2 A sketch of a shaft kiln. Raw meal is entered from the top.

3 CEMENT CHEMISTRY

3.1 Notation

Cement chemists use in general a short hand notation; C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, $\bar{S}$ = SO_3, M = MgO, N = Na_2O and K = K_2O for the main oxides in cement, in addition to H = H_2O to describe hydration processes. It will later be clear how this simplifies the writing of formulas for minerals as well as hydration reactions.

3.2 Production of cement clinker

Portland cement clinker is produced by burning a raw meal at about 1,450°C either in a rotary kiln as sketched in Fig. 1 or in a vertical shaft kiln as depicted in Fig. 2 (mostly in China) as outlined in the introduction (Chapter 1).

The raw meal is composed of a more or less impure limestone (i.e. mainly calcium carbonate, $CaCO_3$) adjusted with components like shale, clay, iron ore etc to obtain a composition as given in Table 1. The raw meal is often composed according to a lime saturation factor, LSF = $m_c/(2.80 \cdot m_S + 1.18 \cdot m_A + 0.65 \cdot m_F)$ where m_x is mass of oxide x. The LSF ranges from 0.90 - 1.04 for ordinary Portland cement (OPC) clinkers, with an average of 0.97. The LSF is actually the ratio between the lime (CaO) in the raw meal and the maximum amount of lime that can be combined with silica, alumina and ferrite in the raw meal during burning and cooling.

The literature refers also to the silica ratio (SR) = $m_S/(m_A + m_F)$ which indicates the solid to liquid ratio in the sintering zone of the cement kiln. The SR lies in general between 1.5 and 4, with favourable values between 2.3 and 2.8.

A third ratio used is the alumina ratio = m_A/m_F , which says something about the nature of the clinker melt. For clinker of normal composition, the alumina ratio lays between 1.5 and 4. However, under otherwise comparable burning conditions, particularly favourable burning characteristics are obtained for an alumina ratio between 1.4 and 1.6.

Table 1 Typical composition of major oxides in a raw meal for ordinary Portland cement clinker

Short hand	Formula	Minimum (%)	Maximum (%)	Average (%)
C	CaO	63	70	66.5
S	SiO_2	19	24	21.5
A	Al_2O_3	3	7	5.5
F	Fe_2O_3	1	5	2.5

Limestone decompose to CaO and CO_2 gas already in the pre-heater and early in the oven, while the alumina and ferrite form a melt phase of which silicate minerals are grown. After the clinker has been rapidly cooled leaving the kiln, it will have a typical mineral composition as given in Table 2.

The chemical system of ordinary clinker is at least quaternary; C-S-A-F, but for simplicity the binary phase diagrams C-S and C-A are presented in Figs. 3 and 5, while the ternary phase diagram C-A-F is reproduced in Fig. 6.

Table 2 Typical composition of major minerals in ordinary Portland cement clinker

Clinker phase	Short hand	Formula	Content (%)	
Tricalcium silicate/ Alite	C_3S	Ca_3SiO_5	Maximum	85
			Average	65
			Minimum	52
Dicalcium silicate/ Belite	C_2S	Ca_2SiO_4	Maximum	27
			Average	13
			Minimum	0.2
Tricalcium aluminate/ Aluminate	C_3A	$Ca_3Al_2O_6$	Maximum	16
			Average	11
			Minimum	7
Tetracalcium aluminoferrite/ Aluminoferrite	C_4AF	$Ca_4Al_2Fe_2O_{10}$	Maximum	16
			Average	8
			Minimum	4
Free lime	C	CaO	Maximum	5.6
			Average	1.2
			Minimum	0.1
Total Magnesium oxide (also in solid solution)	M	MgO	Maximum	4.5
			Average	1.5
			Minimum	0.7

It is clearly seen from Fig. 3 that the major mineral C_3S is incongruently melting at 2,150°C and that it is unstable below 1,250°C decomposing into C and C_2S. Avoiding the latter is one of the good reasons for rapid cooling of clinker. Any content of divalent iron (Fe^{2+}) greatly accelerates this decomposition (Woermann, 1960). It is, therefore, important to burn and cool clinker under oxidizing conditions to keep iron trivalent (Fe^{3+}) so it will enter C_4AF instead.

C_3S has a number of triclinic, monoclinic and rhombohedral crystal modifications stable at different temperatures. The modifications that are metastable at higher temperatures can be stabilized by solid solution of foreign ions in their crystal lattices. One effective stabilizer, for example is zinc, Zn (Stephan et al., 1999a), which depending on concentration stabilizes every modification, with the exception of triclinic type 3 and monoclinic type 3. The solubility limit for ZnO is reached at about 5 % of C_3S (Bigaré et al., 1967, and Hahn et al., 1965). The incorporation of titanium, Ti, up to 1 % promotes the C_3S formation, while higher concentrations inhibit it (Katayal et al., 1999a). However, the main crystal modifications of C_3S found in industrial clinker is monoclinic type 1 and 3 stabilized by magnesium oxide, MgO (M). Clinker with content of $M < 0.8$ % contains only monoclinic type 1, while monoclinic type 3 is present in clinkers with $M > 1.2$ % (Maki and Kato, 1982). The maximum M content in C_3S is 2 %, while the limits for A and F are 1.0 and 1.1 %, respectively. The name alite is actually used for impure C_3S, as it is found in Portland cement clinker. Alite is generally more hydraulic active than pure C_3S and hardens therefore substantially faster (Ono et al., 1966). The crystal lattices of the individually C_3S modifications differ only slightly, which can be recognized from the very low transformation enthalpies of about 0.2 - 4 J/g (Regourd, 1979), so the differences in hydraulic reactivity may well be due mainly to the lattice dislocations caused by the incorporation of foreign ions. Stephan and Plank (2007) studied the effect of multi-doping of alite with MgO, Al_2O_3 and Fe_2O_3 on the crystal lattice parameters by Rietveld analysis of the XRD-profiles as well as the on the setting and hydration rate of C_3S by isothermal calorimetry. Stephan and Plank (2007) also used ^{29}Si MAS (magic angle spinning) NMR (nuclear magnetic resonance) to study the microstructure of doped alite before hydration and thermal analysis (DTA/TG) for further information on hydration.

Dicalcium silicate, C_2S, is formed when the clinker is not fully saturated with C. C_2S melts congruently at 2,130°C as can be seen from Fig. 3. It is a very stable compound that is formed initially in lime-rich mixtures as a solid-state reaction. Dicalcium silicate occurs in five different crystal modifications known as α-, α'_H-, α'_L-, β- and γ-C_2S. The subscripts H and L indicate high and low temperature modifications. A general overview of the transformation between the phases is shown in Fig. 4.

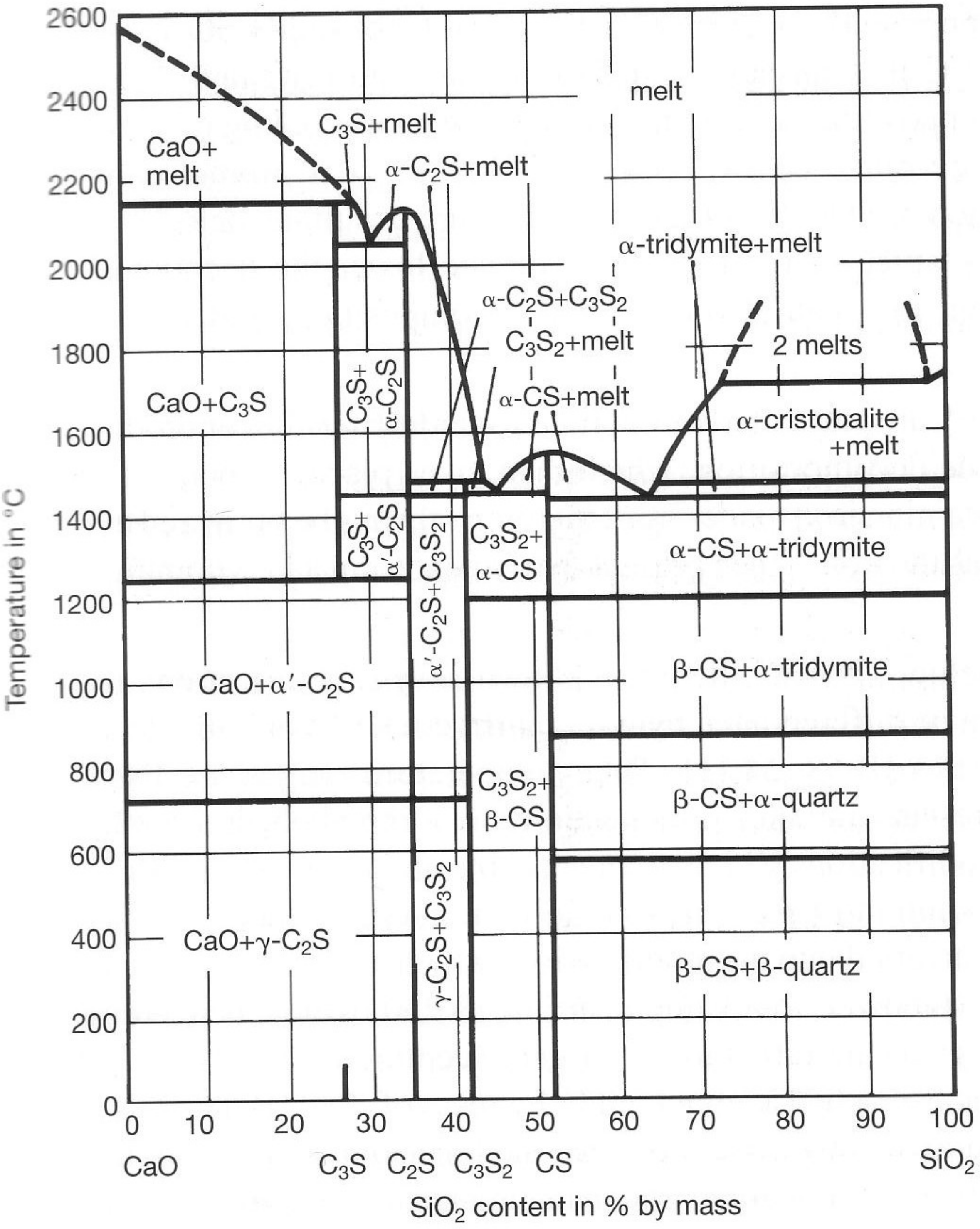


Fig. 3 The binary phase diagram of C - S showing stability of the important cement clinker minerals C_3S and C_2S.

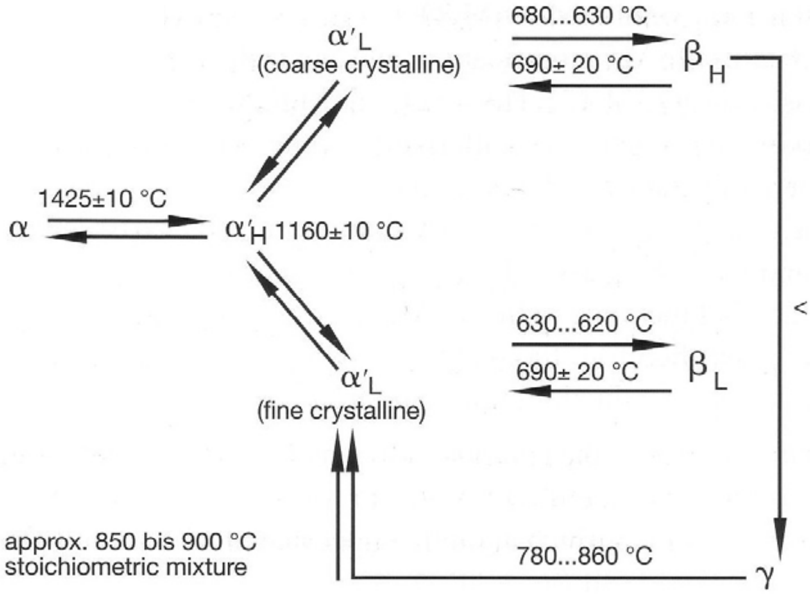


Fig. 4 Conditions for transformation for different dicalcium silicate modifications (Niesel and Thormann, 1967, and Lehmann et al., 1969)

From Fig. 4 it can be seen that the transformations β → γ during cooling and γ → α_L' during heating are not reversible. Furthermore, during the β → γ transformation there is a substantial change in lattice constants, recognisable but the fact that the density of the γ-modification is 2.94 g/cm^3 or about 10 % lower than the β-modification with 3.20 g/cm^3. As a result of this change in modification an originally compact burning product cracks and rapidly disintegrates into dust (so called "dusting") as soon as the temperature during cooling falls below 500°C. Furthermore, the β-modification is hydraulic active while the γ-modification is NOT. This is the second good reason to rapidly cool the clinker leaving the kiln.

Dicalcium silicate modifications can take up more foreign ions in their crystal lattices than tricalcium silicate. Individual modifications can be stabilized in this way so that the modification which is stable at high temperatures is retained on cooling to normal temperatures. The impure β-modification of dicalcium silicate is called belite. Microprobe examinations of industrial clinkers show that belite always contains Al as a foreign ion. Na, Mg, P, S, K, Ti, V, Cr, Mn and Fe may also be present (Barnes et al., 1978).

The high temperature modifications can be stabilized by certain foreign constituents. Depending on the nature and the concentration of the foreign substances or foreign substances it is possible to produce certain modifications selectively. Examples of proven stabilizers are $Ca_3(PO_4)_2$, $Na_4P_2O_7$, V_2O_5, B_2O_3, SrO, BaO, K_2O and combinations of Na_2O and Fe_2O_3 (Ghosh, 1985, Regourd and Guinier, 1974, and Suzuki et al., 1986).

Tricalcium aluminate, C_3A, is the component in the C - A binary system richest in C (see Fig. 5). It melts incongruently at 1,542°C dissociating into solid C and a melt accordingly poorer in C. Pure C_3A occurs only in one cubic crystal modification (Mondal and Jeffrey, 1975). The crystal lattice of C_3A can take up various foreign ions in solid solution, especially Fe^{3+}, Mg^{2+}, Si^{4+}, Na^+ and K^+, as well as Cr^{3+}, Ni^{2+} and Zn^{2+} (Stephan et al., 1999b). The alkalis play a special role as their incorporation into the lattice changes its symmetry from cubic through orthorhombic to monoclinic. Stephan and Plank (2007) studied C_3A doped with Fe_2O_3, SiO_2 and Na_2O in terms of changes to the crystal lattice as well as influence on the hydration. The change in reactivity by doping with foreign oxides was not found to be directly linked with the intensity of changes in the lattice parameters, but more a function of the kind and concentration of doped foreign oxide. Na_2O was found to retard the reactivity of the C_3A in short and medium terms, even when the dosage was kept below the concentration where the crystal structure changes from cubic to orthorhombic (< 2.4 %). The retardation was, however, compensated when the hydration proceeded. The retarding effect of Na_2O on C_3A was amplified by the combined doping with Fe_2O_3.

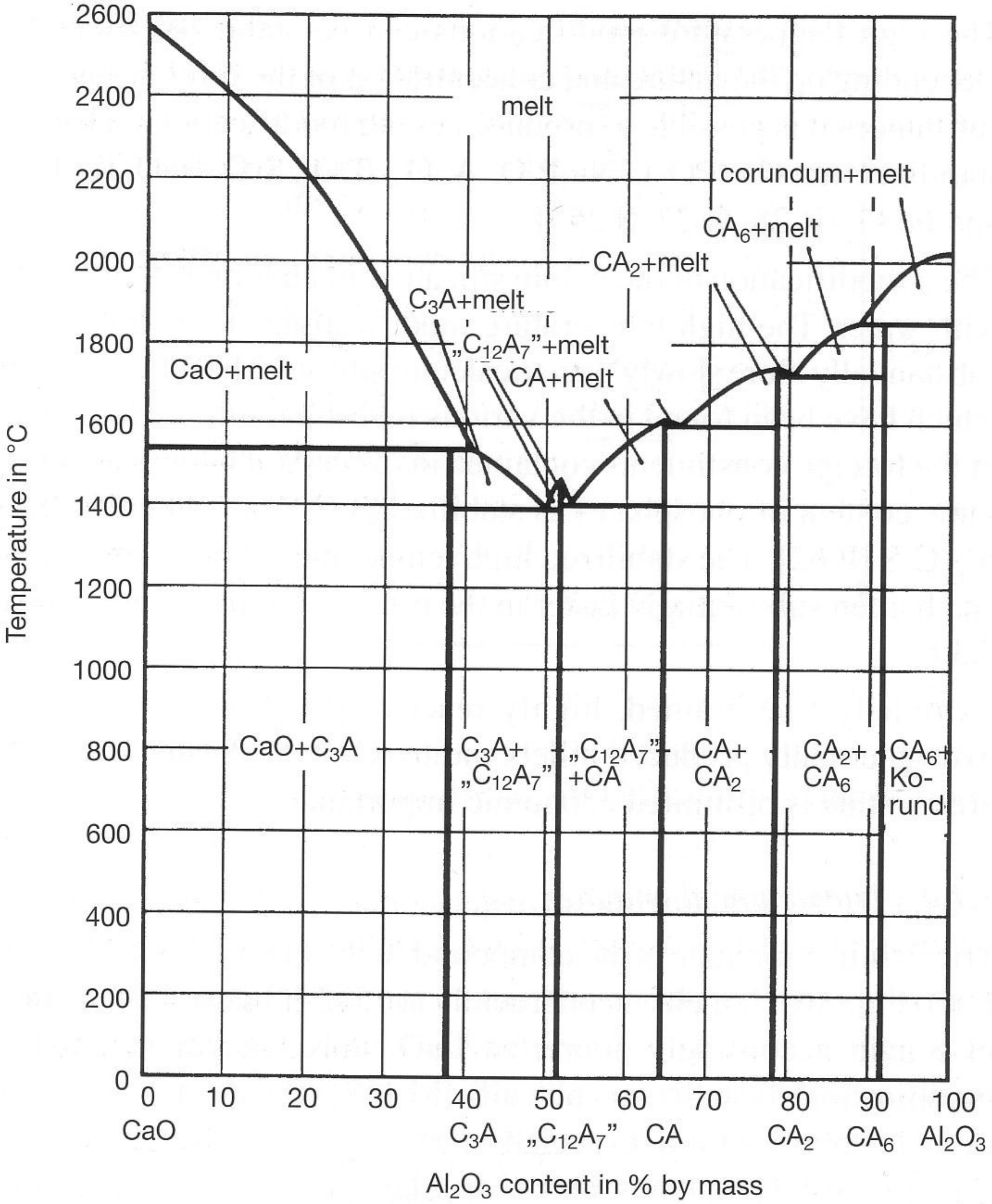


Fig. 5 The binary phase diagram of C - A showing stability of the important Portland cement clinker mineral C_3A.

The Fe_2O_3 compound in the cement clinker was originally assigned a composition corresponding to the formula $Ca_4Al_2Fe_2O_{10}$ or C_4AF in short hand notation (Hansen et al., 1928). It is therefore known as tetracalcium aluminoferrite, and also as brownmillerite after its discoverer. It also occurs as a natural mineral (Hentschel, 1964). C_4AF is a phase from the incomplete solid solution series between dicalcium ferrite, C_2F, which is stable under normal conditions and dicalcium aluminate, C_2A, which only can be produced under high pressure (250 MPa at 1,250°C). This means that the Fe^{3+} and Al^{3+} ions are interchangeable in this compound within certain limits. The mixed crystals of this series should therefore have the formula $C_2(A,F)$. The end member of this solid solution series richest in A consists of 70 % C_2A and 30 % C_2F (Majumdar, 1965). In the part of the ternary phase diagram C-A-F reproduced in Fig. 6, the calcium aluminoferrite solid solution series is represented by a hatched line. The subsidiary triangles into which the ternary system is subdivided indicate the compounds that can coexist in thermal equilibrium. This shows that the calcium aluminoferrite crystal that is in stable equilibrium with C and C_3A has a composition indicated by point B corresponding to 48 mol% C_2A and 52 % C_2F and therefore very close to the composition C_4AF.

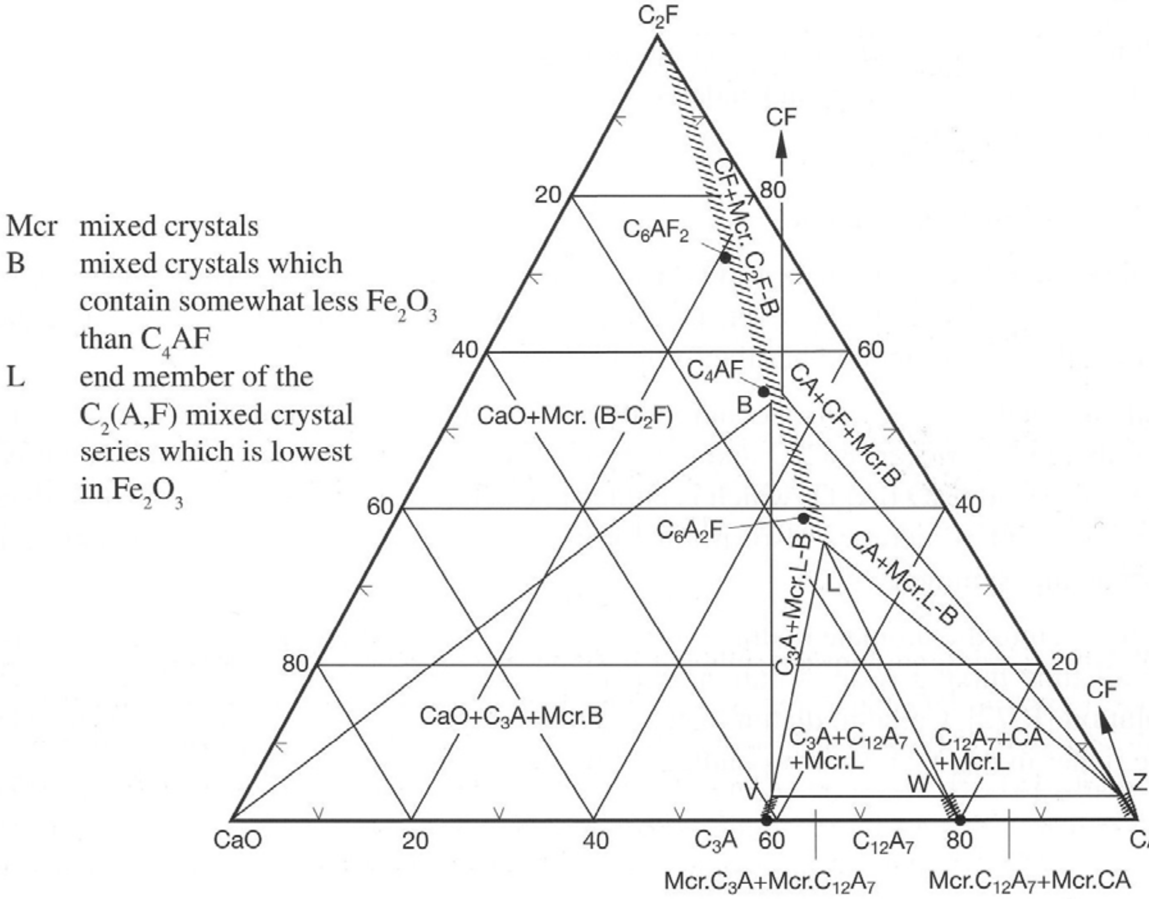


Fig. 6 Calcium aluminoferrite mixed crystal series in the ternary system C-A-F (Newkirk and Thwaite, 1958).

The calcium aluminoferrite mixed crystal can take up foreign ions in the crystal lattice (Stephan et al., 1999b). The incorporation of Mg^{2+} is of particular industrial significance, but it can also take up manganese, Mn^{2+} (Guttmann and Gille, 1929, Goffin and Muβgnug, 1933, Akatsu and Maeda, 1967, Parker, 1952, and Kondo et al., 1978), titanium, Ti^{4+} (Marinho and Glasser, 1984) and chromium, Cr^{6+} (Sakurai and Sato, 1968). Silicon, Si^{4+}, is apparently not incorporated in the crystal lattice (Ono et al., 1981), but is present in the form of C_2S inclusions (Neubauer et al., 1996).

Photos of light-optical micrographs of clinker with high and low content of C_3A are shown in Fig. 7 and taken from Locher (2006). The angular crystals of C_3S and rounded crystals of C_2S can clearly be seen embedded in a white mass of C_4AF with small black streaks of C_3A. The mix of C_3A and C_4AF is often referred to as the *interstitials* since they are surrounding C_3S and C_2S crystals since they were the melt from where the silicates where grown. When such a clinker mass is ground, each resulting grain may be composed of all 4 phases. Thus, one can not simulate cement by blending the 4 pure phases together in their respective amounts.

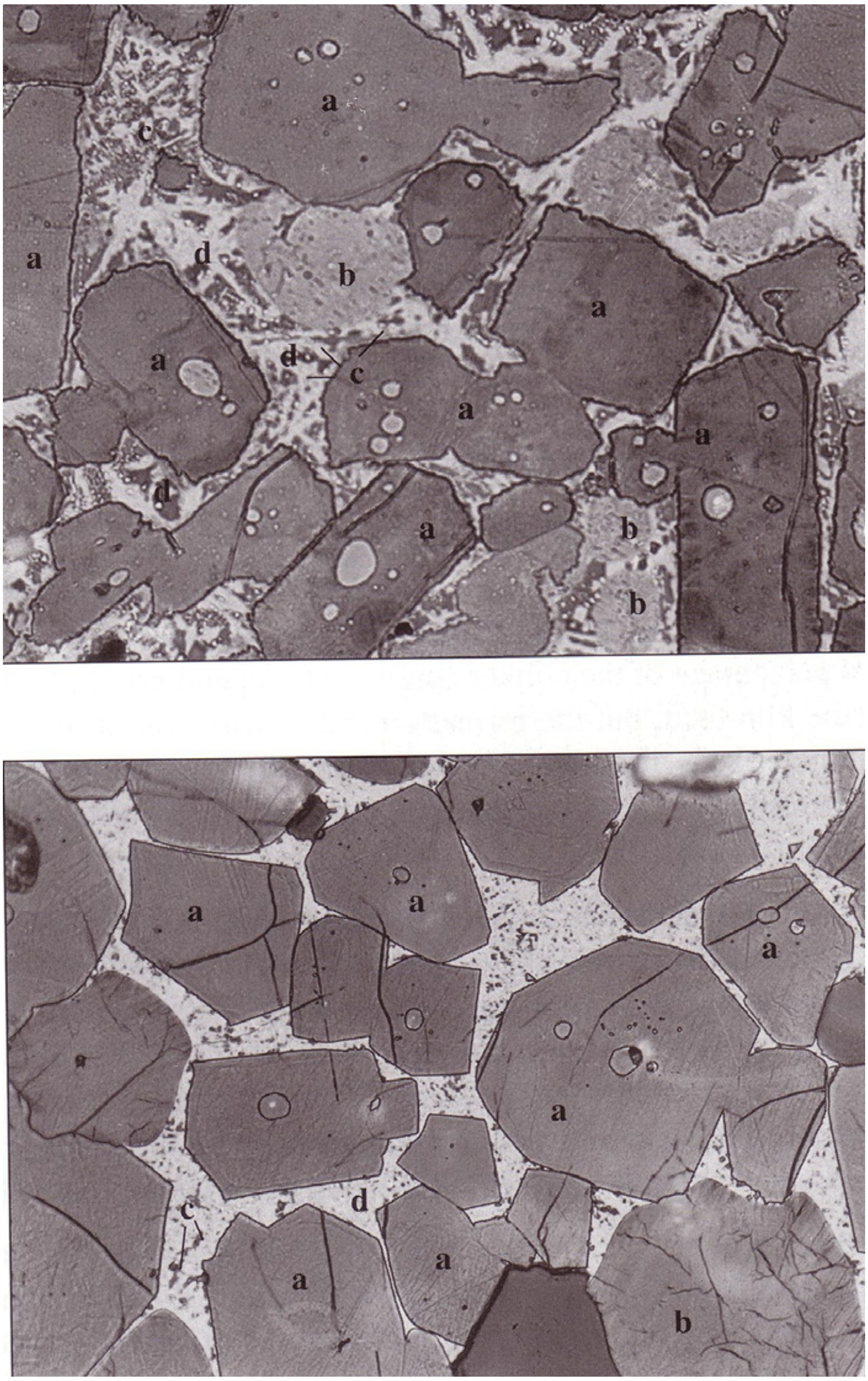


Fig. 7 Light-optical micrographs of polished clinker sections etched with water. Upper and lower parts are clinkers rich and poor in C_3A, respectively. Angular C_3S, rounded C_2S, black streaks of C_3A and white mass of C_4AF are marked a, b, c and d, respectively (Locher, 2007).

3.3 Effect of minor elements in clinker production

3.3.1 General

Minor elements are often added deliberately to the raw meal as mineralisers. They may also be present as contaminations in the raw meal or in alternative fuels and raw materials (AFR), but they will all affect the clinkerization as if the were added as mineralisers. Thus, the effect of mineralizers is of importance to the topic (AR) of this report.

Mineralisers 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 caused by specific elements in the compound added to the cement raw mix. 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.

The effects of mineralizers have been explored during several decades. The literature survey in this sub-chapter is focusing on the effects when the minor elements are introduced by the cement raw mix prior to burning or as AFR. Mineralizers can be active at several stages in the process. A useful picture of the burning process is given in Fig. 8. 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. Fig. 8 shows in principle the main reactions/mechanisms as the temperature increases including:

- Calcinations (decarbonation) of the limestone at 700-900°C: $CaCO_3 \Rightarrow CaO + CO_2$
- transformation of quarts from low to high temperature modification
- formation of calcium aluminates ($C_{12}A_7$), dicalcium silicate (belite = C_2S) and ferrite phase [$C_2(A,F)$] above 700°C
- formation of molten phase at 1,300°C and tricalcium silicate (Alite = C_3S) is formed by the reaction: $C_2S + CaO \Rightarrow C_3S$

Mineralizers are reported to affect decarbonation, the formation of alite and properties of the melt and stabilize the hydraulic belite polymorphs (α- and β-forms). Substances that are affecting the melt properties are also called fluxes. Reaction temperatures are often decreased when applying mineraliser(s) which means increased burnability of the mix.

In view of the main process given in Fig. 8, the effects of adding a mineraliser to the cement raw mix can be the following:

- Decreased burning temperature due to changes in the reactivity and burnability
- Acceleration of the clinkerization reactions (higher activity of the clinker minerals) at lower burning temperatures, e.g. fluorosilicates
- Altered surface tension (e.g. SO_4^{2-}) and viscosity of the melt
- Formation of new intermediate phases as well as more stable phases when approaching firing temperatures
- Controlled polymorphism of the clinker minerals
- Changed 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 and divided them into the following groups, as will adopted in this chapter together with a sub-chapter on rare earth elements that may occur in some ARs:

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

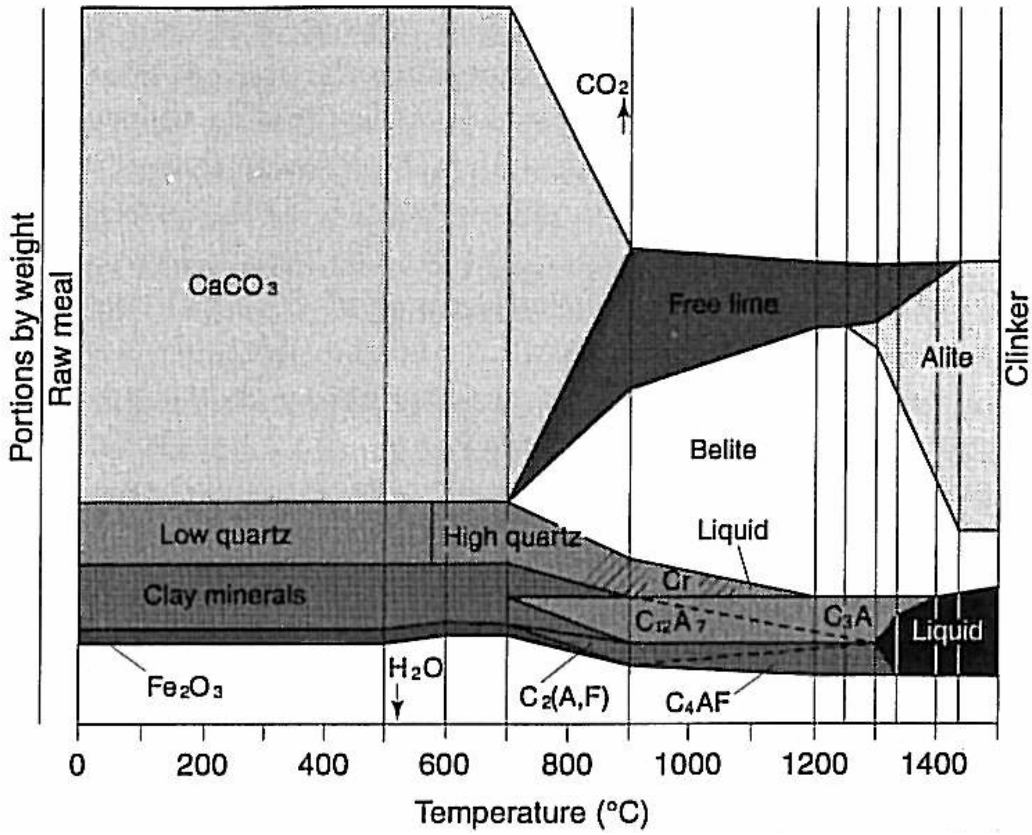


Fig. 8 Reactions taking place in the burning of the raw meal to Portland clinker

Some minor elements are often referred to as "heavy metals", but the definition of these is somewhat arbitrary: *Elements above a certain density (> 5 g/cm^3) and which are toxic, highly toxic or poisonous at low concentrations.* Examples are As, Cd, Cr, Hg, Pb and Tl. Due to low toxicity, Iron (Fe) and titanium (Ti), for example, are NOT considered "heavy metals" in spite of high density (Fe, 7.87 g/cm^3). On could also argue whether Arsenic (As) and Thallium (Tl) actually are metals or not, that's why the definition is "arbitrary" and why "heavy metals" is not used as a special category in this report.

3.3.2 Alkali (Na, K and Li) and alkaline earth (Ba and Sr) oxides

The alkalis sodium (Na) and potassium (K) are derived mainly from the raw materials; their main carrier is clay or shale. Sedimentary rocks, including the carbonates, sometimes contain soluble alkali salts. Sodium and potassium also occur in auxiliary raw materials such as blast furnace slag and fly ash. The alkali oxides Na_2O and K_2O in European fuels range between 0.05-0.6 % and 0.5-2 %, respectively (Bucchi, 1980); for typical raw meal, their concentration levels are 0.13 % and 0.47 %, respectively. The effects of alkalis in cement manufacturing were reviewed in details by Jawed and Skalny (1977, 1978) and Skalny and Klemm (1981). Na_2O and K_2O are volatile in nature, giving rise to a cycle inside the kiln. The extent of alkali volatilization varies with raw material composition; for instance, volatilization of alkalis in clays is higher than for those in feldspar. Alkalis present in the feed are volatilized at a material temperature from 1,400°C-1,500°C as the mix nears the burning zone, but condense at cooler parts of the system, such as the suspension preheater riser ducts or in chain systems in long kilns. The formation of rings and coatings on the kiln lining resulting from this heating-cooling cycle are generally attributed to alkali condensation and reaction with incoming material or refractories. To avoid excessive build-ups in the kiln, a percentage of gases may be led through a by-pass, so that the alkali sulphates and chlorides may be continuously removed and end up in the cement kiln dust (CKD). These CKDs have thus typically high alkali contents.

Usually potassium compounds are more volatile than the sodium compounds. The intensity of the alkali cycle depends upon the nature of their presence in the raw material and on processing and type of kiln (Bucchi, 1981). The retention of alkalis is generally higher for high efficiency kiln systems (Hewlett, 1998).With gas and oil as fuels, the alkalis tend to volatilize more as compared to coal used as a fuel possibly due, at least in part, to the higher hydrogen levels in these fuels, which leads to higher water vapour concentrations in the burning zone.

In the presence of chlorides and sulphate, the volatilization behaviour of both Na and K is modified greatly, as shown by the vapour pressure-kiln temperature relationship in Fig. 9 (Bucchi, 1980). Carbonates have similar effects. In the presence of sulphur, alkalis preferentially form sulphates. If their amount is more than the required stoichiometric balance, the excess will be dissolved in the silicates, aluminates, and ferrites. The common alkali sulphate phases formed are Arcanite (K_2SO_4), sodium potassium-sulphate, also known as Aphthitalite of a general solid solution composition $(K,Na)_2SO_4$, or in short hand $K_3N\bar{S}_4$, and Na_2SO_4, also known as Thenardite (Taylor, 1997).

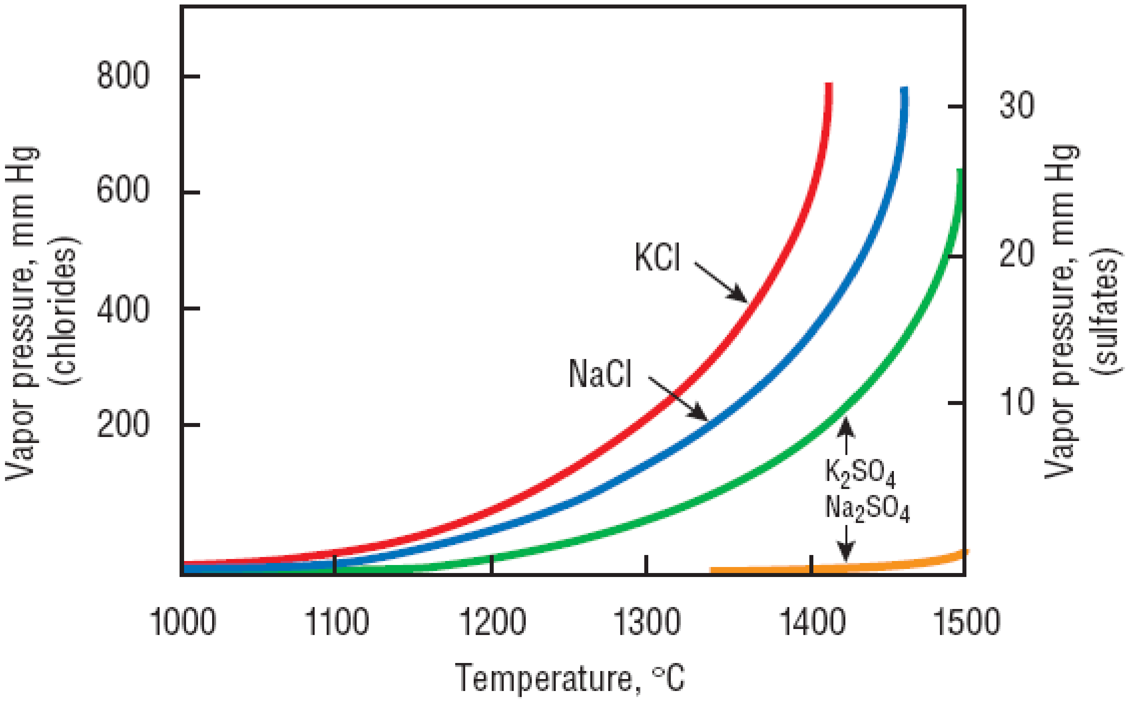


Fig. 9 Vapour pressure of Na and K chlorides and sulphates (Bucchi, 1980).

Burning conditions also significantly influence the formation of double sulphates so that oxidizing conditions produce calcium-potassium sulphate and a reducing condition produces sodium potassium sulphate. Potassium is twice as likely to produce soluble sulphates as sodium. The calcium-potassium double salt, calcium langbeinite $2C\bar{S}\cdot K\bar{S}$, is also sometimes found. Thenardite (Na_2SO_4) is very rare.

The ratio of Na to K in cement raw materials in North America and Europe varies (Skalny and Klemm, 1981). There is usually a substantial excess of K_2O over Na_2O. Therefore, in the presence of sufficient amount of SO_3, a range of double alkali sulphates, as described in this chapter, is formed depending upon the K_2O to Na_2O ratio. If K_2O is in excess of that required to produce Aphthitalite ($K_3N\bar{S}_4$), it forms a single sulphate Arcanite (K_2SO_4).

Introducing SO_3 jointly with K_2O and Na_2O into the clinker melt may lead to phase separation. Since alkalis reduce the melt temperature, and the rate of C_3S formation is proportional to the amount of liquid phase, a positive effect on C_3S formation could be expected.

Alkali sulphate melt and clinker liquid are immiscible phases. Alkalis inhibit the formation of C_3S from C_2S and lime, because they stabilize the lower energy C_2S phase in the absence of sulphates. It might, however, be pointed out that alkalis that are not balanced by sulphur inhibit alite formation far more strongly than, for example, potassium sulphate does. This may be in part because alkali sulphate melt does not participate in the clinkering reaction, whereas alkali in the clinker melt can enter the belite phase and inhibit its conversion to alite.

In Fig. 10 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 Fig. 10. $CaSO_4$ 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 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 the hydraulic activity. In recent studies (Aranda et al., 2007, and de la Torre et al., 2007), 10 laboratory belite clinkers were synthesised with various amounts of alkali (Na, K) carbonate and SO_3 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. 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 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 % K_2O) together with small amounts of Na (0.12 % Na_2O).

The overall clinker reactivity is increased by the presence of alkalis. Gies and Knöfel (1980) showed that Na_2O is incorporated in C_3A in the absence of SO_3 resulting 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°C and also good strength development were found.

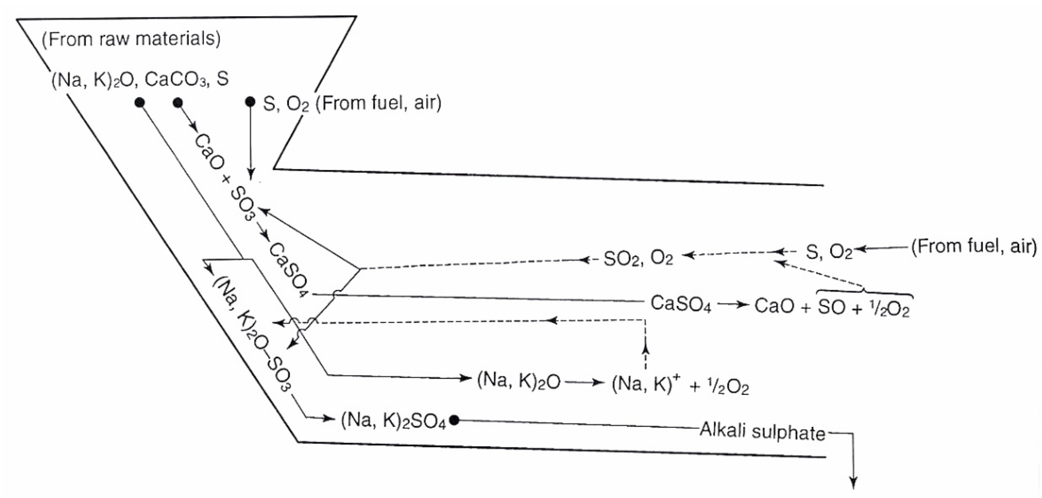


Fig. 10 Overview of the alkali and sulphur cycle in the cement kiln after Hewlett (1998)

Von Lampe 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 was 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 decreased NO_x emissions. It also allows the use of lower grade limestone.

Gartner (1980), and Gies and Knöfel, (1986) reported that in the absence of SO_3, Na_2O is preferentially incorporated in C_3A by replacing CaO and forms "alkali-aluminate" of an approximate composition NC_8A_3, thereby reducing its reactivity. This results in clinkers rich in free lime and aluminate, and can reduce the burnability. Potassium is substituted in C_2S as a compound with an approximate composition of $KC_{23}S_{12}$, and the overall clinker reactivity is decreased due to the slower reaction with CaO to form C_3S in the burning process. In the presence of sulphate, K_2O increases the C_3A reactivity (Strunge et al., 1986). Richartz (1986) reported that SO_3 reduces the extent of alkali solid solution in C_3A and hence the reactivity, but improves the cement properties.

It might be mentioned that although alkalis, Na_2O in particular, may act as fluxes, they are technically less desirable compounds than many of the minor compounds (Bucchi, 1980). If present in excess, alkalis often lead to higher pH and better early strength, but lower later strengths. They are not desirable because of the deleterious alkali-silica reaction (ASR) with reactive aggregates that leads to expansive reactions and can cause serious cracking in concrete. The deleterious effects of alkalis on the mechanical properties of cement may be reduced by gypsum addition to the raw feed, because of the possible elimination of solid solutions of alkalis with clinker minerals (Butt et al. 1971). One possible speculation is that gypsum would either increase the volatilization, or eliminate NC_8A_3 or $KC_{23}S_{12}$ formation. The latter explanation is probably more likely. According to Lokot and Azelitskaya (1969), the addition of gypsum to raw feed produces cement of high 28-day strength, enhanced kiln output and fuel savings.

Lithium (Li) is found in some waste materials such as used lubricants, but occurs only in traces in typical raw materials and fuels.

Lithium would tend to form a relatively non-volatile oxide (Li_2O) at elevated kiln temperatures. Gouda (1980) reported that Li_2O is the most reactive among the alkalis in lowering the temperature of the initial liquid phase. Rangarao (1977) pointed out that up to 1 % of Li_2O in the raw mix imparts a mineralizing effect, but lime fixation is impaired thereafter. At a lower Li_2O addition (0.1-0.3 % by weight), limestone dissociation energy is reduced, and mineral formation becomes more intensive; this appears to be a contradiction to the usual behaviour of mineralizers and clinker poisons.

Li_2O has also been reported to increase the reactivity of the raw mix (Bhatty, 1995, and 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 (Kolovos et al., 2002a) the reactivity was measured in terms of the remaining free lime (fCaO) at 1200 and 1450°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 1,200°C. This was explained by the earlier decomposition of $CaCO_3$ as shown in their TGA measurements. At 1,450°C they only found marginal positive effects.

Apart from the major element calcium (Ca) and minor element magnesium (Mg) in the usual raw meal as treated in earlier chapters, the most relevant alkaline earth elements in clinkerization are barium (Ba) and strontium (Sr).

Barium (Ba) occurs in varying amounts in limestone, mostly as barite ($BaSO_4$). It can also occur in clayey sediments in appreciable amounts. The presence of barium in a raw mix can reduce the firing temperature from 1,450°C to 1,400°C and result in increased clinker production. The clinker would also be produced with improved mineralogical composition (Timashev et al., 1974). However, Kurdowski (1974) reported only a marginal usefulness of BaO when added in small amounts, stating that it did not significantly affect either the properties of the liquid phase or the rate of lime assimilation; Ba replaced Ca in all clinker phases, except for the ferrite. The optimum BaO concentration was 0.3 % to 0.5 %, preferably for clinker containing less flux (silica modulus $m(SiO_2)/[m(Al_2O_3)+m(Fe_2O_3)] > 3.0$ where m(x) is mass of oxide x) and high C_2S content.

Several studies have found Ba to be an effective activator of hydration and strength. The strength obtained from Ba-incorporated clinkers is 10-20 % higher than that of regular clinker of all ages tested under identical conditions (Kurdowski, 1974; Butt and Timashev, 1968; Kurdowski and Szummers, 1968; Kruvchenko et al., 1970; Peukert, 1974).

Barium has been reported to decrease the clinkering temperatures, accelerate reactions and stabilise β-C_2S (Katyal et al., 1999b, Bhatty, 1995, and Ghose et al., 1983). The effect of $BaCO_3$ on pure C_3S was studied by Katyal et al. (1999b). 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°C. Above this level C_3S was destabilised and disintegrated into C_2S and free CaO. According to Kolovos et al. (2002a) 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 1,200 and 1,450°C. This illustrates 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 have 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 like in the case of barium. Improved mineralizing effects are also often encountered when more than one active compound are considered (e.g. the use of AR). Mullick et al. (1997) improved the burnability (decrease in fCaO) by the use of barite together with fluorspar. Rajczyk et al. (1992) used a barium containing by-product in the study of belite cements.

A major portion of strontium (Sr), found in clinker as SrO, comes from limestone and aragonite. Strontium frequently occurs in clinkers between 0.05-0.4 % (Blaine et al., 1965). The mean value quoted by Moir and Glasser, (1992) was 0.059 %. Brisi and Appendino (1965) and Gilioli et al. (1972) demonstrated that small amounts of SrO favour alite formation, but at 4-5 % addition, Sr preferentially distributes in belite rather than alite, and inhibits the formation of alite. Phase equilibrium studies indicate that it also favours free lime formation, with SrO preferably going into solid solution and displacing CaO from other compounds. The tendency of free CaO release during clinkering makes $SrCO_3$ more adverse than $SrSO_4$, and the clinkers having a high lime saturation factor (LSF) may be more vulnerable to free lime expansion during hydration.

3.3.3 First series of transition metal oxides

To recapitulate, 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 above 1,340°C, will increase the diffusivity of the clinkering species. This, in turn, leads to increased rate of combining C_2S with free CaO and thus enhanced C_3S formation. Distinguishing between fluxing and mineralizing effects will in this section not necessarily be pointed out.

The 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 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 these transition metals and the viscosity of the melt was established by Timashev (1980). He 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 metal-oxide (Me-O) bond. This nice relationship is shown in Fig. 11. The same author found similarly decreased surface tension with increased oxidation state, though with a larger scattering.

When exploring the mineralising effects of the transition metals it is very useful to recall which principle clinker phases we expect the different metals to incorporate in. Hornain (1971) found that the main concentrations of the first series transition metals were found in the ferrite phase (C_4AF), as shown in Fig. 12. The exceptions were Cr and V (vanadium) which also concentrate in C_2S and C_3S.

Inclusion of transition metals can also influence the grindability of the final clinker. Tsivilis and Kakali (1997) found that grindability decreased in the following order of included transition metals; $MnO > Cr_2O_3 > NiO > ZrO_2 > CuO > Co_2O_3 > V_2O_5 > MoO_3 > TiO_2 > ZnO$.

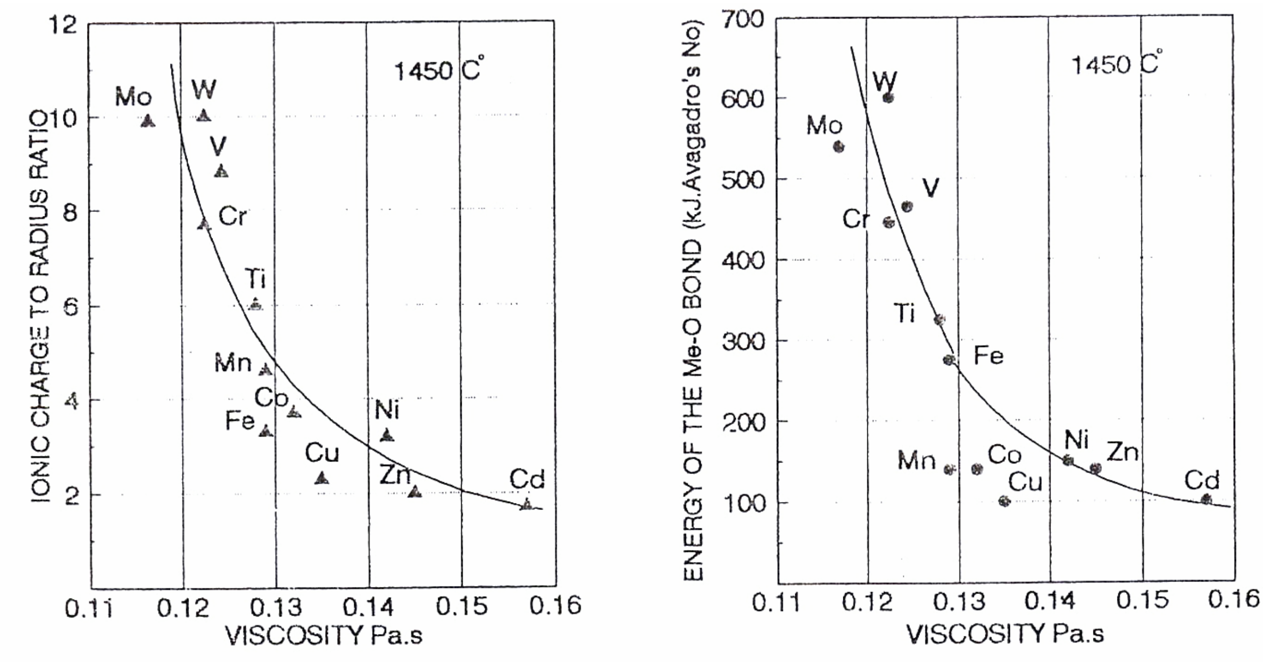


Fig. 11 Effects of the ionic charge and the energy of the Me-O on the viscosity of clinker melt (Timashev, 1980)

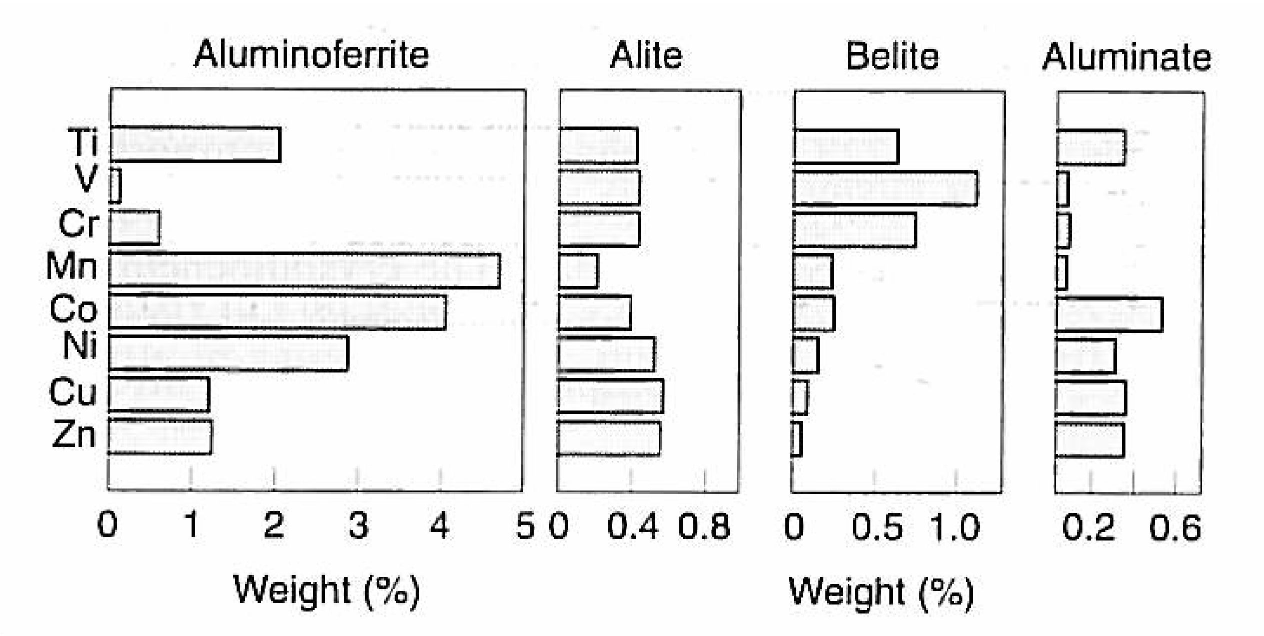


Fig. 12 Distribution of some transition elements in the principle clinker phases (Hornain, 1971)

3.3.3.1 Ti, V, Cr and Mn

Titanium (Ti) as oxide may be present in typical cement raw material at the 0.02-0.4 % level by weight (Bucchi, 1980). Gartner (1980) reported a higher concentration of 0.1-1.0 % TiO_2 in most raw mixes. Concentrations of TiO_2 in some of the auxiliary raw materials are even higher. Blast furnace slag, for instance, can contain 1.7 % TiO_2, and bauxites may have between 2-8 % TiO_2 by weight. Note that AF containing waste paper or paint may contain substantial amounts of TiO_2 as pigment.

TiO_2 is a refractory material (boiling point 2,500-3,000°C) and is essentially incorporated in clinker. At low levels the effects of Ti on the manufacturing of cement are insignificant (Miller, 1976); higher levels of up to 2 % may improve the compressive strength of clinker (Knöfel, 1979). Hornain (1971) and Marinho and Glasser (1984) reported that TiO_2 is preferentially distributed in the ferrite phase. Titanium additions to kiln feed from ilmenite ($FeTiO_3$) have been used to produce buff-coloured cement. Kolovos et al. (2002a) have reported that addition of 1 % TiO_2 to the raw mix can reduce free lime in clinker by 30-60 %. Knöfel (1977) observed a sharp reduction in alite with equivalent increase in the belite phase when TiO_2 was increased in the raw mix, while the variation in ferrite and aluminate was not significant.

Titanium promotes decarbonation of limestone, decreases the clinker melt temperature and the free lime content, but it is strongly dependent of concentration according to Bhatty (1995) and Katyal et al. (1999a).

Calcium titanate ($CaTiO_3$) is apparently a major titanium containing phase present in clinker. It has been reported that about 1 % TiO_2 addition in the raw mix reduces the melt temperature by 50°C-100°C, probably because of a favourable relationship between ionic potential and the melt viscosity as shown in Fig. 11.

Vanadium (V) occurs at a measurable level in cement raw materials (10-80 ppm in limestone, 98-170 ppm in clay/shale, and 30-50 ppm in coal) according to Sprung (1985). It is also present in fly ash where it tends to concentrate in fine fractions (Coles et al., 1979). Fairly high levels of vanadium are also reported in crude oils (Gartner, 1980). Weisweiler and Krčmar (1990) reported nearly 800 ppm vanadium in some petroleum cokes used in cement manufacturing. Ash from petroleum coke also contains very high levels of V_2O_5 (up to 60 %). But the low overall ash content in the petroleum coke contributes with only up to 0.08 % V_2O_5 in clinker produced in modern cement plants that use 50 % petroleum coke as a substitute for regular fuel (Moir and Glasser, 1992).

Use of vanadium is known to decrease the melt viscosity primarily due to its higher ionic potential. Vanadium is present as V_2O_5 in cement clinker. It concentrates in alite and forms larger crystals. However, according to Hornain (1971), vanadium preferably resides in belite rather than alite, as shown in Fig. 12. V_2O_5 (decomposes at 1,750°C) is unlikely to vaporize at normal kiln temperatures. On the other hand, vanadium present in fuel does not have adequate contact with the reacting mass in the kiln and largely ends up in CKD or the gas dust as suggested by Weisweiler and Krčmar (1990).

Presence of 1 % V_2O_5 can significantly reduce the free lime in clinker when fired at 1,200°C (Odler and Abdul-Maula, 1980a). V_2O_5 has also been used for stabilizing β-C_2S in clinker apparently by substituting VO_4^{3-} for SiO_4^{4-}. According to Bhatty (2003), presence of vanadium produces belite with ragged edges. Vanadium also imparts tan colour to clinker. A concentration of 1.5 % V_2O_5 is reported to increase hydration of alite; however, higher concentrations adversely affect the grindability of resulting clinkers. High V_2O_5 levels could also deteriorate kiln lining in some cases (Gartner, 1980). V_2O_5 in clinker can also increase sulphate expansion under certain circumstances.

Vanadium is reported to decrease the melt temperature, favour formation of big alite crystals and stabilize β-C_2S (Moir and Glasser, 1992). Of the transitions metals, only Cr^{6+}, V^{5+} and Mn^{7+} seem to stabilize the β-C_2S phase (Xiuiji and Shizang, 1986). Among these elements, in turn, only chromium (Cr) had the ability to increase the C_2S activity (Moir and Glasser, 1992). Andrade et al. (2003) confirmed that V showed a preferred partition towards C_2S in their clinker studies.

Chromium (Cr) can be present in raw feed in measurable quantities. Sprung (1985) has reported up to 16 ppm in limestone and nearly 100 ppm in clay and shales. Coals and used oils may contain up to 80 ppm and 50 ppm Cr, respectively. Some of the auxiliary raw materials, such as bauxites, which are used up to 4 % in cement manufacturing, may contain 0.04-0.4 % Cr_2O_3. In addition, a small amount of Cr can also enter cement from the grinding media during raw meal preparation, cement finish milling, and refractory linings.

The presence of Cr in raw materials is known to reduce the viscosity of clinker melt due to its high ionic charge as is shown in Fig. 11 (Timashev, 1980). Miller (1976) has reported improved clinker burnability at 1 % Cr_2O_3 addition. Chromium can exist in a number of oxidation states in clinker, the most stable being Cr^{3+} and Cr^{6+}. Their formation is sensitive to the oxygen level in the kiln. A high oxygen content tends to form Cr^{6+}. These compounds are readily soluble in water and markedly affect the hydration characteristics of the paste. Reducing conditions favour the formation of Cr^{3+} compounds which are less soluble in mix water.

Under oxidation conditions, Cr can also exist as Cr^{4+} and Cr^{5+} in C_2S, which can then be disproportionate to the more stable Cr^{3+} and Cr^{6+} upon mixing with water (Feng and Yan, 1990). Hornain (1971) reported that Cr preferentially resides in belite followed by ferrite, alite, and aluminates, as shown in Fig. 12. Although Cr^{6+} can be present in both alite and belite, it is reported to stabilize the β-C_2S form (Hornain, 1971, and Kondo, 1963). Suba Rao and Narang (1987) developed active belite-rich cement from raw feed containing 4-5 % Cr_2O_3 by weight. Imlach (1975) used 0.11-1.32 % Cr_2O_3 in the raw feed as a flux. The resulting cement exhibited improved 8- and 24-hour strengths, but 28-day strengths always decreased.

A significant portion of Cr can also enter the finished cement from chrome-rich grinding media. The level of Cr^{6+} in ground cement can be almost doubled by the use of high chromium alloy balls during finished grinding.

Kolovos et al. (2002a) have reported that addition of 1 % Cr_2O_3 to the raw mix can cause an increase in free lime content of the clinker. According to Stephan et al. (1999a and b, 2001), however, up to 0.5 % addition of chromium lowers the free lime, but 2.5 % chromium leads to decomposition of alite to form more belite and consequently more free lime. Chromium is mainly found in belite, but if potassium is high in the clinker, K_2CrO_4 and/or $K_2Cr_2O_7$ can also form.

Although a major portion of chromium incorporated in clinker is usually tied up in belite, ferrite or sulphate phases, chromium oxide is somewhat volatile and can end up in the CKD. Between 100 and 1000 ppm of Cr has been reported in CKD (Lee and von Lehmden, 1973). Delles et al. (1992) have shown Cr contents between 0.01 and 264 ppm in CKDs produced by burning conventional fuels, and between 0.01 and 299 ppm in CKDs produced by waste fuels. Levels of 20.6 mg/s and 12.5 mg/s have also been found in kiln emissions using conventional as well as waste fuels respectively (Mantus et al., 1992). In U.S. cement, total chromium is reported to be between 20 ppm and 450 ppm.

Bhatty (2003) has shown that chromium addition enlarges the alite crystal size. However, at higher chromium contents, decomposition of alite becomes persistent with ragged edges while belite becomes dendritic. Chromium also imparts dark green colour to the clinker.

Stephan et al. (1999a) prepared C_3S 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 that this positive effect disappeared above this level. In the following study, Stephan et al. (1999b) prepared pure C_3A and C_4AF with the same metals at the same elevated concentrations levels. They found no change in the modification of these phases. When the metal concentration was as high as 5 %, significant amounts of fCaO could be detected in the C_3A. In contrast, addition of these metals did not affect the C_4AF 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. In 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. Stephan et al. (1999b) found that Cr^{6+} existed as the separate phase $C_4Al_6O_{12}CrO_4$, as well as in solid solution with C_4AF.

According to Magistri et al. (2007), even when the raw material contains Cr^{3+}, due to the highly oxidizing and alkaline conditions of the kiln during clinker production it is partially converted to hexavalent chromium and probably fixed as alkaline or calcium chromate (Na_2CrO_4, K_2CrO_4, $CaCrO_4$) even though a fraction may enter the clinker minerals as contaminants as discussed above. As a result, the Portland clinkers and cements contain soluble chromates (usually in the range of 5 – 20 ppm or mg/kg, while the total chromium can reach 200 ppm) that are reported to cause skin irritation (allergic contact dermatitis). This is the reason why the European Community has recently introduced the obligation (Directive 2003/53/EC) to maintain the level of soluble chromates below 2 ppm (EUR-LEX, 2003). The reduction of soluble chromates (obtained with the addition of stannous or ferrous salts during cement grinding) has a great impact on the cement industry, and some European Companies report a total cost of about 10-15 million €/year. A number of patents report the use of inorganic reducing agents to control the Cr^{6+} leaching from cement. Most of these patents are of European origin and use ferrous sulphate heptahydrate, ammonium-ferrous sulphate, and manganese sulphate during intergrinding to convert Cr^{6+} to Cr^{3+}, which is more stable in an alkaline aqueous environment as cement and is not a significant health risk. Since fresh concrete is highly alkaline (pH 13-13.5) hexavalent chromium will be as CrO_4^{2-} in solution and any divalent iron would have precipitated as $Fe(OH)_2$ or remain in solution as $Fe(OH)_3^-$. The reduction mechanism is then;

$$CrO_4^{2-} + 3\ Fe(OH)_2 + 4\ H_2O = Cr(OH)_3 + 3\ Fe(OH)_3 + 2\ OH^- \qquad [1]$$

Trivalent chromium hydroxide precipitate as a solid or will enter calcium aluminate hydrates as in solid solution (see hydration of cement in section 3.5). The interactions between hexavalent chromium and cement hydration have been studied from the point of view of heavy metals immobilization and waste managements. AF_m phases and Ettringite are reported to be able to immobilize chromates (Klemm, 1998, and He and Suito, 2002). He and Suito (2002) studied the immobilization of Cr^{6+} by calcium aluminates and sulphoaluminates. By hydrating tricalcium aluminate in chromium containing solution they found a complete fixation of chromium after six hours. The main hydration products were C_3AH_6 and C_4AH_{19} and it was possible to verify (using a microprobe analysis) that the chromium was present only in the C_4AH_{19}. The authors concluded that this phase is responsible for the immobilization and that the chromate takes the place of one of the hydroxide ions in the coordination sphere of aluminium. It is also known that the chromate, having the same charge and a similar ionic radius of sulphate can have a similar behaviour and give Ettringite-like structures.

The chromate analogue of Ettringite has been studied by several authors. Teramoto and Koie (1976), studying the effect on cement hydration of several hazardous elements, noted the formation of an Ettringite-type phase containing chromate. Pöllman et al. (1993) synthesized a chromate substituted Ettringite and studied the solid solutions of sulphate and chromate Ettringite. Perkins, in his Ph.D. work (2000), synthesized the chromate analogous of Ettringite and measured its solubility after a set of dissolution and precipitation experiments. On this basis, he evaluated the solubility product and several thermodynamic properties (free energy and enthalpy of formation). Only a few studies have applied the same concept to the release of chromates from cement itself (Magistri and Padovani, 2006) and the results obtained are the following:

1. The amount of chromates released from a clinker and from cement produced with the same clinker can be very different: The presence of gypsum has a great influence.
2. Pure tricalcium aluminate fully immobilizes hexavalent chromium from an aqueous solution while a mixture of C_3A and gypsum does not.
3. The immobilization of chromates by C_3A is reversible: If the amount of sulphates in solution increases, the chromium already immobilized is released.

Magistri et al. (2007) verified the effect of fineness, type and amount of gypsum and presence of additives on chromium immobilization by pure C_3A. They also studied the release of chromates from real cement and presented a hypothesis about the chromate immobilization/release mechanism.

Ahn et al. (2007) studied the degree of substitution of tri- and hexavalent chromium into the Ettringite structure in order to evaluate the immobilization potential in the field. They found that Cr^{3+} substituted Al^{3+} in both Ettringite and monosulphate, while CrO_4^{2-} failed to compete with sulphate (SO_4^{2-}) in the formation of Ettringite.

Shimosaka et al. (2007) investigated how hexavalent chromium could be reduced during commercial clinker burning. They classified chromium in Portland cement clinker as follows;

1) "Total Chromium" means chromium as an element, regardless of the oxidizing state.
2) "Chromium (VI)" represents 50 to 80 % of the total chromium in clinker. It will mainly be incorporated into belite as (IV) and (V) and will become (VI) in water by disproportionation and is regarded as "total chromium (VI)"
3) "Soluble chromium (VI)" is the portion of the total chromium (VI) that rapidly dissolves in water. It represents, on average, approximately 20 % of the chromium in clinker. It is believed to exist as chromate (i.e. CrO_4^{2-}).

Shimosaka et al. (2007) focused on the fact that clinker burning consumes a large amount of fuel that has a reducing potential. Thus, there might be a burning condition under which the total and/or soluble chromium (VI) in the clinker is reduced. In order to control the burning atmosphere, large amounts of secondary fuels were injected into the rotary kiln systems. In these trials, two injection points, corresponding to the calcining zone and the cooling zone of the rotary kiln, were examined, as illustrated in Fig. 13. The one corresponding to the calcining zone was at the raw feed inlet of the rotary kiln, that is, underneath the final cyclone of the preheater. The other one, corresponding to the cooling zone, was at the clinker outlet of the rotary kiln, that is, adjacent to the main burner. These points were referred to the "kiln-tail" and "kiln-head." At the former injection point, waste tires were allowed to fall into the raw feed flow. For the latter, a mixture of coarse flammable waste (waste tire chips, waste plastics and waste wood chips) was pneumatically injected with a velocity of 60 m/s so that they directly impacted the clinker flow. A reducing atmosphere at 700°C or higher will reduce the chromium (VI) amount in a commercial clinker. The amount of sulphide in the clinker might be usable as an indicator of a reducing atmosphere for clinker burning. Pisters (1966) investigated the chromium amount in approximately 300 cements and found that, on average, approximately 20 % of the total chromium content exists as soluble chromium (VI) and this is still valid except for chromium reduced cements. According to Fig. 14 reproduced from Shimosaka et al. (2007), kiln-tail injection (Trial #3) needed more secondary fuel than kiln-head injection (Trial #4) to obtain the same ratio of total or soluble chromium (VI). It should be noted that kiln-tail injection had no effect on these chromium (VI) ratios in the lower consumption ranges. In addition, with kiln-head injection, they sometimes observed flaming fuel particles in the clinker cooler.

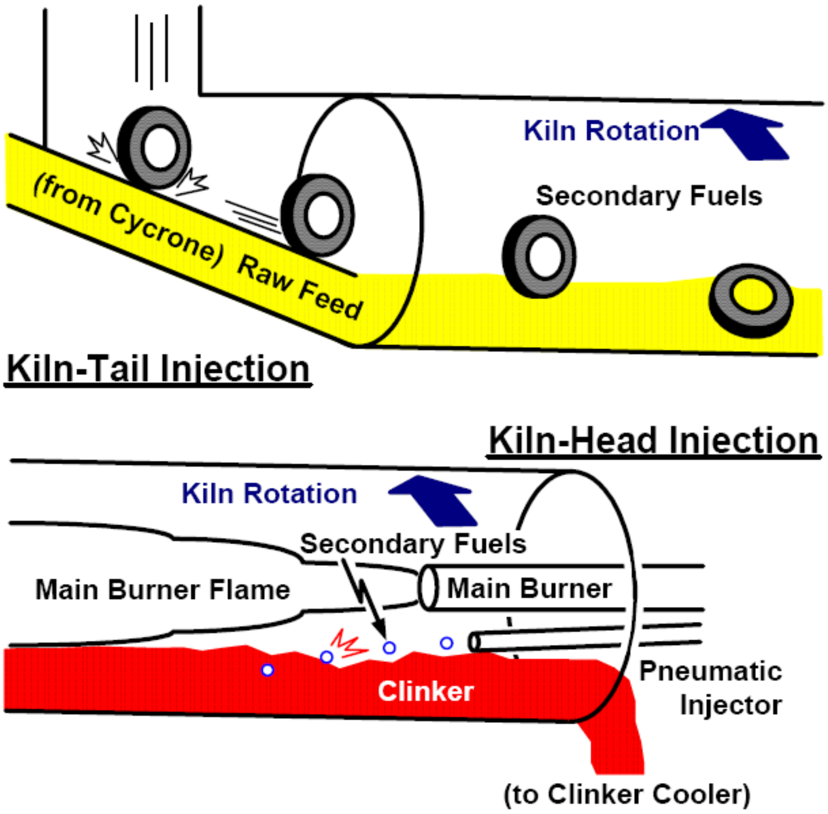


Fig. 13 Two methods of injecting the secondary fuels into the kiln system.

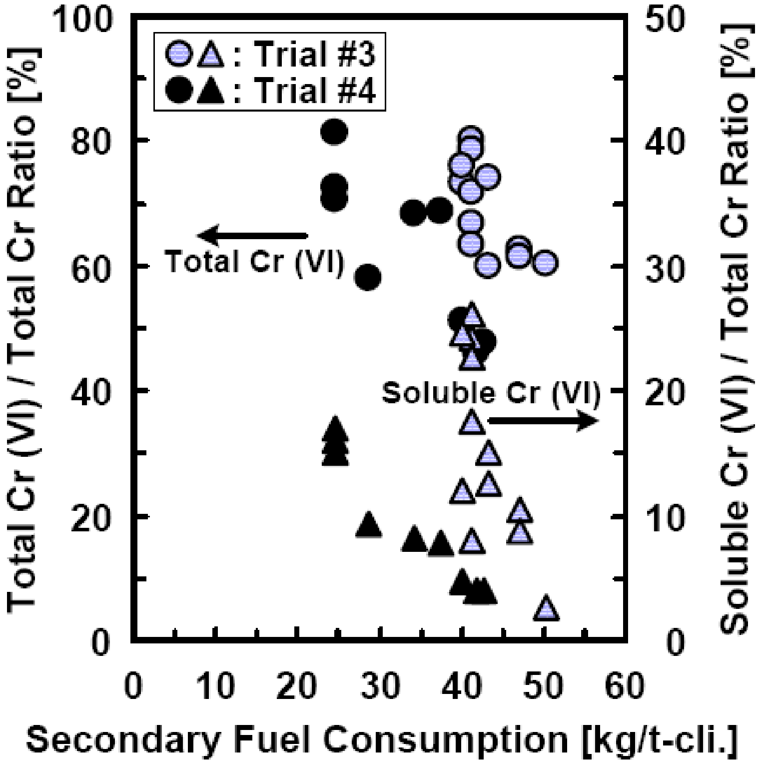


Fig. 14 Variations in the ratios of total (circles) and soluble (triangles) hexavalent chromium to total chromium as a function of secondary fuels consumption in Trials #3 (kiln tail injection) and #4 (kiln head injection).

The results from the study of Shimosaka et al. (2007) were summarized as follows:

1) Chromium (VI) in clinker was able to be reduced at 700 °C or higher temperature in a reducing atmosphere.
2) The amount of chromium (VI) in clinker was intentionally made variable via kiln operation. Increasing coarse-sized secondary fuel consumption, injecting secondary fuels into the clinker flow in the cooling zone of rotary kiln, or both, reduced chromium (VI) in commercial clinker.
3) Imperfectly flamed fuel particles that reached the cooling zone would decrease chromium oxidization in the cooling zone of a rotary kiln and/or clinker cooler, realizing a chromium reduction in the clinker.
4) The amount of sulphide in clinker is a somewhat rough chromium reduction indicator. It should be applied with restrictions to local conditions and facilities.
5) Chromium (VI) leaching from soils stabilized by such clinker described was decreased.

Tamás et al. (2007) investigated the use of different fuels and reducing slag to reduce hexavalent chromium during clinker production, and claimed that coal firing gave the best results. However, they recommended still to add a reducing agent when milling the clinker to cement. A similar statement was made by Opockzky et al. (2003) in their study on various heavy metals in cement in connection with co-processing waste.

Manganese (Mn) in clinker comes both from the primary and auxiliary raw materials. Limestone may contain up to 1.91 % Mn_2O_3 as the carbonate mineral rhodochrosite, whereas shales and bauxite could have up to 58.9 % and 36.7 % by weight, respectively (Bucchi, 1981). Mn_2O_3 could be present up to 1.2 % in blast furnace slag, and 1.44 % in coal fly ash.

Cement produced from slag can contain more than 1 % Mn_2O_3, which usually imparts a brown colour to cement (Hewlett, 1998). The polymorphism of silicate in clinker is affected by the presence of manganese oxides in the raw material. Knöfel et al. (1984) reported that the limit of Mn_2O_3 substitution in C_3S is approximately 2.2 % at 1,550°C. At lower concentrations, say ~0.1 % Mn_2O_3, single substitution of Si^{4+} by Mn^{4+} takes place, whereas at 2.2 % Mn_2O_3 concentration, a double substitution of Si^{4+} by Mn^{4+} and Ca^{2+} by Mn^{2+} is possible. The stabilized C_3S polymorph was identified as monoclinic, while Gutt and Osborne (1969) reported it to be triclinic. Miller (1976) demonstrated that at low levels (< 0.7 %) Mn stabilizes monoclinic alite, but at high levels and in the presence of fluoride, trigonal alite with markedly high hydration activity is formed.

Manganese can occur in a number of oxidation states depending upon the burning conditions in the kiln and can impart different colours in clinkers, ranging from reddish-brown to blue. Xiuji and Shizang (1986) reported that Mn^{4+} was not able to stabilise β-C_2S in contrast to its 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 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 Si^{4+} and that 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 % respectively and are thus confirming the selectivity.

Alite content of clinker increases with Mn addition, with maximum alite attained at 0.5 % MnO_2 and 1 % Mn_2O_3 (Knöfel and Gies, 1983). According to Hornain (1971), high Mn content promotes the formation of belite in the silicate phases, but is preferentially incorporated into the ferrite phase through the formation of “alumino-manganite,” such as “C_4AMn”. This reduces C_3A and marginally increases free lime, thus reducing the early strength of cement.

Manganese will not volatilize at kiln temperature (boils at 1,960°C) and is unlikely to concentrate in the CKD. Manganese at higher levels may impart a dark brown colour to clinker (Bhatty, 2003).

3.3.3.2 Co, Cu, Ni and Zn

Cobalt (Co) is present in traces in the raw mix. The maximum reported concentration is 23 ppm CoO. It has, however, been found at much higher levels (up to 1.27 %) in some of the coal fly ashes that could be used as a component for cement raw feed (Bucchi, 1981). The majority of cobalt that is present in the raw mix is incorporated in the clinker. The CoO level reported in cement is < 130 ppm, but the amounts detected in the alite and belite phases are only traces, since the bulk of cobalt is concentrated in the ferrite phase (see Fig. 12), by Co^{3+} replacing Fe^{3+} (Bhatty, 1995) and forming the “C_4ACo” phase. Cobalt can also give a darker colour to cement.

Studies by Odler and Abdul-Maula (1980a and b) showed that Co to some extent enhance the combination of C_3S and reduce the fCaO at 1,200°C. This effect increased at 1,300°C.

Sychev and Korneev (1964) demonstrated that Co somewhat reduces the hydraulic activity of alite and increases clinker hardness. According to Miller (1976), cobalt increases the water demand and marginally reduces the late strength of cement paste.

Cobalt and its oxides are unlikely to vaporize in the kiln or report to the CKD.

Copper (Cu) is also found in small amounts in the raw materials. Bucchi (1981) has quoted an average of 16 ppm cupric oxide (CuO) in the raw mixes, and up to 0.13 % in coal fly ashes. An average of 90 ppm CuO occurs in commercial clinkers. Copper preferentially concentrates in the ferrite phase, followed by alite, aluminate, and belite (see Fig. 12).

Miller (1976) reported that under oxidizing conditions, the small amount of copper present as CuO stabilizes alite, whereas under reducing conditions, copper as Cu_2O adversely affects both alite and belite phase formations. CuO can also function as a flux, as it decreases the melt temperature considerably (Rumyanstev and Kozlov, 1968). Odler and Abdul-Maula (1980a and b) measured significant reduction in fCaO at both 1,200 and 1,300°C for CuO. In fact Cu acted both as mineraliser 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 in the temperature region 1,000-1,300°C. Moreover, the sintering temperature was lowered. Kolovos et al. (2002a) basically confirmed the positive effect of CuO (at 1,200 and 1,450°C) among the elements most encountered in the field of mineralizers. Fig. 15 gives a nice overview of some of their results and illustrates the effect of CuO. 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 1,200-1,450°C. This proves that Cu is applicable to different clinker types (high C_2S and high C_3S).

It should be remembered that CuO accelerates C_3S formation, whereas Cu_2O inhibits it. Copper also imparts a dark tan colour to clinker (Bhatty, 2003).

Copper oxides are volatile at kiln temperature (melting points for CuO is 1,326°C and for Cu_2O 1,235°C). Thus, copper contents up to 500 ppm has been found in some cement kiln dusts (CKDs) in USA.

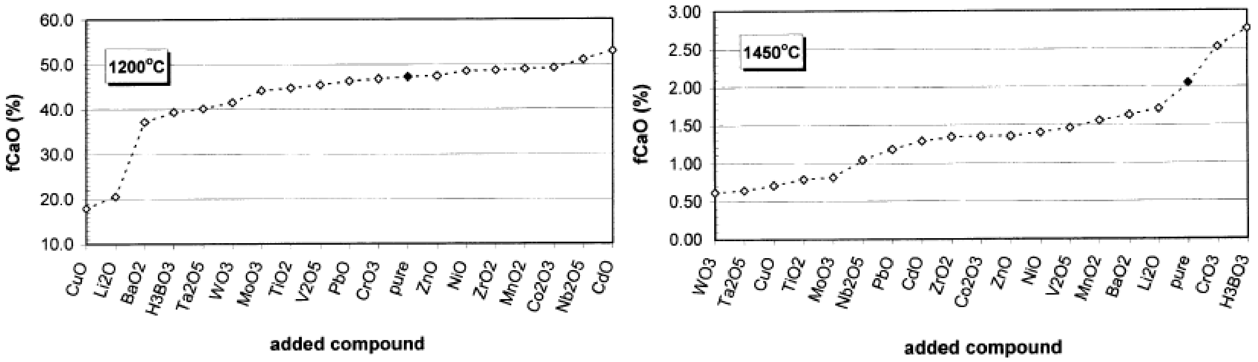


Fig. 15 Effect of different elements on the burnability (fCaO) at 1200 and 1450°C (Kolovos et al., 2002a).

Nickel (Ni) may occur in both raw materials and in fuels. Sprung (1985) has reported traces of nickel (Ni) in limestone (1.5-7.5 ppm), clay or shale (61-71 ppm), coal (20-80 ppm), used oil (3-30 ppm), and petroleum coke (208 ppm). In coal fly ashes, NiO may be present up to 1.9 % (Bucchi, 1981).

Nickel preferentially concentrates in the ferrite phase, followed by the alite, aluminate, and belite phases, as shown in Fig. 12 (Hornain, 1971). Between 0.5 to 1.0 % nickel stabilizes alite (Rangarao, 1977). NiO substitutes for CaO up to 4 mole% in alite and stabilizes the monoclinic form (Enculescu, 1974). This alite modification apparently enhances cement compressive strength.

The mineralizing effect of nickel (Ni) is reported to be marginal as concluded by Stephan et al. (1999a and b, 2001) where the effects of NiO on the formation of C_3S, C_3A and C_4AF were studied. Fig. 12 shows that Ni preferentially concentrates in the C_4AF phase and from Fig. 15 it is seen that some effect on the burnability was achieved only at the normal firing temperature of 1,450°C. Stephan (1999b) reported that increased liberation of heat was measured during hydration of C_4AF.

In clinkers with high magnesium levels, a new compound $MgNiO_2$ could form, whereas the remaining nickel goes to the interstitial phases. Nickel imparts dark brown colour to clinker (Bhatty, 2003).

Most Ni compounds are non-volatile, but owing to the volatile nature of some compounds (mostly $Ni(CO)_4$) nickel could end up in the kiln dust, although Delles et al. (1992) have shown a maximum of 50.5 ppm Ni in the CKD. In previous studies, concentrations between 100 and 1,000 ppm have been recorded in CKDs from certain U.S. cement plants (Lee and von Lehmden, 1973). An average concentration of 17.3 mg/s has also been found in the cement kiln emissions using conventional fuel, compared to 11.0 mg/s using waste fuels (Mantus et al., 1992).

The last first series transition metal in the periodic table is zinc (Zn). Zinc is a trace element in the raw mix, comprising 22-24 ppm in limestone, 59-115 ppm in clay or shale, and 16-220 ppm in coal. However, it can be present at up to 3,000 ppm in used oil as a potential secondary fuel, or 10,000 ppm in used automobile tires. Its concentration is also reported to be significant in alternative raw materials such as metallurgical slag (Miller, 1976).

Between 80-90 % of the ZnO in the raw mix becomes incorporated in clinker (Sprung and Rechenberg, 1978; Knöfel, 1978). Approximately half of the zinc is distributed in silicates with preference for alite over belite; the other half is distributed into the matrix with preference for the ferrite phase (Knöfel, 1978; Tsuboi et al, 1972). According to Hornain (1971), zinc in clinker is preferentially retained in ferrite followed by alite, aluminate, and belite (Fig 12). ZnO additions accelerate clinker formation, as would be expected from the relative levels substituted in the alite and belite phases. Formation of alite and C_4AF is enhanced at the expense of belite and C_3A due to ZnO doping (Odler and Schmidt, 1980).

Stevula and Petrovic (1981) prepared triclinic modifications of C_3S of the types TI-TII from mixtures of 0.75-1.5 % ZnO and pure C_3S which were fired at about 1,600°C and slowly cooled. Addition of 3.0 and 4.5 % ZnO formed rhombohedral C_3S with no free ZnO. Boikova (1986) noted changes in C_3S symmetry from triclinic to monoclinic and to rhombohedral with increasing ZnO additions. Stephan et al. (1999a and b, 2001) also noted that that zinc becomes incorporated in C_3S lattice by replacing calcium.

Odler and Abdul-Maula (1980a) found that 1 % ZnO promoted the clinkerization at 1,300°C whereas smaller effects were measured at 1,200°C in agreement with the trend shown in Fig. 15. 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* clinkering temperatures (1,450°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. Murat and Sorrentino (1996) added 10 % of $ZnCl_2$ (among other metal salts) to the raw mix. Approximately 50 % was found to be taken up in the clinker phases. They also confirmed that alite crystal sizes increases with increasing amount of Zn and high Zn amounts will eventually retard the setting of the cement.

Odler and Schmidt (1980) stated that the clinker could contain up to 0.5 % Zn without having negative effects of the cement properties. Up to 1.0 % ZnO in the raw mix decreases free lime considerably, retards the hydration, and reduces strength when added in excess of 1.0 % (Odler and Abdul-Maula, 1980a and b). Similar observations were reported by Knöfel (1978). Miller (1976) suggested the possibility of reducing contents of Zn in clinker by preferentially vaporizing it where the liquid phase is low, thus reducing the potentially deleterious effects on cement setting.

Barbarulo et al. (2007) reviewed the somewhat conflicting reports on the influence of zinc on cement properties as follows: It is well known that zinc added to cement strongly delays cement hydration (Arliguië and Grandet, 1985). The impact of zinc in the raw-mix on clinker reactivity has also been studied (Stephan et al., 1999c, Bolio-Arceo and Glasser, 2000, Kakali et al., 2003), but the effective impact and threshold level of ZnO addition inducing delay in hydration varies from one publication to another. Most authors (Stephan et al., 1999c, Kakali et al., 2003, Akatsu et al., 1968, Knöfel, 1978, Murat and Sorrentino, 1996, and Bordoloi et al., 1998) report a delay in cement hydration when ZnO is added to the raw-mix. According to Akatsu et al. (1968), the setting time seems to increase proportionally to CaO substitution by ZnO (+ 45 minutes for 1.0 % ZnO). Bolio-Arceo and Glasser (2000), on the other hand, find no negative (sometimes positive) effect on the setting time, even for high intakes of ZnO (up 1.5 %). The retarding effect of zinc in cement systems has to be considered if one wants to understand why different results are found in literature. According to Arliguië and Grandet (1982, 1985 and 1990a,b) and Arliguië et al. (1979 and 1982), who mainly studied the effect of zinc added to cement, the delay induced by zinc in cement systems is due Zn^{2+} ions in solution. Arliguië proposes the following mechanism: Zn^{2+} in solution react with hydroxyl ions to form an amorphous layer of $Zn(OH)_2$ around cement grains, resulting in a slower dissolution of clinker phases. When calcium concentration in solution reaches a sufficient level, hydrated calcium hydroxizincate $Ca(Zn_2(OH)_6)\cdot 2H_2O$ precipitates, thus dissolving the previous $Zn(OH)_2$ layer, and hydration can resume. The mechanism inducing a delay when ZnO is added to the raw-mix is probably the same, the main difference being that the Zn^{2+} concentration in solution will depend on the release of zinc from the dissolution of the zinc-bearing phases of clinker. Zinc has been reported to enter alite structure up to 2.5 % (Stephan et al., 1999a). However, in a Portland cement clinker, zinc is mainly present in the interstitial phase, the concentrations in alite and belite being closer to 0.1 % than 1 % (Bolio-Arceo and Glasser, 2000). Apart from what is found in the melt, more zinc is found in alite than in belite (Andrade et al., 2003). Zinc is also frequently found in Periclase, MgO, according to Andrade et al. (2003). When a large amount of ZnO (> 1 %) is added to the raw-mix, the X-ray diffraction peaks of aluminate (C_3A) are reduced while those of ferrite (C_4AF) are increased (Akatsu et al., 1968, and Bolio-Arceo and Glasser, 1998). Bolio-Arceo and Glasser (1998) showed that this corresponds to the apparition of a new phase, $(CaO)_6(ZnO)_3(Al_2O_3)_2$ (short hand notation $C_6Z_3A_2$ with Z meaning ZnO). This phase was previously described as $C_{14}Z_6A_5$ (Barbanyagre, 1997). The zinc aluminate phase $C_6Z_3A_2$ is reactive within a few hours or days and is considered as a cementitious material (Bolio-Arceo and Glasser, 2000). MgO can substitute ZnO in $C_6Z_3A_2$, giving the $C_6(Z_{1-x}M_x)_3A_2$ solid-solution (Bolio-Arceo and Glasser, 2000). Some authors find ZnO by energy dispersive analyses of X-rays (EDAX) using scanning electron microscopy (SEM) as Murat and Sorrentino (1996). Bolio-Arceo and Glasser (2000) reported that synthetic $C_6Z_3A_2$ added to cement delays the setting time by a factor of about 2. When the equivalent quantity of ZnO was added to the raw-mix, no delay was observed. There may thus be a difference of reactivity (and a difference of zinc release into solution) between synthetic $C_6Z_3A_2$ and the phase obtained during clinker sintering. This difference could come from MgO substitution: ZnO substitution in Periclase has been reported by Andrade et al. (2003), and ZnO substitution in $C_6(Z_{1-x}M_x)_3A_2$ by Bolio-Arceo and Glasser (2000).

Barbarulo et al. (2007) showed how the presence of MgO in the raw mix can reduce the negative effect of zinc on cement hydration as reproduced in Fig. 16. This was explained by a solid solution of ZnO into MgO in accordance with the phase diagram in Fig. 17. Thus, clinkers with high MgO content can tolerate a higher dosage of zinc, which can explain the different conclusions in the literature.

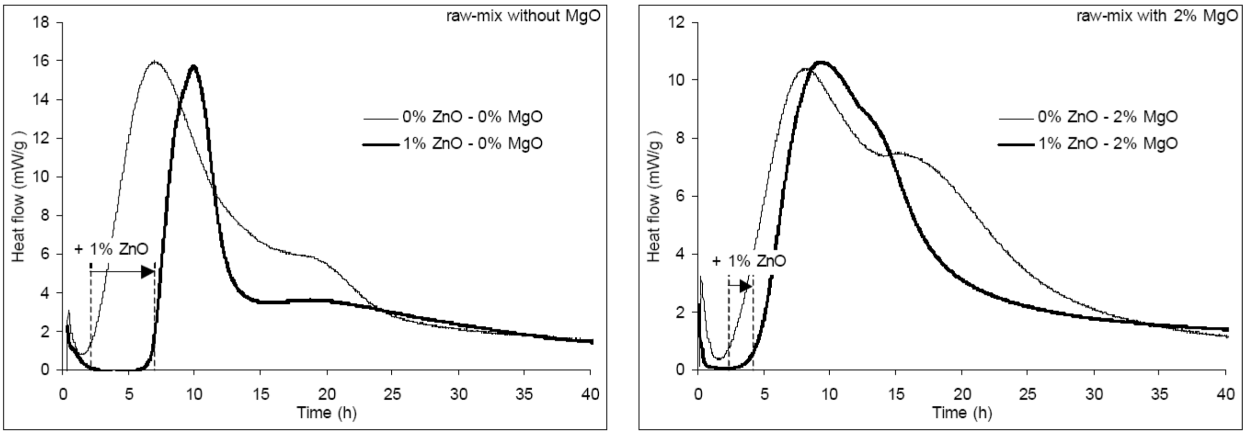


Fig. 16 The effect of 1 % ZnO on hydration of cement from clinkers with no MgO (left) and with 2 % MgO (right) as measured by isothermal calorimetry (Barbarulo, 2007).

According to Sprung and Rechenberg (1978), the volatility of zinc in preheater kilns could be 10-20 %. For a multi-stage preheater kiln, the capture of ZnO would be more effective and could result in the total incorporation into the clinker. An average of 149 ppm zinc is reported in the CKD from the U.S. plants using conventional fuel and 150 ppm for those using waste fuel (Delles et al., 1992); the corresponding zinc emission rates were only 2.97 mg/s and 1.53 mg/s, respectively.

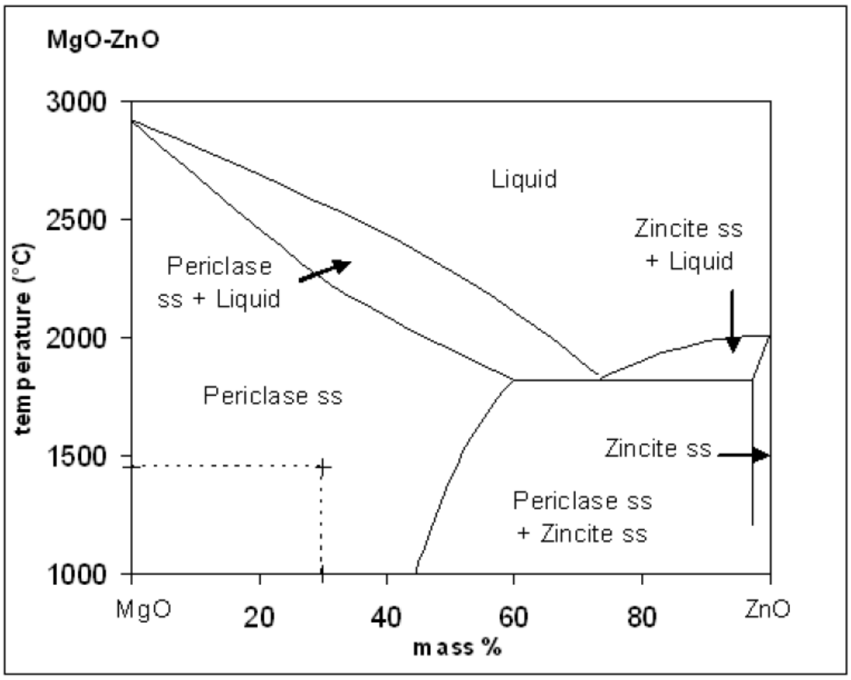


Fig. 17 Schematic representation of the MgO-ZnO phase diagram (www.adcis.net), with + indicating a composition investigated by Barbarulo et al. (2007).

3.3.4 Second series of transition metal oxides

The elements in the second series of transition metals that are of some interest to cement clinkerization are yttrium (Y), zirconium (Zr), niobium (Nb), molybdenum (Mo) and cadmium (Cd).

Isomorphism between yttrium (Y) and calcium frequently occurs in natural materials; for instance fluoroapatite, $Ca_5(PO_4)_3F$, can contain up to 10.6 % Y_2O_3, but presumably in cement raw materials, yttrium occurs only in traces.

Yttrium substitutes for Ca in both C_3S and C_2S according to Boikova (1986). It yields both triclinic and monoclinic forms of C_3S. In a C_2S-$Y_4(SiO_4)_3$ system, the region of homogeneity can exist up to 35 % $Y_4(SiO_4)_3$ by weight (Toropov and Fedorov, 1962b, and Toropov and Boikova, 1963).

Since yttrium is unlikely to volatilize at kiln temperature (melts at 1,522°C), it can hardly be expected to concentrate in the kiln dust.

Zirconium (Zr) is concentrated mostly in siliceous ores used as a component of kiln raw feed (Miller, 1976). Blaine et al. (1965) reported about 0.5 % zirconium, in the fully oxidized form of ZrO_2, in U.S. clinkers.

Kakali et al. (1990) found no significant change in the burning and cooling conditions for clinker prepared with 0.73-1.45 % ZrO_2; the principal phases, alite, belite, aluminate, and ferrites, were satisfactorily crystallized. However, ZrO_2 changed the size and shape of alite, while belite was modified. ZrO_2 also imparted a noticeable color change to clinker.

A significant retarding effect and a subsequent delay in strength for cements prepared with ZrO_2 containing raw mixes was also reported (Kakali et al., 1989). However, earlier studies by Blaine et al. (1965) indicated that smaller ZrO_2 additions increased the early strength of cement.

Niobium (Nb) is another element found in traces in raw materials. Weisweiler and Krčmar (1990) have reported more than 30 ppm niobium in the raw feed of a German plant.

Because of its low concentration in the raw mix, niobium would be expected to have very little effect on clinker formation. Kakali et al. (1990) reported a very feeble effect of Nb^{5+} addition (up to 1.5 % by weight) on the mineralogical texture and viscosity of clinker melts because of its low ionic charge to atomic radius ratio. Cement prepared from these clinkers did not show any noticeable change in setting or strength properties when compared to regular cement (Kakali et al., 1989).

Because niobium oxide is a high temperature oxide (melts at 2,468°C), it would be unlikely to concentrate in the kiln dust or stack emissions.

Molybdenum (Mo) is potentially an important trace element in AF, like lubricating oil (Gartner, 1980). In coal fly ash, MoO_3 could be as high as 1.5 % by mass. Up to 0.05 % of Mo has been reported in clinkers (Blaine et al., 1965). Molybdenum having a small radius and a high charge number is an effective reducer of the clinker melt viscosity as shown in Fig. 11. Kakali et al. (1990) reported the formation of larger and rounder alite crystals with some modified belite in clinker prepared with up to 1.5 % MoO_3 addition. However, cements made from these clinkers showed no adverse effects on their physical properties (Kakali et al., 1989). Kolovos et al. (2002a) have reported that addition of 1 % MoO_3 to the raw mix can reduce free lime in clinker by 30-60 %.

Cadmium (Cd) occurs in traces in the raw materials and fuels. Cadmium in the raw feed reacts with the constituent of kiln gas and can form halides or sulphates, both of which are readily vaporized at peak kiln temperature. The form of cadmium incorporated in clinker is not known; however, with increasing chloride input in the kiln, the concentration of Cd in clinker decreases. The addition of $CdCl_2$ to the raw mix has the same effect. In a cyclone preheater kiln, 74-88 % of the total Cd entering the kiln is incorporated in clinker as opposed to 25-64 % for that produced in the grate preheater kilns. The remaining Cd is captured in the kiln dust (Weisweiler and Krčmar, 1990).

Cadmium is volatile in nature, although not as volatile as thallium or chlorine (Sprung et al., 1984). CdO reportedly increased the burnability of the clinker by lowering the melt temperatures whereby Cd^{2+} most likely entered the silicate phases (Ramankulov et al., 1964). Improved clinker burnability with CdO addition was also noted by Odler and Abdul-Maula (1980a). The fact that cadmium is a carcinogenic metal significantly reduces the use of such a mineraliser.

3.3.5 Third series of transition metal oxides

The elements in the third series of transition metals that are of some interest to cement clinkerization are tantalum (Ta), wolfram (W) and mercury (Hg).

Tantalum (Ta) is present only in traces in cement raw materials. It is reported to be present at < 9 ppm in raw materials and 0.3 ppm in the oil coke used as fuel in cement (Weisweiler and Krčmar, 1990). Since tantalum is present as trace in both the raw feed and fuel, it is unlikely to impart any noticeable effect on clinker formation or cement use. Weisweiler and Krčmar (1990) reported 14.3 and 3.3 ppm tantalum respectively in clinker and kiln dust prepared from a raw material containing 8.9 ppm tantalum. Kolovos et al. (2002a) have reported that addition of 1 % Ta_2O_5 to the raw mix can reduce free lime in clinker by 30-60 %.

Wolfram (W), also called tungsten, is a trace metal in the raw mix and is expected to appear in traces in the clinker. Kakali et al (1990) noted that the addition of up to 1.5 % WO_3 in the raw mix changed the shape of alite crystals, making them bigger and rounder; the belite formed was of Type III and, to some extent, contained secondary dendritic crystals, probably because of excessive Si^{4+} replacement by W^{6+}. Dissolution of W^{6+} in the melt decreased the viscosity because of its large charge to radius ratio, as also exhibited in Fig. 11. Kolovos et al. (2002a) reported that addition of 1 % WO_3 to the raw mix can reduce free lime in clinker by 30-60 %. Ivashchenko (1991) reported that addition of W^{6+} also improved the granulometric composition of clinker and decreased dusting. Improved hydration rate was expected because of enhanced activity of ferrite and alite modification in the clinker. However, cement pastes prepared from these clinkers did not show any significant change in the setting or strength properties when compared to regular cements (Kakali et al., 1989). Wolfram is a very high temperature melting metal (melts at 3,410°C). Since it will not volatilize at kiln temperatures, partition of wolfram to the CKD is highly unlikely.

Mercury (Hg) is a trace element. It is highly volatile and vaporizes at very modest temperatures (boiling point = 557°C). Mercury is somewhat inert, and very little is known about its interaction in the clinker making process. It is very likely that mercury and its compounds would volatilize in the pre-calcination region at temperatures closer to 400°C and escape with the stack gases. Mantus et al. (1992) have shown that the emission levels of mercury from cement plants burning waste fuel (2.14 mg/s) are noticeably higher than those using conventional fuel (0.984 mg/s). Mercury levels in the respective kiln dusts are the same (0.4 ppm).

3.3.6 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 and so is ash from municipal waste incineration. 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.

The formation of the stable yet volatile alkali chlorides NaCl (boiling temperature = 1,413°C) and KCl (subliming temperature = 1,500°C) at clinkering temperature is well known. Both chlorides volatilize in the burning zone and condense in the cooler parts to form kiln rings or preheater build-ups which impair plant performance. Bhatty and Muhammad (1985) also concluded that agglomeration due to the presence of molten alkali chlorides was one of the major reasons for the build-ups. In cases of plants without preheater, the volatile chlorides end up in the kiln dust. In preheater kilns, up to 99 % of the chlorides are recaptured by the incoming feed in the calcining zone (Ritzmann, 1971); the concentration of chloride at that point could be extremely high (> 1 %) compared to that of raw feed (≈ 0.01 %).

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. The chloride content is also restricted to a level in the finished cement that will not initiate reinforcement corrosion. This means that not much chloride can be added for cements to be used in concrete with reinforcement. Mineralising effects of chlorides have been reported by Odler and Abdul-Maula (1980a) and levels of 0.5-1.5 % $CaCl_2$ were actually found to reduce the combination of lime. 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 1,200°C and received much interest in the early1980s. 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 1,200°C (Damao and Daxi, 1985, and Cheng and Fang, 1989). Note that the Chinese cement standard is under revision and will set a requirement to cement to contain < 0.06% Cl^-, while there was no stated limit in earlier versions.

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. Instead, a double substitution with Al^{3+} for Si^{4+} and of F^- for O^{2-} occurs in order to fulfil the electro-neutrality principle in the crystal (Shame and Glasser, 1986). This leads to extensive solid solution formation and increased thermodynamic stability of C_3S relative to C_2S as illustrated in Fig. 18. The lower stability limit was obtained at a temperature below 1,100°C compared to a normal limit at 1,250°C. Moreover, addition of fluoride seems to stabilise the high-temperature 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. Fluoroaluminates tend to increase the early strength development and form 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 1,320°C or with lower cooling rate than with conventional clinker. Fluoroaluminate cement is one of the many special types of cement produced in China (Sui and Yao, 2003).

If x = 0.15 (15 mol %) in Fig. 18 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 %. 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 than the 0.5 % F above, as the concentration needed for C_3Sss to be stable is below 1,100°C (Fig. 18).

Fluoride in combination with sulphates is a far more effective mineraliser than fluoride alone (Moir and Glasser, 1992). The $CaSO_4$-CaF_2-Ca_2SiO_5 system is explained in Giminez-Molina et al. (1991). The apatite like structure fluorellestadite, $3C_2S{\cdot}3CaSO_4{\cdot}CaF_2$, was found to be stable up to the incongruent melting point at around 1,240°C. It was recommended to avoid the composition that favoured fluorellestadite due to its inertness. Emmanuelson et al. (2003) investigated F^- and SO_4^{2-} mineralised 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 mineralisers. This proves the complexity of assessing specific mineralising effects. Moreover, rhombohedral as well as monoclinic alite was identified in the two different clinkers tested.

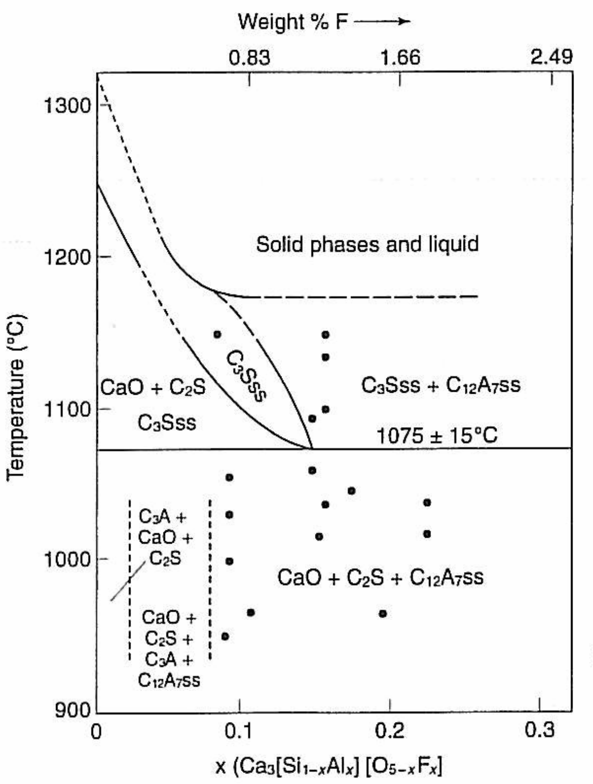


Fig. 18 C_3S stabilised by addition of fluoride showing extensive formation of solid solution (ss) and that C_3Sss theoretically is stable as low as 1075°C when x = 0.15 (Glasser and Marr, 1980).

With some exceptions, bromine (Br) plays a minor role in cement manufacturing. Bromine occurs only as a minor element in raw materials, for example lime stone (6 ppm), clay (10-58 ppm) and coal (7-11 ppm) according to Akstinat and Rott (1988) and Sprung (1985). Bromine has also been detected at measurable levels in some of the fly ashes generated at coal-operated power plants, and may of course exist in higher amounts in some special wastes (e.g. bromated flame retarders). Bromine is volatile and expected to end up in stack emissions (Akstinat and Rott, 1988). Under oxidizing conditions, bromine gas (Br_2) would form and end up in emissions. Retention of bromine in clinker is negligible. Alkali bromide may be found in low concentration in clinker kiln dust (CKD).

Iodine (I) is very seldom present in any considerable amounts. Iodine salts are however volatile in nature and would mostly end up in dust and as emissions (Bhatty et al., 2004).

3.3.7 P-block elements

The most encountered elements in this group are sulphur (S) and phosphorus (P) and to a lesser extent boron (B), arsenic (As), tin (Sn), antimony (Sb), thallium (Tl) and lead (Pb).

Sulphur participates in the alkali sulphate cycle in the cement kiln as explained in section 3.3.2. Emmanuelson et al. (2003) found the mineralising mechanism of sulphur on the silicates to be 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 mineraliser 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 content of free CaO in the finished clinker, and additions of these mineralisers 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. Emmanuelson et al. (2003) showed that the accumulated reaction heat of the clinker mineralised with CaF_2 was higher than the reference after hydration for half a day as shown in Fig. 19.

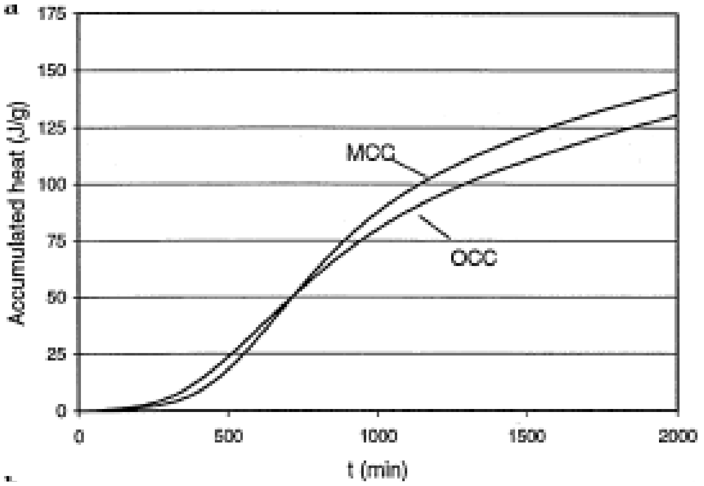


Fig. 19 Accumulated heat of reaction for hydration of ordinary cement clinker (OCC) and CaF_2 mineralised cement clinker (MCC) after Emmanuelson et al. (2003).

Phosphorous (P) is relevant as mineraliser since it occurs both in primary raw materials (limestone and shale) as apatite in certain parts of the world (Bucchi, 1981, and Moir and Glasser, 1992) and in industrial by-products, which may be used as secondary raw materials (slags from the metal extractive industries). The partial replacement of fossil fuel with meat and bone meal (MBM) used as alternative fuel represents a source for an additional amount of P_2O_5 present in clinker. Inorganic phosphorus compounds present in these materials would combine mainly with the silicates formed during clinkering (Gutt, 1968, and Nurse, 1952).

It has been shown that a high level of phosphorus inhibits the alite formation. Halicz and Nathan (1994) obtained synthetic clinkers prepared from oil shale containing up to 5 % P_2O_5 as a secondary component. Although C_3S contents decreased considerably when the P_2O_5 amount increased, satisfactory C_3S contents were achieved by taking the P_2O_5 concentration into account in the silica modulus formula. Gutt (1968) showed that the limit of inclusion of phosphate ions in alite solid solution is about 1.1 % P_2O_5. High amounts of phosphate led to preferential formation of phosphatic dicalcium silicate solid solution. Diouri and Boukhari (1997) studied the effect of combination of manganese and phosphorus elements on the formation of solid solutions, by heterovalent substitution of corresponding ions in C_3S lattice. They observed that the monoclinic type 3 polymorph of alite was formed at Mn and P inclusions less than 0.69 % Mn_2O_3 and 0.62 % P_2O_5. At higher amounts of these oxides, the alite phase is not formed and solid solutions of C_2S phase along with $2CaO \cdot MnO_2$ and CaO are obtained.

The Fe_2O_3 and P_2O_5 additions to a mixture with molar ratio $CaO/SiO_2 = 2$ induce a reduction of the onset decarbonation temperature and stabilize β, ά, and α forms for amounts less than 9.50 % Fe_2O_3 and 8.45 % P_2O_5 (Benarchid et al., 2004). The hydraulic activity evaluated by heat evolution was reported to be higher for β-phase than for $\acute{\alpha}_L$-phase in the case of dicalcium silicate doped with phosphorus (Fukuda and Taguchi, 1999). This effect was attributed to twin boundaries that appear in β form and behave like active centres for the reaction with water. On the contrary, the crystal fragments of $\acute{\alpha}_L$ -phase were nearly uniform with occasional line defects. As a result, the hydration rate of the β-phase was, during the early stage of the process, much higher than that of the $\acute{\alpha}_L$ -phase, leading to the higher cumulative heat evolution of the former phase.

Kolovos et al. (2001) studied the effect of adding different anions to the raw mix at 1,200 and 1,450°C. It was found that the chemical form (speciation) of the mineraliser added did not affect the fCaO content determined for sulphur and fluorine as can be seen in Fig. 20. For phosphorus, however, it 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 $CaHPO_4$ is equivalent to 0.6 % and 0.7 % PO_4^{3-} respectively, i.e. below this limit.

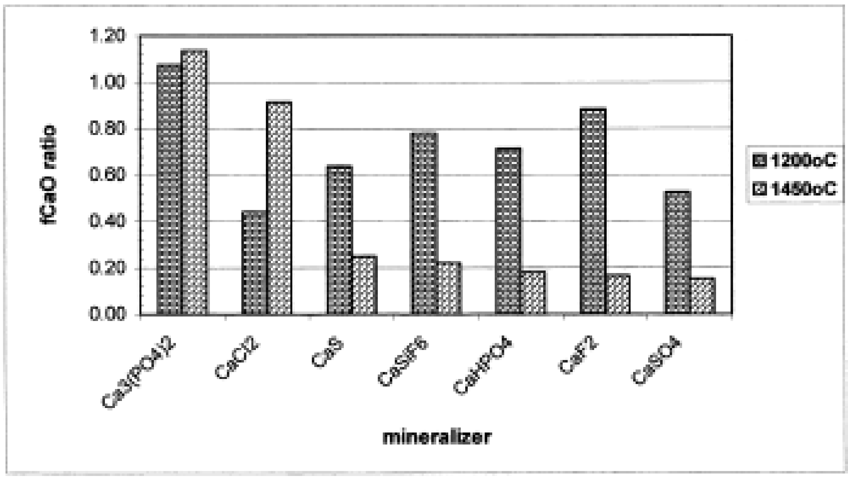


Fig. 20 The fCaO ratio of mineralised samples relative to the reference sample (Kolovos et al., 2001).

Boron (B) is generally found in traces (3 ppm) in most cement raw materials, particularly those containing iron ore. Boron may, however, be present in alternative raw materials (AR) and may very well act as a mineraliser as well as a fluxing agent. However, the overall effect on C_3S is negative whereas boron stabilise C_2S. According to Kolovos et al. (2002a) it still is debateable, concerning the C_3S formation, whether boron stabilise C_2S or destabilise C_3S. However, Moir and

Glasser (1992) pointed out that B_2O_5 was not found to be present as C_3S solid solution and the decomposition (destabilisation) of C_3S was the likely explanation: $C_3S \Rightarrow C_2S + CaO$.

Concerning the boron mineralising effect on C_2S, extensive solid solution formation was found by 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 ($x = \sim 0.3$) α-like C_2S polymorphs were formed. In view of these findings it seems that boron might be used in production of belite clinkers. In Fig. 15 one can see the effect of 1 % H_3BO_3 addition. The determined fCaO (free CaO) at 1,200°C was largely reduced whereas a significant negative effect was found at 1,450°C. This is in good agreement with our overall picture; enhancement of the belite phase and inhibition of the alite phase.

Arsenic (As) bearing minerals arsenolite or claudite As_2O_3 (or As_4O_6) occur only in small amounts in coal and used oils, and are unlikely to influence cement manufacturing in any way. Smith et al. (1979) have indicated that in coal-fired power plants, both As and Sb tend to concentrate in the fly ash, but their concentration levels are extremely low. It tends to concentrate in the fine fractions of fly ash (Coles et al., 1979). Weisweiler and Krčmar (1989) have reported up to 5 ppm of As in raw material and only 0.6 ppm in petroleum coke.

Tin (Sn) is a trace element in both the raw feed and fuel. Elemental tin is reasonably non-volatile (boils at 2,265°C). Tin oxide (SnO) or natural cassiterite melts at 1,630°C and sublimes between 1,800°C and 1,900°C. It is very likely that tin will remain in the clinker. Not much is known about the effect of tin in clinker manufacture.

Antimony (Sb) occurs as traces in cement raw materials. It has been reported to occur at 0.08 ppm in the raw feed and 0.0429 ppm in petroleum coke (Weisweiler and Krčmar, 1989). A considerable portion of antimony gets incorporated in clinker in the form of low volatile calcium antimonates under oxidizing kiln conditions at high temperatures (Weisweiler and Krčmar, 1989). The oxides, Sb_2O_3, natural seranmontite, and valentinite, are not very volatile at kiln temperatures; they sublime at 1,550°C. However, some high levels of Sb have been reported in the kiln dust from some cement plants by Lee and von Lehmden (1993). Gartner (1980), however, argued that the limited nature of this data might not be very reliable. Bhatty (2003) has shown that the addition of antimony reduces the formation of ferrite to the benefit of aluminates. Additionally, alite formation is improved, however the size of both alite and belite are reduced.

Thallium (Tl) is found only in traces in raw material; its concentration in coal is only 1.1 ppm. Thallium may also be present in some pyritic minerals used as an iron source for raw feed; it is sometimes found in coal fly ashes, or is present in industrial by-product iron sources. Although thallium occurs in traces in the raw feed, it is the most volatile element after mercury in the kiln (melting at 303°C), and is most likely to concentrate in the kiln dust. Since thallium may be present in the fly ash used in cement raw feed, or as Sprung et al. (1984) discovered, in industrial by-product iron sources, it tends to build up in extremely large internal cycles in cement kilns and may lead to contents greater than 10,000 ppm in CKD if no dust is discarded.

Lead (Pb) is often present in trace amounts in raw materials – mainly clay and shale. It is present at appreciable levels in coals (11-270 ppm), used oils (10-21700 ppm), lubricating oils, and scrap tires. In fly ash, lead tends to concentrate in the fine fractions (Coles et al., 1979).

The effect of lead in cement manufacturing and cement properties has been studied in some detail. Lead compounds are fairly volatile. They tend to vaporize in the kiln and exit the kiln as fines, and are collected in the kiln dust. Mantus et al. (1992) have shown that the lead concentration levels in the CKD from cement plants burning certain waste fuel (277 ppm) can be much higher than those plants using conventional fuel (83.1 ppm). There is also evidence that despite the partitioning of lead into the CKD, the bulk of the lead can still be retained in the clinker (Berry et al., 1975). However, this would have no adverse effect on the cement properties if present below 70 ppm. The effect of lead levels higher than that in clinker is uncertain (Sprung and Rechenberg, 1978).

Andrade et al. (2003) synthesized clinker with lead (0.67 % PbO) and found that Pb concentrated in some minute spherules (separate compound) and partitions towards alite in only small amounts. Leaching test on cement from the clinker (Maringolo, 2001) revealed a very low mobility of Pb.

3.3.8 Rare earth elements

Elements 51-71 in the periodic table are commonly known as “the rare earths” or “lanthanides.” They are present only as traces in raw materials and cement clinkers. Owing to their presence at extremely low levels, they have not been the subject of extensive studies in cement manufacturing. Since the rare earths have very similar properties to one another, it is assumed that they all will have somewhat similar effects on the clinker formation. The following section discusses the findings from reported literature data.

Boikova et al. (1964), Boikova and Toropov (1966) and Boikova (1986) and Toropov et al. (1962a and b, 1963) observed the substitution of rare earths for Ca in both C_3S and C_2S. The solid solution of C_3S with oxyorthosilicate of lanthanum (La) and scandium (Sc) results from the similarities in ionic size, and chemical properties between Ca, La and Sc. Formation of C_3S solid solution with gadolinium (Gd) and neodymium (Nd) have also been reported. Jantzen and Glasser (1979) reported that nearly 15 % of $Nd_4 \cdot Si_3O_{12}$ could be dissolved into β-C_2S, which has identical hydration activity to that of regular β-C_2S. La stabilizes all modifications of C_3S solid solutions (Stevula and Petrovic, 1981, and Sinclair and Groves, 1984). Gd gives the triclinic and monoclinic formulations, whereas Sc produces only the triclinic C_3S solid solutions. Leaching of Nd stabilized in cement pastes is fairly low.

Lanthanum also stabilizes the solid solution of C_2S by substituting for Ca^{2+} (Toropov et al., 1962a and b, 1963). Boikova (1986) assumed, based on the observations on selected rare earths such as La, Nd, Gd, and Sc, that the remaining rare earths with similar chemical and ionic characteristics would isomorphously substitute for Ca^{2+} in C_3S and C_2S. As a result, a preferential distribution of rare earths in wastes could be expected in the clinker silicate phases. Rumyantsev and Skotnikova (1970) reported that the addition of La_2O_3 in the raw mix accelerates the formation of clinker under laboratory conditions; the engineering properties of the resulting cements are also enhanced when compared to reference.

Studies of rare earths in cement manufacturing also stemmed from the possibility of using low to medium level radioactive wastes that might contain significant amounts of rare earth elements as mineralizers. Studies by Jantzen and Glasser (1979), Jantzen et al. (1982) and Boikova (1986) indicated that raw mixes with 20-30 % radioactive waste composed of La_2O_3, UO_3, Ce_2O_3, and other oxides, give optimum elemental distribution in clinker when fired at 1,100-1,200°C. This prevents volatilization and activation of radionuclides which occurs at 1,200°C. On the other hand, full radionuclide partitioning of raw mixture with radioactive wastes will not occur at temperatures below 1,100°C.

Jantzen and Glasser (1979) developed clinkers by incorporating 15-20 % by weight of radioactive wastes and firing at about 1,200°C. The clinkers were slow to react, but the ultimate hydration products were primarily stable insoluble calcium silicates hydrates with reasonable distribution of the radionuclides. Sichov (1968) reported that La, Nd, and Ce enhanced the hydration activity of alite. Rare earths have low volatilities (Klein et al., 1975) and are very unlikely to end up in the kiln dust.

3.4 Dry cement

Portland cement is clinker ground together with calcium sulphate to regulate setting, sometimes ferrous sulphate to reduce chromium and minor additives like grinding aids. In a specification sheet of a dry cement, the main elements are given, either determined by X-ray fluorescence (process control) or analytical chemistry (according to codes for specification), and given as the corresponding oxides. Assuming that the only minerals in the cement are alite, C_3S (i.e. Ca_3SiO_5), belite, C_2S (i.e. Ca_2SiO_4), aluminate phase, C_3A (i.e. $Ca_3Al_2O_6$), ferrite phase, C_4AF (i.e. $Ca_4Al_2Fe_2O_{10}$) and anhydrite, $C\bar{S}$ (i.e. $CaSO_4$), the content of these minerals may be calculated through mass balances (i.e. Bogue calculations). The first four minerals are formed during equilibrium conditions in the burning of the cement clinker, while the anhydrite (or alternatively gypsum, $C\bar{S}H_2$, or hemihydrate, $C\bar{S}H_{0.5}$) is added to the mill when clinker is ground to cement.

The content of other oxides is also usually given; N (i.e. Na_2O), K (i.e. K_2O) and M (i.e. MgO). Note that the alkalis often are found as the mineral $K_3N\bar{S}_4$ or in solid solution in the main minerals. "Free lime" is the content of free CaO due to insufficient burning or the decomposition of C_3S into C_2S and "free lime" if the cooling rate is too low.

The specific surface area (m^2/kg) of cement is commonly determined directly by an air permeability method called the Blaine method. In addition to the specific surface, the particle size distribution is of importance for the hydration rate of cement, since the hydration takes place at the interface between the cement grain and the water phase. However, it is important to realise that the surface of a cement grain is inhomogeneous as sketched in Fig. 21. The distribution of C_3S/C_2S- and C_3A/C_4AF-domains are determined by the milling process and the difference in resistance against fracture of the clinker minerals (see Fig. 7). Note that since cement grains are composite grains with may be all 4 major phases in one grain (as indicated for a large grain in Fig. 21), efforts to simulate cement by adding corresponding amounts of individual minerals will fail.

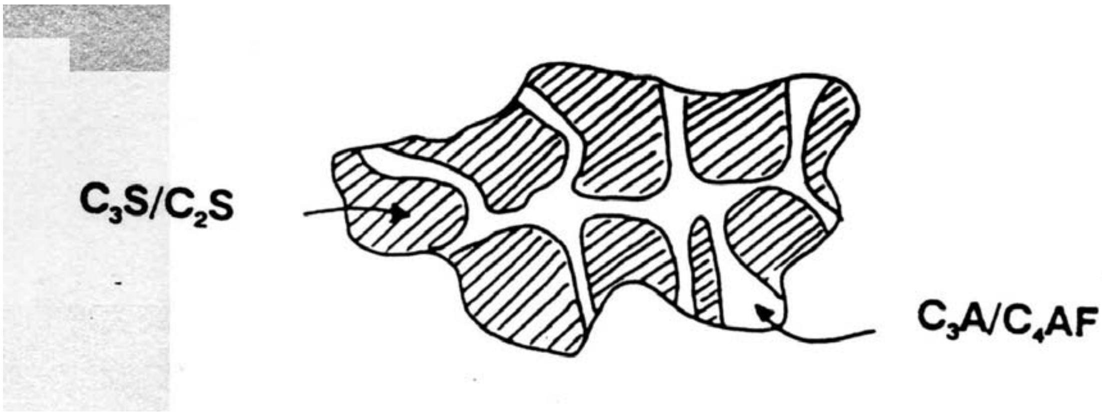


Fig. 21 The inhomogeneous nature of a cement grain showing domains of C_3S/C_2S and C_3A/C_4AF.

Nowadays, many of the cements on the market are blended. That means that supplementary cementing materials (SCM) are interground with the cement clinker. SCMs can be blast furnace slag, fly ash etc as outlined in chapter 3.4.1. It is important to notice that the definition of common cements according to the European standard EN 197-1 is composition based (see section 3.4.1), while the definition according to the American standard ASTM is performance based (see section 3.4.2). Both are outlined here to illustrate the complexity of cements in the market as well as background for the next chapter on hydration of cement recommended to understand binding of heavy metals etc in a concrete. The Chinese standard which is under revision is review in section 3.4.3.

3.4.1 Definition of common cements according to EN 197-1

EN 197-1 classifies cements based on calcium silicate hydrates for hardening and which are for general use. The constituents for these cements are;

1. Portland cement clinker (K)
2. Granulated blastfurnace slag (S)
3. Pozzolanic material (P and Q)
4. Fly ash (V and W)
5. Burnt shale (T)
6. Limestone (L, LL)
7. Silica fume (D)
8. Minor additional constituents
9. Calcium sulfate
10. Additives

The constituents of cement are sub-divided into main and minor additional constituents. Main constituents are the substances listed above from 1 to 7, provided their content in the cement exceeds 5 % by mass. Minor additional constituents can all be the substances listed under 1 to 8, provided they have a maximum content of 5 % by cement mass, as well as inorganic mineral substances from clinker production. The data concerning the cement composition, and also concerning the proportions of calcium sulfate and additives, always relate to the total of all main and minor additional constituents in the cement without taking the calcium sulfate and additives into account.

1. Portland cement clinker (K)
Portland cement clinker is also known as cement clinker or just clinker. At least 2/3 of it consists of the two calcium silicates, namely tri- and di-calcium silicate, which are richest in CaO and can react with the mixing water and harden reasonably rapidly. Portland cement clinker is therefore a hydraulic substance.

2. Granulated blastfurnace slag (S)
Granulated blastfurnace slag is a granulated, rapidly cooled, and therefore predominantly glassy, basic blastfurnace slag. It is a latent hydraulic substance because it reacts only slowly with water. It reacts and hardens, however, relatively rapidly with the formation of calcium silicate hydrates when mixed with activators such as cement clinker. Granulated blastfurnace slag must consist of at least 2/3 by mass of glassy slag and at least 2/3 of CaO, MgO and SiO_2 in order to be defined as blastfurnace slag by EN 197-1.

3. Pozzolanic material (P and Q)
Pozzolanic materials are natural or industrial substances which, because of their content of reactive silicon dioxide, SiO_2, react when finely ground in the presence of water at normal

ambient temperature with dissolved calcium hydroxide, form calcium silicate hydrates, and as a result can harden hydraulically. Reactive silicon dioxide, which is present either as free SiO_2 or combined in aluminosilicate, is therefore essential for the pozzolanic hardening. Calcium aluminate hydrates, which can also contribute to the strength formation, are also formed. The proportion of reactive CaO is unimportant. The content of reactive SiO_2 content must be at least 25 % by mass. Although fly ash and silica fume have pozzolanic properties they are dealt with separately in points 4 and 7.

Natural pozzolana (P) are usually materials of volcanic origin or sedimentary rock of suitable chemical and mineralogical composition. This also includes trass.

Industrial pozzolana (Q) can be thermally treated and activated clays and shales, and air-cooled slags from the extraction of lead, copper or zinc, provided they contain sufficient concentrations of reactive SiO_2.

4. Fly ash (V and W)
Fly ash is obtained by electrostatic or mechanical precipitation of dust particles from the furnace exhaust gases. It may only be used for cement production if it comes from a furnace fired with pulverized coal. The fly ash is either an aluminosilicate or a calcium silicate depending on how the silicon dioxide is chemically combined. Because of the content of reactive silicon dioxide both types have pozzolanic properties. Calcium silicate fly ash has also hydraulic properties. In order to limit the content of incompletely burnt substances the loss on ignition must not exceed 5.0 % by mass.

Siliceous fly ash (V) is a fine powder, consisting predominantly of spherical and glassy particles, which has pozzolanic properties. It must contain less than 5 % by mass of reactive CaO and at least 25 % by mass of reactive SiO_2.

Calcareous fly ash (W) is a fine powder with hydraulic and/or pozzolanic properties. The content of reactive CaO must be ≥ 5 % by mass. Calcareous fly ash, containing between 5 and 15 % by mass of reactive CaO, must contain more than 25 % by mass of reactive SiO_2.

5. Burnt shale (T)
Burnt oil shale has particular importance as a constituent of hydraulic binders. It is produced in a special furnace at approximately 800°C. Because of the content of calcium carbonate and sulfur in the natural starting material the burnt oil shale contains clinker phases, mainly dicalcium silicate and monocalcium aluminate, as well as small quantities of free CaO and calcium sulfate and larger proportions of pozzolanic substances. In a finely ground state such burnt shales therefore exhibit not only hydraulic properties, such as those of Portland cement, but also pozzolanic properties.

During strength testing in mortar after moist storage, finely ground burnt oil shale must reach a compressive strength of 25.0 N/mm^2 at 28 days. It must also be sound (i.e. pass the expansion in the Le Chatelier test) when mixed with 70 % by mass of Portland cement.

6. Limestone (L and LL)
Limestone must meet the following requirements:

a) The limestone must contain at least 75 % by mass of $CaCO_3$ calculated from the CaO content
b) The clay content, determined by the methylene blue adsorption on the pulverized limestone, must not exceed 1.20 g/100 g limestone

c) The total content of carbon (TOC) as a measure of the content of organic constituents must not exceed 0.2 % by mass for limestone LL and 0.50 % for limestone L.

7. Silica fume (D)
Silica fume consists of very fine spherical particles with a content of amorphous silicon dioxide SiO_2 of at least 85 % by mass. Silica fume must meet the following requirements:
a) The loss on ignition must not exceed 4.0 % by mass.
b) The specific surface area (BET) must be at least 15 m^2/g.

8. Minor additional constituents
Minor additional constituents are natural or synthetic inorganic mineral substances which, after appropriate preparation, improve the physical properties of the cement, e.g. its workability or water retention, through their particle size distribution. They can be inert or have slightly hydraulic, latent hydraulic or pozzolanic properties. However, no requirements are set for them in this respect. They must be correctly prepared, i.e. selected, homogenized, dried and comminuted, to suit their state of production or delivery. They must not increase the water demand of the cement appreciably, impair the resistance of the concrete or mortar, or reduce the corrosion protection of the reinforcement.

9. Calcium sulfate
Calcium sulfate, in the form of gypsum ($CaSO_4 \cdot 2H_2O$) or β-anhydrite (β-$CaSO_4$), or as a mixture of these compounds, is added in small quantities to the cement during its manufacture to control the setting. β-anhydrite is the naturally occurring modification of water-free $CaSO_4$, and is also known as anhydrite II. α-anhydrite (anhydrite I) is the high-temperature modification of $CaSO_4$ and is stable only at temperatures above 1180°C. If part of the water content of gypsum is removed, Hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$) is formed, while complete dehydration produces "soluble" γ-anhydrite (γ-$CaSO_4$) also known as anhydrite III. The Hemihydrate occurs in two forms, known as α- and β-Hemihydrate. They both have the same crystal lattice and differ only in the way they are formed, and are therefore not polymorphic modifications. The more coarsely crystalline α-Hemihydrate with lower water demand is formed when gypsum is dehydrated in an autoclave, and β-Hemihydrate with a substantially greater specific surface area and higher water demand is formed by "dry" dewatering in rotary kilns, boilers at temperatures from 120°C to 180°C or simply due to the heat in the mill where the constituents and gypsum are ground to cement.

Gypsum and β-anhydrite occur naturally, but the calcium sulfates which are generated in various industrial processes can also be used as setting regulators. This applies in particular to chemical gypsum, which is generated during the extraction of phosphoric acid from calcium phosphates (phosphogypsum) or during the extraction of hydrofluoric acid from fluorspar (fluogypsum) as well as to FGD gypsum (i.e. gypsum from flue gas desulphurization plants) mainly in power stations.

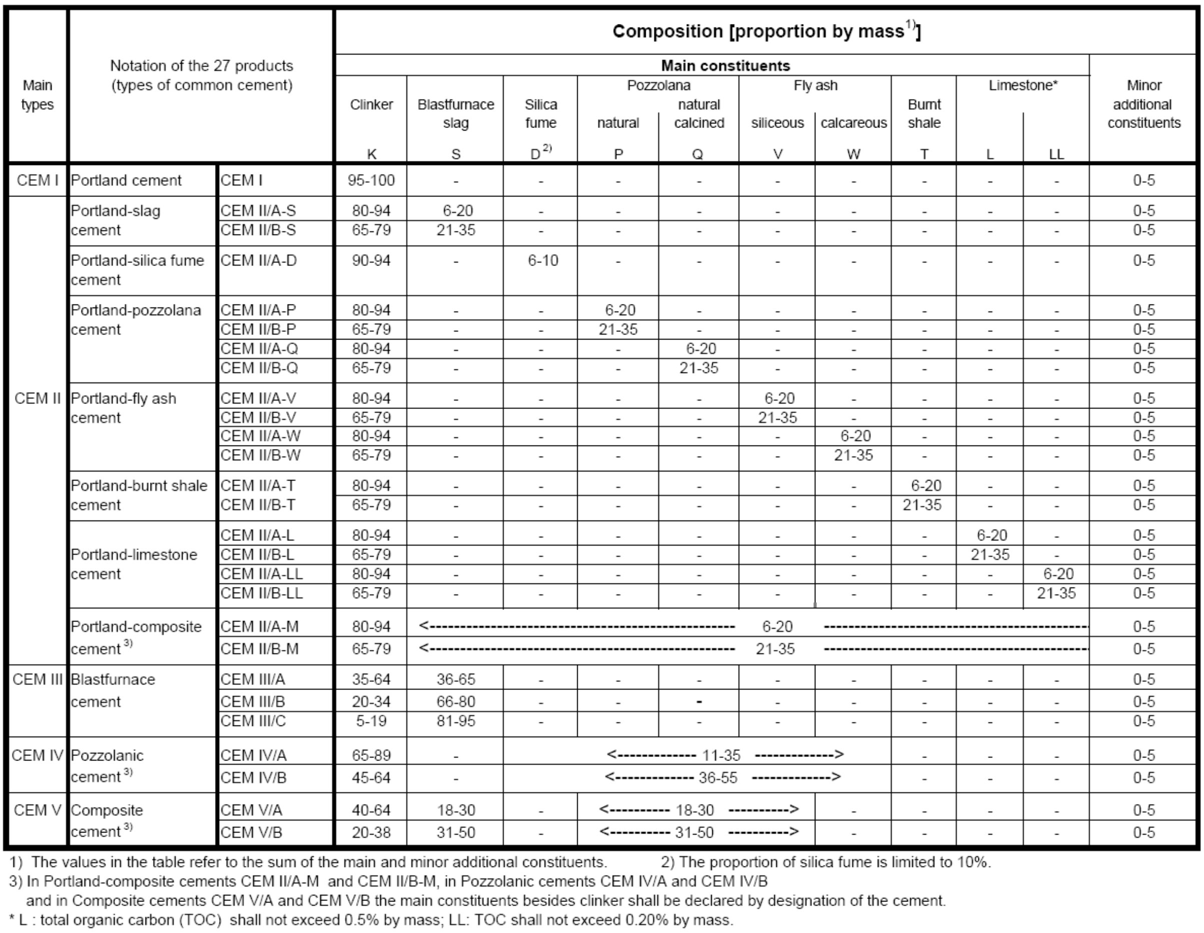
10. Additives
For the purpose of the European and German standards cement additives are constituents which are used to improve the manufacture or properties of cement, e.g. grinding aids. The total quantity of these additives should not exceed 1 % by mass, and the dry content of organics shall not exceed 0.5 %. If this value is exceeded the precise quantity must be stated on the packaging and/or on the delivery document. These additives must not promote corrosion of reinforcement or adversely affect the properties of the cement or the concrete or mortar made from that cement.

EN 197-1 contains cements for general use, and not cements with special properties. It differentiates between the following five main categories:

CEM I Portland cement
CEM II Portland-composite cement
CEM III Blastfurnace cement
CEM IV Pozzolanic cement
CEM V Composite cement

The subdivision of these five main categories into a total of 27 types of cement together with their designations is shown in Table 3.

Table 3 The 27 products in the family of common cements according to EN 197-1: 2000



Main types	Notation of the 27 products (types of common cement)		Composition [proportion by mass 1)]										
			Main constituents										Minor additional constituents
			Clinker	Blastfurnace slag	Silica fume	Pozzolana		Fly ash		Burnt shale	Limestone*		
						natural	natural calcined	siliceous	calcareous				
			K	S	D 2)	P	Q	V	W	T	L	LL	
CEM I	Portland cement	CEM I	95-100	-	-	-	-	-	-	-	-	-	0-5
CEM II	Portland-slag cement	CEM II/A-S	80-94	6-20	-	-	-	-	-	-	-	-	0-5
		CEM II/B-S	65-79	21-35	-	-	-	-	-	-	-	-	0-5
	Portland-silica fume cement	CEM II/A-D	90-94	-	6-10	-	-	-	-	-	-	-	0-5
	Portland-pozzolana cement	CEM II/A-P	80-94	-	-	6-20	-	-	-	-	-	-	0-5
		CEM II/B-P	65-79	-	-	21-35	-	-	-	-	-	-	0-5
		CEM II/A-Q	80-94	-	-	-	6-20	-	-	-	-	-	0-5
		CEM II/B-Q	65-79	-	-	-	21-35	-	-	-	-	-	0-5
	Portland-fly ash cement	CEM II/A-V	80-94	-	-	-	-	6-20	-	-	-	-	0-5
		CEM II/B-V	65-79	-	-	-	-	21-35	-	-	-	-	0-5
		CEM II/A-W	80-94	-	-	-	-	-	6-20	-	-	-	0-5
		CEM II/B-W	65-79	-	-	-	-	-	21-35	-	-	-	0-5
	Portland-burnt shale cement	CEM II/A-T	80-94	-	-	-	-	-	-	6-20	-	-	0-5
		CEM II/B-T	65-79	-	-	-	-	-	-	21-35	-	-	0-5
	Portland-limestone cement	CEM II/A-L	80-94	-	-	-	-	-	-	-	6-20	-	0-5
		CEM II/B-L	65-79	-	-	-	-	-	-	-	21-35	-	0-5
		CEM II/A-LL	80-94	-	-	-	-	-	-	-	-	6-20	0-5
		CEM II/B-LL	65-79	-	-	-	-	-	-	-	-	21-35	0-5
	Portland-composite cement 3)	CEM II/A-M	80-94	<-- 6-20 --									0-5
		CEM II/B-M	65-79	<-- 21-35 --									0-5
CEM III	Blastfurnace cement	CEM III/A	35-64	36-65	-	-	-	-	-	-	-	-	0-5
		CEM III/B	20-34	66-80	-	-	-	-	-	-	-	-	0-5
		CEM III/C	5-19	81-95	-	-	-	-	-	-	-	-	0-5
CEM IV	Pozzolanic cement 3)	CEM IV/A	65-89	-	<------------- 11-35 ------------->					-	-	-	0-5
		CEM IV/B	45-64	-	<------------- 36-55 ------------->					-	-	-	0-5
CEM V	Composite cement 3)	CEM V/A	40-64	18-30	-	<---------- 18-30 ---------->			-	-	-	-	0-5
		CEM V/B	20-38	31-50	-	<---------- 31-50 ---------->			-	-	-	-	0-5

1) The values in the table refer to the sum of the main and minor additional constituents. 2) The proportion of silica fume is limited to 10%.
3) In Portland-composite cements CEM II/A-M and CEM II/B-M, in Pozzolanic cements CEM IV/A and CEM IV/B and in Composite cements CEM V/A and CEM V/B the main constituents besides clinker shall be declared by designation of the cement.
* L : total organic carbon (TOC) shall not exceed 0.5% by mass; LL: TOC shall not exceed 0.20% by mass.

CEM 1 is Portland cement containing at least 95 % by mass of Portland cement clinker. CEM II covers cement which, in addition to clinker, contain one or more main constituents in a proportion of between 6 and 35 % by mass (silica fume up to maximum 10 % by mass). This proportion is subdivided again at 20 % by mass. The cement with the lower proportion is designated as A and the cement with the higher proportion as B. CEM III is the designation for three types of blastfurnace cement A, B and C containing between 36 % and 95 % by mass of granulated blastfurnace slag with subdivisions at 65 % and 80 % by mass of granulated blastfurnace slag. CEM IV denotes two types (A and B) of pozzolanic cement containing between 11 and 55 % by mass of pozzolana, with a subdivision at 35 %

by mass of pozzolana. These cements must pass the pozzolana test. CEM V comprises composite cements which, in addition to cement clinker (K), contain 36 % to 80 % by mass of granulated blastfurnace slag (S) and/or pozzolana of natural (P) and/or industrial (Q) origin and/or siliceous fly ash (V), and are subdivided into A and B at 60 % by mass.

The different categories of cement are associated with 3 strength classes; 32.5, 42.5 and 52.5, based on the standard strength measured at 28 days as outlined in Table 4. The three classes are further sub-divided on the basis of the initial strength into normal hardening (code letter N for normal) and rapid hardening (code letter R for rapid).

EN 197-1 also specifies some physical and chemical requirements to the common cements. The initial setting tested in accordance with EN 196-3 must not start before 75, 60 and 45 minutes for the strength classes 32.5, 42.5 and 52.5, respectively. There is no limit for the final setting time. The soundness must not exceed 10 mm expansion during the Le Chatelier test defined in EN 196-3. The chemical requirements to be fulfilled by the cements complying with EN 197-1 are listed in Table 5.

Table 4 Strength classes of cements as defined in EN 197-1

Strength class	Compressive strength (N/mm^2 or MPa)			
	Early strength		Standard strength at 28 days	
	≥ at 2 days	≥ at 7 days	Minimum	Maximum
32.5 N	-	16	32.5	52.5
32.5 R	10	-	32.5	52.5
42.5 N	10	-	42.5	62.5
42.5 R	20	-	42.5	62.5
52.5 N	20	-	52.5	-
52.5 R	30	-	52.5	-

Table 5 Chemical requirements for the cements as defined in EN 197-1

Property	Test method	Cement type	Strength class	Requirement (%)
Loss on ignition	EN 196-2	CEM I and III	All	≥ 5.0
Insoluble residue	EN 196-2[1]	CEM I and III	All	≥ 5.0
Sulfate content (as SO_3)	EN-196-2	CEM I CEM II[2] CEM IV CEM V	32.5 N 32.5 R 42.5 N	≥ 3.5
			42.5 R 52.5 N 52.5 R	≥ 4.0
		CEM III[3]	All	
Chloride content	EN 196-2	All[4]	All	≥ 0.10[5]
Pozzolanicity	EN 196-1	CEM IV	All	satisfies test

[1] Determination of the residue insoluble in hydrochloric acid as well as sodium carbonate solution

[2] Cement type CEM II/B-T may contain ≤ 4.5 % SO_3 in all strength classes

[3] Cement type CEM III/C may contain ≤ 4.5 % SO_3

[4] Cement type CEM III may contain > 0.1 % Cl^-, but in that case the content must be declared on the package

[5] For application in the manufacture of prestressed concrete elements, cements with lower chloride content may be produced. In such a case the lower value shall replace 0.1 % and be declared in the delivery note.

In Norway, for instance, there are two blended cements on the market. One CEM II/A-V 42.5 R based on intergrinding 20 % siliceous fly ash (V) produced as the standard cement on the Norwegian market by the Norwegian cement manufacturer, and one imported CEM II/B-S 52.5 N blended with 30 % ground blast furnace slag.

3.4.2 Cements as defined by North American standards

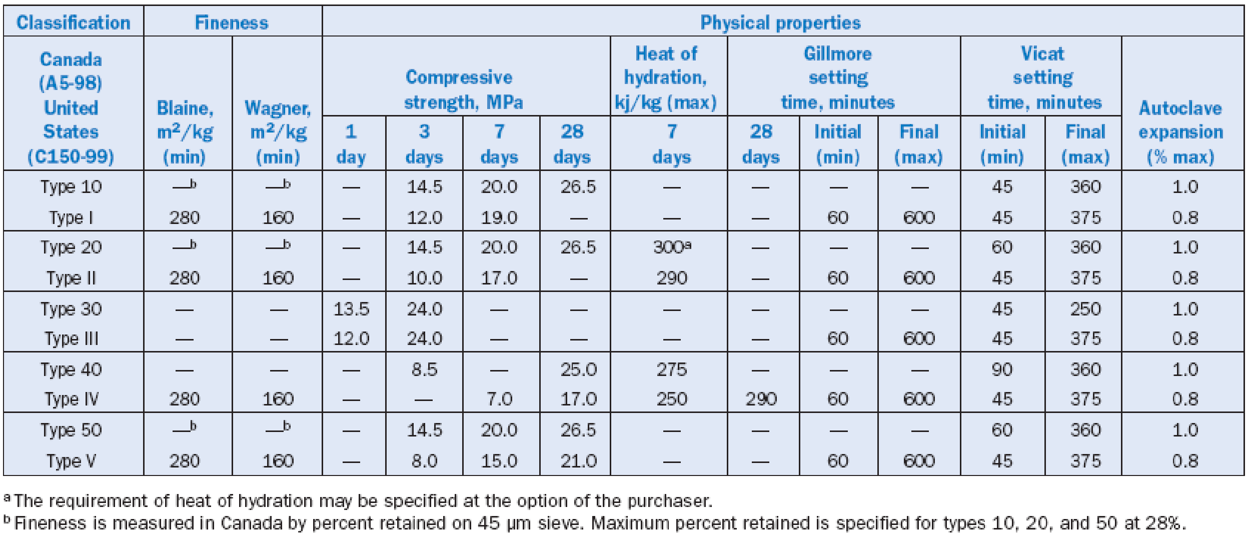
Tables 6 and 7 provide a comparison of the important chemical and physical properties of Portland cement in specifications prepared by the Canadian Standards Association (CSA) in Canada (CSA, 1998) and ASTM in the United States (ASTM, 1999). The standards compared are CSA A5-98 and ASTM C 150-99. Table 8 presents new designations for Canadian cements effective in 2004.

In the United States, the American Association of State Highway and Transportation Officials (AASHTO) also prepares standards for Portland cement used in transportation structures. These standards are similar to the ASTM standards, but there are some differences. The most significant is the requirement related to tricalcium silicate (C_3S) content for Types II and IIA cements. AASHTO M85-98, “Standard Specification for Portland Cement” (AASHTO, 2000), places a maximum limit on C_3S of 55 % for these types, while ASTM C 150-99 does not include a limit.

Additionally, AASHTO revised M85 in August 2000 to include the requirement that quantities of processing additions used in the manufacturing of Portland cement shall not be greater than 1 % by mass. ASTM C 150-99 does not include such a prescriptive limit, but refers to a performance specification, ASTM C465, “Standard Specification for Processing Additions for Use in the Manufacture of Hydraulic Cements.”

Changes in CSA A3001-03 include new nomenclature for Portland cements: two-letter descriptive type designations (see Table 8). The former Type 20 cement was split into two types by intended use; MS for moderate sulphate resistance and MH for moderate heat of hydration.

Table 6 Comparison of physical properties of Portland Cements in CSA A5-98 (CSA, 1998) and ASTM C150-99 (ASTM, 1999) after Bhatty et al (2004).



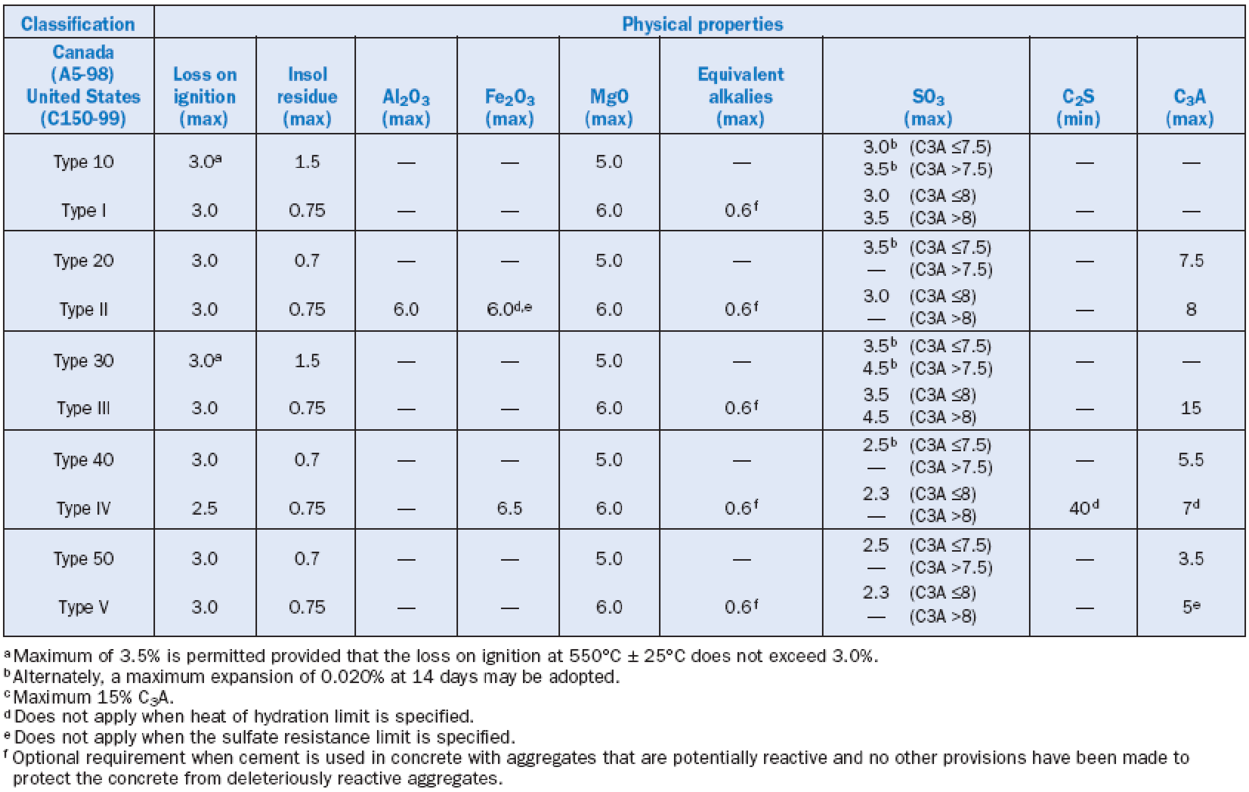
Classification	Fineness		Physical properties										
Canada (A5-98) United States (C150-99)	Blaine, m^2/kg (min)	Wagner, m^2/kg (min)	Compressive strength, MPa				Heat of hydration, kj/kg (max)	Gillmore setting time, minutes			Vicat setting time, minutes		Autoclave expansion (% max)
			1 day	3 days	7 days	28 days	7 days	28 days	Initial (min)	Final (max)	Initial (min)	Final (max)	
Type 10	—[b]	—[b]	—	14.5	20.0	26.5	—	—	—	—	45	360	1.0
Type I	280	160	—	12.0	19.0	—	—	—	60	600	45	375	0.8
Type 20	—[b]	—[b]	—	14.5	20.0	26.5	300[a]	—	—	—	60	360	1.0
Type II	280	160	—	10.0	17.0	—	290	—	60	600	45	375	0.8
Type 30	—	—	13.5	24.0	—	—	—	—	—	—	45	250	1.0
Type III	—	—	12.0	24.0	—	—	—	—	60	600	45	375	0.8
Type 40	—	—	—	8.5	—	25.0	275	—	—	—	90	360	1.0
Type IV	280	160	—	—	7.0	17.0	250	290	60	600	45	375	0.8
Type 50	—[b]	—[b]	—	14.5	20.0	26.5	—	—	—	—	60	360	1.0
Type V	280	160	—	8.0	15.0	21.0	—	—	60	600	45	375	0.8

[a] The requirement of heat of hydration may be specified at the option of the purchaser.

[b] Fineness is measured in Canada by percent retained on 45 μm sieve. Maximum percent retained is specified for types 10, 20, and 50 at 28%.

The nomenclature for blended hydraulic cements has been modified to a three-letter descriptive designation to address its equivalent performance to Portland cements with up to three supplementary cementing materials (see Table 8). Upon request, the designations for blended cements can also provide information on the composition of blended hydraulic cements. The designations then follow the form: BHb-Axx/Byy/Czz, where BHb is the blended hydraulic cement type and A, B, and C are the supplementary cementing materials (SCMs) used in the cement in proportions xx, yy, and zz respectively. Covered supplementary cementitious materials include ground granulated blast furnace slag (S), silica fume (SF), natural pozzolana (N), and fly ash (Classes F, CI, and CH). Class F, CI, and CH fly ashes are low (less than 8 % CaO by mass), medium (between 8 % and 20 % CaO by mass), and high calcium oxide contents (more than 20 % CaO by mass), respectively.

Table 7 Comparison of chemical properties of Portland Cements in CSA A5-98 (CSA, 1998) and ASTM C150-99 (ASTM, 1999) after Bhatty et al (2004).



Classification	**Physical properties**								
Canada (A5-98) United States (C150-99)	**Loss on ignition (max)**	**Insol residue (max)**	**Al_2O_3 (max)**	**Fe_2O_3 (max)**	**MgO (max)**	**Equivalent alkalies (max)**	**SO_3 (max)**	**C_2S (min)**	**C_3A (max)**
Type 10	3.0^{a}	1.5	—	—	5.0	—	3.0^{b} (C3A ≤7.5) 3.5^{b} (C3A >7.5)	—	—
Type I	3.0	0.75	—	—	6.0	0.6^{f}	3.0 (C3A ≤8) 3.5 (C3A >8)	—	—
Type 20	3.0	0.7	—	—	5.0	—	3.5^{b} (C3A ≤7.5) — (C3A >7.5)	—	7.5
Type II	3.0	0.75	6.0	6.0^{d,e}	6.0	0.6^{f}	3.0 (C3A ≤8) — (C3A >8)	—	8
Type 30	3.0^{a}	1.5	—	—	5.0	—	3.5^{b} (C3A ≤7.5) 4.5^{b} (C3A >7.5)	—	—
Type III	3.0	0.75	—	—	6.0	0.6^{f}	3.5 (C3A ≤8) 4.5 (C3A >8)	—	15
Type 40	3.0	0.7	—	—	5.0	—	2.5^{b} (C3A ≤7.5) — (C3A >7.5)	—	5.5
Type IV	2.5	0.75	—	6.5	6.0	0.6^{f}	2.3 (C3A ≤8) — (C3A >8)	40^{d}	7^{d}
Type 50	3.0	0.7	—	—	5.0	—	2.5 (C3A ≤7.5) — (C3A >7.5)	—	3.5
Type V	3.0	0.75	—	—	6.0	0.6^{f}	2.3 (C3A ≤8) — (C3A >8)	—	5^{e}

[a] Maximum of 3.5% is permitted provided that the loss on ignition at 550°C ± 25°C does not exceed 3.0%.
[b] Alternately, a maximum expansion of 0.020% at 14 days may be adopted.
[c] Maximum 15% C_3A.
[d] Does not apply when heat of hydration limit is specified.
[e] Does not apply when the sulfate resistance limit is specified.
[f] Optional requirement when cement is used in concrete with aggregates that are potentially reactive and no other provisions have been made to protect the concrete from deleteriously reactive aggregates.

Blended SCMs are designated as BMb and have reporting requirements similar to blended hydraulic cements.

Other points of interest in the new A3000-03 include:
- Provisions are given for blended hydraulic cements consisting of a portland cement and up to three supplementary cementing materials and blended supplementary cementing materials containing up to three components
- A provision has been included for the testing of processing additions when slag, fly ash, or natural pozzolana are present
- The C_3A limit for MH and MS (A3001-98 Type 20) has been revised to 8 % maximum, similar to ASTM C 150 Type II
- The maximum silica fume content of blended hydraulic cements has been increased to 15 %

- A definition for hydraulic cement has been added: hydraulic cement is defined as either Portland cement, blended hydraulic cement, mortar cement, or masonry cement
- The uniformity requirements clause has been modified to clarify that the uniformity requirement is intended for the predominant product
- Annex C has been added to explain the changes to the nomenclature of Portland and blended hydraulic cement types
- Annex D has been added as a guide for the evaluation of alternative supplementary cementing materials for use in concrete

CSA A3000-03 is available in English and French and can be obtained at www.csa.ca.

Table 8 Type designations for Canadian Portland and blended hydraulic cements

New type designation CSA A30001-03		Type descriptions hydraulic cement	Previous type designations		U.S. type designations	
Portland cement	Blended hydraulic cement		Portland cement	Blended cement	ASTM C 150	ASTM C1157
GU	GUb	General Use	10	10E-x	I	GU
MS	MSb	Moderate Sulphate resistant	20	20E-x	II	MS
MH	MHb	Moderate heat of hydration	20	20E-x	II	MH
HE	Heb	High Early strength	30	30E-x	III	HE
LH	LHb	Low Heat of hydration	40	40E-x	IV	LH
HS	HSb	High Sulphate resistance	50	50E-x	V	HS

Examples: MS – Portland cement (with no supplementary cementitious materials) for use when moderate sulphate resistance is required. GUb-30F/5SF – general use blended cement containing 30 % by mass Class F fly ash (F) and 5 % silica fume (SF).

Bhatty et al. (2004) concluded that Portland cement standard specifications and test methods have been evolving in North America for well over 100 years. These standards continue to be generally prescriptive in nature, but steps are being taken to move toward standards which specify the desired performance of the Portland cement. This move towards performance standards from empirical prediction of performance to prediction based on materials science offers the opportunity to develop performance specifications which can lead to an overall improvement in the quality of concrete structures.

3.4.3 Chinese cement standards

According to Yan (2007), the Chinese standard is similar to EN 197-1 and defines 6 Portland cements as listed in Table 9 and 4 strength classes shown in Table 10 referring to testing after 28 days curing. China also produces a number of special cements (Sui and Yao, 2003).

Table 9 The 6 Portland cements defined in the Chinese standard and their output in 2005 (Yan, 2007)

Type	Cement Name	Clinker replacement	Output in 2005
P	Portland	≤ 5 % mineral	8 %
PO	“Ordinary” Portland	5-20 % mineral	69 %
PS	Slag Portland	21-70 % GGBS[1]	8 %
PF	Fly Ash Portland	21-40 % fly ash	0.5 %
PP	Pozzolan Portland	21-50 % pozzolan	1 %
PC	Complex Portland	21-50 % of 2 minerals	14 %

[1] Ground glassy blastfurnace slag

Table 10 The strength classes in the Chinese standard and their relative use in China, Germany and France (Yan, 2007)

Year	Country	Strength class (MPa or N/mm^2) at 28 days			
		32.5	42.5	52.5	62.5
2002	China	54.5 %	41.4 %	3.9 %	0.2 %
1997	Germany	61.6 %	32.4 %	5.2 %	-[1]
1997	France	48.2 %	11.3 %	32.6 %	-[1]

[1] Not defined class in EN 197-1:2000

The Chinese cement standard is currently under revision according to Sui (2007). Changes are made so the following will apply;

- P (Portland cement to be equivalent to EN 197-1:2000)
- PO can contain 6-20 % SCM, but strength class 32.5 removed
- PSa can contain 20-50 % GGBS
- PSb can contain 50-70 % GGBS
- PP can contain 20-40 % SCM and grinding aid ≤ 0.5 %
- Chloride level ≤ 0.06 % for all cements, (no earlier chloride demand)

According to Yan (2007), 200 Mt/y industrial wastes are utilized during the production of cement. In 2006 China produced 1240 Mt cement, which is > 45 % of the global output (Yan, 2007). One thing is the SCMs milled together with clinker as outlined for the cement types in Table 9, another is the SCMs (mostly fly ash) added directly to the concrete mixer. Of the > $2{\cdot}10^9$ m^3 concrete (density about 2200 kg/m^3) China produces per year, > $100{\cdot}10^6$ t was added mineral admixtures (Yan, 2007).

The Chinese code for co-processing wastes in cement kilns is under drafting (project started 2006) according to Sui (2007).

3.5 Cement hydration

In the discussion of binding of foreign elements in cement, it is of importance to know something about the hydration products, the porosity and the pH of the pore solutions, in particular with respect to leaching of for instance heavy metals (Connor, 1990). This chapter is written for chemists with no particular knowledge of cement hydration. More detailed information can be found in the cement chemistry books by Taylor (1997), Hewlett (1998) and Bensted and Barnes (2002).

3.5.1 Hydration of the interstitial phases C_3S/C_4AF

In the absence of calcium sulphates the first hydration product of C_3A is gel-like with no detectable XRD lines, which appear to grow at the C_3A surface. Later this material transforms into hexagonal crystals corresponding to the phases C_2AH_8 and C_4AH_{19}, with additional amounts precipitating from the liquid phase. The formation of the hexagonal phases slows down further hydration of C_3A as they function as a hydration barrier covering the C_3A surface. Finally the hexagonal phases convert to the thermodynamically stable cubic phase C_3AH_6, the diffusion barrier is disrupted and the hydration proceeds again with a fairly high speed. The overall hydration process may thus be written;

$$2\ C_3A + 27\ H \rightarrow \underset{\text{(hexagonal phases)}}{C_2AH_8 + C_4AH_{19}} \rightarrow \underset{\text{(cubic phase)}}{2\ C_3AH_6} + 15\ H \qquad [2]$$

In the presence of calcium sulphate (as in a Portland cement) the amount of hydration of C_3A in the initial state of hydration is distinctly reduced when compared to that consumed in the absence of $C\bar{S}$. Needle formed crystals of Ettringite (trisulphate) is formed as the main product of hydration;

$$C_3A + 3\ C\bar{S}H_2 + 26\ H = C_6A\bar{S}_3H_{32} \qquad [3]$$

Minor amounts of the monosulphate $C_4A\bar{S}H_{12}$ or even C_4AH_{19} may also be formed if an imbalance exists between the reactivity of C_3A and the dissolution rate of calcium sulphate, resulting in an insufficient supply of SO_4^{2-} ions.

The Ettringite formation is accompanied by a significant liberation of heat. After a rapid initial reaction, the hydration rate is slowed down significantly. The length of this dormant period may vary and increases with increasing amounts of calcium sulphate in the original paste.

A faster hydration, associated with a second heat release maximum, gets under way after all the available amount of calcium sulphate has been consumed. Under these conditions the Ettringite, formed initially, reacts with additional amounts of tricalcium aluminate, yielding calcium aluminate monosulphate hydrate (monosulphate) as the product of reaction;

$$C_6A\bar{S}_3H_{32} + 2\ C_3A + 4\ H = 3\ C_4A\bar{S}H_{12} \qquad [4]$$

As Ettringite is gradually consumed, hexagonal calcium aluminate hydrate (C_4AH_{19}) also starts to form. It may be present in the form of a solid solution with $C_4A\bar{S}H_{12}$ or as separate crystals.

The origin of the dormant period, characterised by a distinctly reduced hydration rate, is not obvious and several theories have been forwarded to explain it. The theory most widely accepted assumes the build-up of a layer of Ettringite at the surface of C_3A that acts as a barrier responsible for slowing down the hydration. Ettringite is formed in a through-solution reaction and precipitates at the surface of C_3A due to its limited solubility in the presence of sulphates. The validity of this theory has been questioned arguing that the deposited Ettringite crystals are not dense enough to account for the retardation of hydration. The four proceeding alternative theories have been proposed;

i) The impervious layer consists of water-deficient hexagonal hydrate stabilised by incorporation of SO_4^{2-}. It is formed on the surface of C_3A and becomes covered by Ettringite.

ii) C_3A dissolves incongruently in the liquid phase, leaving an aluminate rich layer on the surface. Ca^{2+} ions are adsorbed on it, thus reducing the number of active dissolution sites and thereby rate of C_3A dissolution. A subsequent adsorption of sulphate ions results in a further reduction of the dissolution rate.

iii) SO_4^{2-} ions are adsorbed on the surface of C_3A forming a barrier. Contrary to this theory it has been found that C_3A is not slowed down if calcium sulphate is replaced by sodium sulphate.

iv) Formation of an amorphous layer at the C_3A surface that acts as an osmotic membrane and slows down the hydration of C_3A

The termination of the dormant period appears to be due to a break down of the protective layer, as the added calcium sulphate becomes consumed and Ettringite is converted to monosulphate. In this through-solution reaction both C_3A and Ettringite dissolve and monosulphate is precipitated from the liquid phase in the matrix.

The composition of the calcium aluminoferrite phase (ferrite phase), usually written as C_4AF, may vary between about $C_4A_{1.4}F_{0.6}$ and $C_4A_{0.6}F_{1.4}$. Under comparable conditions the hydration products formed in the hydration of the ferrite phase are similar in many respects to those formed by C_3A although the rates differ and the aluminium in the products are partially substituted by ferric ions. The reactivity of the ferrite may vary over a wide range, but seems to increase with increasing A/F ratio.

3.5.2 Hydration of the main mineral alite, C_3S

The hydration of alite can be divided into 4 periods:

a) Pre-induction period. Immediately after contact with water, an intense, but short-lived hydration of C_3S gets under way. An intense liberation of heat may be observed in this stage of hydration. The duration of this period is typically no more than a few minutes.

b) Induction (dormant) period. The pre-induction period is followed by a period in which the rate of reaction slows down significantly. At the same time the liberation of heat is significantly reduced. This period lasts typically a few hours.

c) Acceleration (post-induction) period. After several hours the rate of hydration accelerates suddenly and reaches a maximum within about 5-10 h. The beginning of the acceleration period coincides roughly with the beginning of the second, main heat evolution peak. The $Ca(OH)_2$ concentration in the liquid phase attains a maximum at this time and begins to decline while crystalline calcium hydroxide starts to precipitate. The initial set as determined by Vicat-needle is often just after the start of this period and the final setting time just before the ending of it.

d) Deceleration period. After reaching a maximum the rate of hydration starts to slow down gradually; however, a measurable reaction may still persist even after months of curing. The reason is that the hydration reaction becomes diffusion controlled due to hydration products growing around the unhydrated cement core in increasingly thickness.

The overall alite hydration reaction may ideally be written as

$$2\ C_3S + 7\ H = C_3S_2H_4 + 3\ CH \qquad [5]$$

The calcium hydroxide, CH, is crystalline, while the calcium silicate hydrate is amorphous with a variable composition and therefore often simply denoted CSH-gel. The CSH-gel is the real hydraulic binder in concrete.

The mechanism of hydration and setting of C_3S is not yet fully known and different existing theories are summarised in Table 11.

Table 11 Theories on the mechanism of C_3S hydration

Theory on Mechanism	Impermeable hydrate layer		Electrical double layer	CH nucleation	CSH nucleation
Pre-induction period	First stage CSH formed				
Beginning of Induction period	First stage CSH acts as diffusion barrier		Impedes passage of ions	Supersaturation of liquid phase with respect to CH stops further rapid dissolution of C_3S	
Changes during Induction period	Ageing of CSH	Osmotic pressure increases	Gradually weakening of double layer	Slow nucleation of CH	Slow nucleation of second stage CSH
End of Induction period	Increased permeability of CSH	Bursting of CSH layer	Breakdown of double layer	CH nuclei reach critical size	Nuclei of second stage CSH reach critical size
Acceleration period	Accelerated dissolution of C_3S and growth of second stage CSH and CH				

3.5.3 Hydration of belite, C_2S

Belite forms essentially the same hydration products as alite, but it reacts much more slowly and contributes little to the early strength. Note that it produces about 1/3 the amount of calcium hydroxide in the idealized reaction;

$$2\ C_2S + 5\ H = C_3S_2H_4 + CH \qquad [6]$$

3.5.4 Hydration and setting of ordinary Portland cement

The overall hydration development and setting of ordinary Portland cement is sketched in Fig. 22. It contains basically a combination of the description of the interstitial phase with gypsum and alite as discussed in preceding sections. However, which of the two that dominates setting is still a matter of discussion and probably depends on the cement composition.

Even though very little seems to happen in the induction or "dormant" period after the first heat peak usually assigned to water adsorption and initial Ettringite formation (Eq. 3) according to isothermal calorimetry (see Fig. 22), there is also a continuing hydration of alite (C_3S).

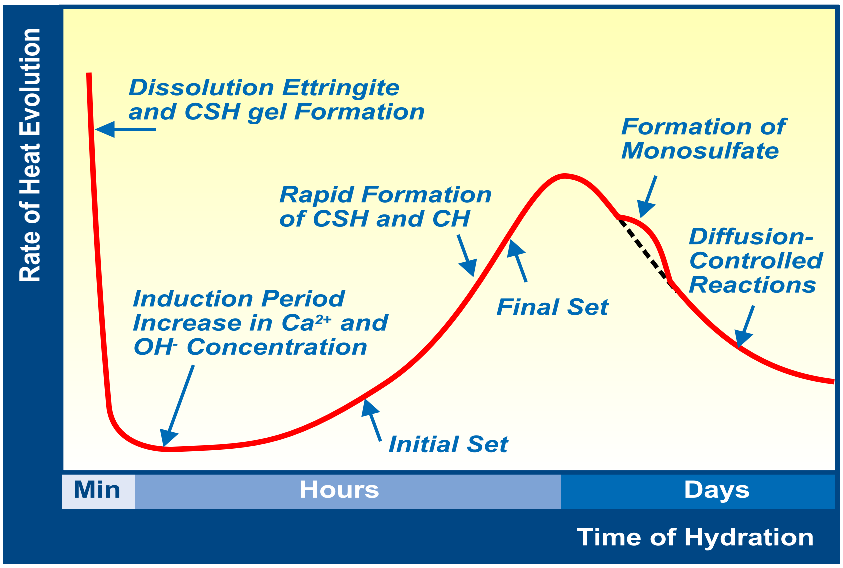


Fig. 22 Principal sketch of Portland cement hydration development and setting.

3.5.5 Hydration products of supplementary cementing materials (SCMs)

The chemically simplest SCM is silica fume (SF) since it usually consist of > 90 % amorphous SiO_2 (S) spheres with average individual diameter of 0.15µm, although these may be agglomerated. It is a pozzolan, meaning that it reacts with calcium hydroxide (CH) forming additional binding CSH-gel as shown by the overall reaction

$$CH + S = CSH \qquad [7]$$

However, this reaction would take months if it was not for the catalytic action of alkali hydroxides in the pore water of hardened cement bringing it to days as shown in the reaction loop (Justnes, 2007);

$$\begin{array}{lll} S\ (s) \ + & (N,K)H\ (aq) \rightarrow & (N,K)SH\ (aq) \\ & \uparrow & + \\ CSH\ (s) + & (N,K)H\ (aq) \leftarrow & CH\ (aq\ or\ s) \end{array} \qquad [8]$$

using cement chemist's short hand notation; C = CaO, S = SiO_2, N = Na_2O, K = K_2O and H = H_2O.

Blast furnace slag is not a pozzolan, but has self-cementing properties when activated by sulphates or alkali hydroxides. Blast furnace slag has a typical composition of 47 % CaO+MgO, 35 % SiO_2 and 12 % Al_2O_3. When activated with gypsum together with cement, the hydration products are generally the same as for ordinary Portland cement (OPC); CSH-gel, Ettringite and monosulphate (Schmolczyk, 1965, and Uchikawa, 1986). The formation of Strätlingite (C_2ASH_8) is only to be expected if alkali hydroxide is added to the slag cement (Richartz, 1966) or if the blast furnace slag is activated with alkali hydroxide (Regourd, 1980, and Forss, 1983).

Siliceous fly ash consisting of a glassy aluminosilicate (AS) phase forms a mixture of calcium silicate hydrate (CSH) gel, Strätlingite (C_2ASH_8) and calcium aluminate hydrates (e.g. C_3AH_6) in reaction with calcium hydroxide (CH). The following pozzolanic reaction is unbalanced since there are too many unknowns;

$CH + AS + H \rightarrow CSH + C_2ASH_8 + C_3AH_6$ [9]

Pozzolans like calcined clays (e.g. metakaoline) will give essentially the same hydration products as sketched in reaction 9.

There is a trend to make Portland cement blended with limestone (at least in Europe). Many think of limestone as inert. Matschei et al. (2007a, b and c), however, showed that limestone will react with calcium aluminate hydrates (e.g. C_3AH_6) and monosulphate ($C_4A\bar{S}H_{10}$), but not Ettringite ($C_6A\bar{S}_3H_{32}$). Since there is only a small amount of monosulphate for limestone to react with in ordinary Portland cement, it has been thought of as inert. However, the situation may change if limestone is combined with slag or pozzolana producing more alumina hydrates (Eq. 9). The calcium carbonate ($C\bar{C}$) will then be able to react with the calcium aluminate hydrate and form calcium carboaluminate hydrate transferring even more liquid water into hydrates thereby lowering the porosity and increasing the strength;

$C_3AH_6 + C\bar{C} + 5\ H = C_4A\bar{C}H_{11}$ [10]

Reaction 10 is quite fast as Matschei et al. (2007c) synthesized pure $C_4A\bar{C}H_{11}$ by letting stoichiometric amounts of C_3A and $C\bar{C}$ hydrate together for 14 days. Limestone will also react with monosulphate to form carboaluminate hydrate and Ettringite binding even more liquid water;

$2\ C\bar{C} + 3\ C_4A\bar{S}H_{12} + 18\ H = 2\ C_4A\bar{C}H_{11} + C_6A\bar{S}_3H_{32}$ [11]

where C = CaO, $\bar{C} = CO_2$, A = Al_2O_3, $\bar{S} = SO_3$ and H = H_2O.

3.5.6 Porosity of hardened cement paste, mortar or concrete

It is possible to estimate the porosity of hardened cement paste (i.e. cement and water) by assuming the degree of hydration (α) and the amount of chemical (23 %) and physical (17 %) bound water per mass of reacted cement. In addition, there will be contraction pores resulting from the chemical shrinkage as the reaction products have a smaller volume than the reactants (i.e. cement minerals and water). Contraction pores are empty ("vacuum") while non-reacted water constitutes water filled capillary pores. The water will always redistribute so the finest pores will be water filled on the expense of coarser ones due to capillary forces.

While cement paste is composed of cement, water and admixtures, mortar has in addition sand (d_{max} usually 8 mm) in a cement/sand ratio of 1/3. Concrete is graded aggregates (sand and gravel, d_{max} usually 20 mm) glued together with cement paste where the cement/aggregate ratio of 1/6. Since the porosity of the aggregate in mortar and concrete is very low, the porosity of mortar and concrete can be estimated as "diluted" cement paste using an average density of aggregate of 2.67 kg/m^3. Unlike cement paste, mortar and concrete will also have entrained air bubbles as pores.

Before showing how to estimate total porosity, a more detailed description of chemical shrinkage leading to contraction pores is given. Knowing the density, ρ (g/ml), of reactants and products of a chemical reaction, it is possible from the molar weight, M (g/mol), of the involved compounds to calculate the volume change, ΔV (ml), pr mass, m (g), reactant remembering the basic relations $n = m \cdot M$ (mol) and $\rho = m/V$.

The simplest example, the recrystallisation of hemihydrate to gypsum will per gram hemihydrate;

$CaSO_4 \cdot ½H_2O$	+	1½ H_2O	=	$CaSO_4 \cdot 2H_2O$	[12]
m = 1.00 g		0.19		1.19	
M = 145.15 g/mol		18.02		172.17	
n = 6.89 mmol		10.33		6.89	
ρ = 2.74 g/ml		1.00		2.32	
V = 0.365 ml		0.186		0.511	

give a shrinkage of $\Delta V = 0.511-(0.365+0.186) = -0.040$ ml.

The densities (g/ml) & molar weights (g/mol) of the following common substances in cement chemistry; C_3S, C_2S, C_3A, C_4AF, $C\bar{S}H_2$, $C\bar{S}H_{0.5}$, $C_{4.7}S_{3.1}H_{5.9}$, CH, $C_6A\bar{S}_3H_{32}$, $C_4A\bar{S}H_{12}$, C_3AH_6, C_4AH_{13} and C_2AH_8, are ≈3.15 g/ml & 228.32 g/mol, 3.28 & 172.24, 3.03 & 270.20, ≈3.73 & 485.97, 2.32 & 172.17, 2.74 & 145.15, 2.49 & 552.3, 2.24 & 74.09, 1.78 & 1255.26, 2.02 & 622.58, 2.52 & 378.29, ≈2.02 & 560.48 and 1.95 & 358.24, respectively.

In this way one can also estimate the shrinkage of the initial Ettringite formation;

C_3A	+	3 $C\bar{S}H_2$	+	26 H	=	$C_6A\bar{S}_3H_{32}$	[13]
m = 1.00 g		1.91		1.73		4.64	
M =270.20 g/mol		172.17		18.02		1255.26	
n = 3.70 mmol		11.10		96.20		3.70	
ρ = 3.03 g/ml		2.32		0.998		1.78	
V = 0.330 ml		0.823		1.733		2.607	

$\Delta V = 2.607 - (0.330+0.823+1.733) = -0.273$ ml/g C_3A, while the chemical bound water is 1.73 g/g reacted C_3A, meaning that the chemical shrinkage is about 16 % of the chemical bound water.

The shrinkage of the alite reaction can be estimated in a similar manner, but the magnitude is strongly dependent of the composition and density of the CSH-gel formed. Justnes and Kjellsen (2003) estimated the density of a 28 days CSH gel of composition $C_{4.7}S_{3.1}H_{5.9}$ to 2.49 g/ml, which leads to the chemical shrinkage of this balanced reaction;

C_3S	+	3.39 H	=	0.325 $C_{4.7}S_{3.1}H_{5.9}$	+	1.48 CH	[14]
m = 1.00 g		0.268		0.786		0.480	
M = 228.32 g/mol		18.02		552.3		74.09	
n = 4.38 mmol		14.84		1.42		6.48	
ρ = 3.15 g/ml		0.998		2.49		2.24	
V = 0.317 ml		0.268		0.316		0.214	

$\Delta V = (0.316+0.214) - (0.317+0.268) = -0.055$ ml/g C_3S, while the chemical bound water is 0.27 g/g C_3S, meaning that the chemical shrinkage is about 8 % of the chemically bound water. It is important to note that the chemical shrinkage of the C_3A reaction is much higher (≈ 5 times) than the reaction of C_3S.

The chemical shrinkage of Portland cement being a mixture of a number of minerals is in general considered to be about 0.06 ml/g cement (or about 25 % of the chemical bound water of 0.23 g/g cement reacted) according to Copeland and Hayes (1953).

The total porosity of a cement paste based on 1 g cement of density 3.15 g/ml and water-to-cement ratio (w/c) of 0.50 can then be calculated as follows assuming a degree of hydration α = 0.80;
Chemical bound water = 0.23·0.80 = 0.184 g/g cement
Physically bound water = 0.17·0.80 = 0.136 g/g cement
Liquid water with density 1.0 g/ml = capillary porosity = 0.50-(0.184+0.136) = 0.18 ml/g cement
Contraction pores = 0.25·0.184 = 0.046 ml/g cement
Total porosity is then (0.18+0.046) ml·100 vol %/(1/3.15 + 0.5/1) ml = 27.6 vol %

When it comes to leaching from concrete it is not only the total porosity that matters, but also the fineness of the pores. The addition of pozzolana will often lead to a pore size refinement since they convert crystalline calcium hydroxide to amorphous CSH gel with very fine pores, but also due to increased water binding. If the SCM is fine enough, like in the case of silica fume, it will also lead to a pore size refinement simply because of improved particle packing. This is exemplified in Fig. 23 for cement pastes designed for oil-well cementing immediately after setting when very little has reacted (Justnes 2007). The figure shows that silica fume alone reduced the average pore size openings from about 250 nm to 25 nm.

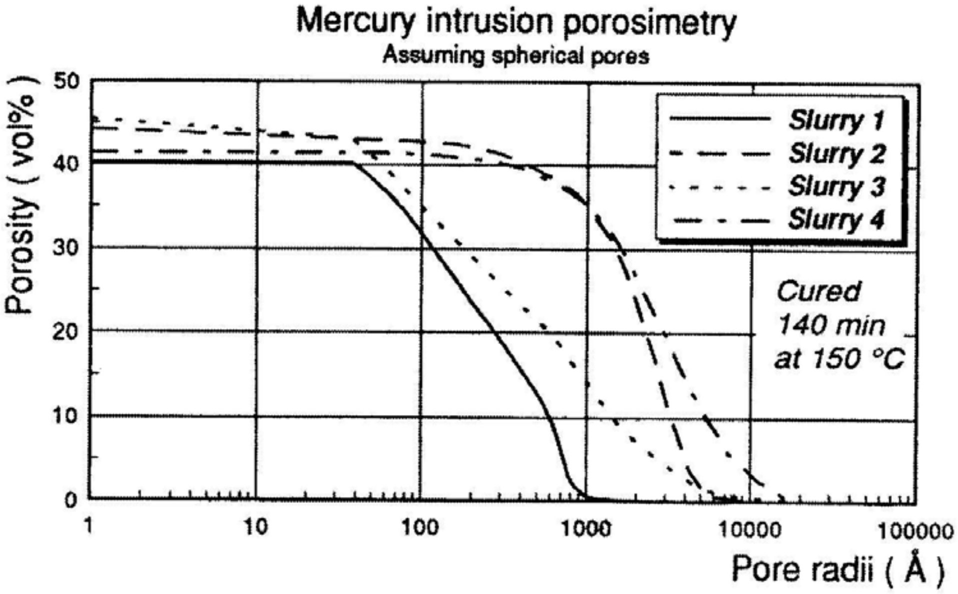


Fig. 23 Pore size distribution of oil well cement slurries immediately after set at 150°C: 1) complete composition, 2) lacking SF, 3) lacking weight material and 4) lacking both SF and weight material (Justnes, 2007).

3.5.7 pH of pore water in hardened cement paste, mortar or concrete

The pH of the pore water in hardened cement paste, mortar and concrete is governed by the cement and its reaction products. The calcium silicates produce a lot of sparingly soluble calcium hydroxide (Eqs. 5 and 6) that will act as a pH buffer corresponding to 12.5 according to its solubility product, k_{sp}, at 25°C;

$Ca(OH)_2$ (s) = Ca^{2+} + 2 OH^- $k_{sp} = [Ca^{2+}]\cdot[OH^-]^2 = 5.5\cdot10^{-6}$ [15]

In pure water the concentration of calcium is half that of hydroxide; $[Ca^{2+}] = ½\cdot[OH^-]$ which inserted in Eq. 15 gives $[OH^-]^3 = 11\cdot10^{-6}$ or a concentration of hydroxides of 0.0222 mol/litre which corresponds to pH =12.35 or a solubility of 1.64 g calcium hydroxide /litre. The solubility of calcium hydroxide is in Lange's Handbook of chemistry given as 1.89, 1.82, 1.73 and 1.60 g/litre at 0, 10, 20 and 30°C, respectively, and it is thus an anomalous compound with decreasing solubility with increasing temperature.

Portland cement may also contain about 1 % alkalis given as sodium oxide equivalents (Na_2O_{eq}) even though they are present as easy soluble sulphates in the fresh state or in solid solution in the minerals. The alkalis are liberated gradually as hydration proceeds. Anyway, they will all end up as soluble hydroxides as exemplified in Eq. 16 and increase the pH of the pore water to 13.0-13.5;

Na_2SO_4 (aq) + $Ca(OH)_2$ (s) + 2 H_2O = 2 NaOH (aq) + $CaSO_4\cdot2H_2O$ (s) [16]

The relation between concentration of hydroxyl ions, $[OH^-]$, and pH is

$pH = 14 + \log [OH^-]$ or $[OH^-] = 10^{(pH-14)}$ [17]

so a typical pH of 13.2 gives $[OH^-]$ = 0.158 mole/litre. Considering a cement with 1 % Na_2O_{eq} and w/c = 0.50, the hydroxyl concentration in the water should be $[OH^-]$ = 2,000 g · 0.01 · 2 / (62 g/mole · 1 litre water) = 0.645 mol/litre corresponding to a pH of 13.8, assuming that all alkalis are released at once. The fraction of alkalis in the cement minerals will, however, be released later as they hydrate, and the amount of liquid will be reduced. Thus, pH in the remaining pore water can be quite high after some hydration.

In practice, however, concrete will be affected by the carbon dioxide in the air. The CO_2 in the air is on average 300 ppm, but can be much higher in traffic loaded areas (e.g. tunnels) or rooms crowded with people (exhaling carbon dioxide). The concrete will carbonate in the presence of CO_2;

$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$ [18]

and for instance

2 NaOH (aq) + CO_2 (aq) = Na_2CO_3 (aq) + H_2O [19]

The pH of the carbonated area will drop to 8-9 and the steel reinforcement in the concrete will no longer be passive with respect to corrosion. However, this is a diffusion controlled process that is slow with a maximum rate at a relative humidity of 60 %. However, when the concrete later is crushed for recycling or used as a road base, the carbonation may be much faster and so might be the leaching of elements to the environment.

The solubility of heavy metals are very pH dependent as shown in Fig. 24, and can actually be much lower in the carbonated zone of concrete (pH 8-9) than in sound concrete (pH 13-14). However, not only the pH matter, but also the cations available. Since concrete is rich in calcium hydroxide, many of the heavy metals soluble in a sodium hydroxide system will precipitate as calcium salts (e.g. zinc as calcium zincates).

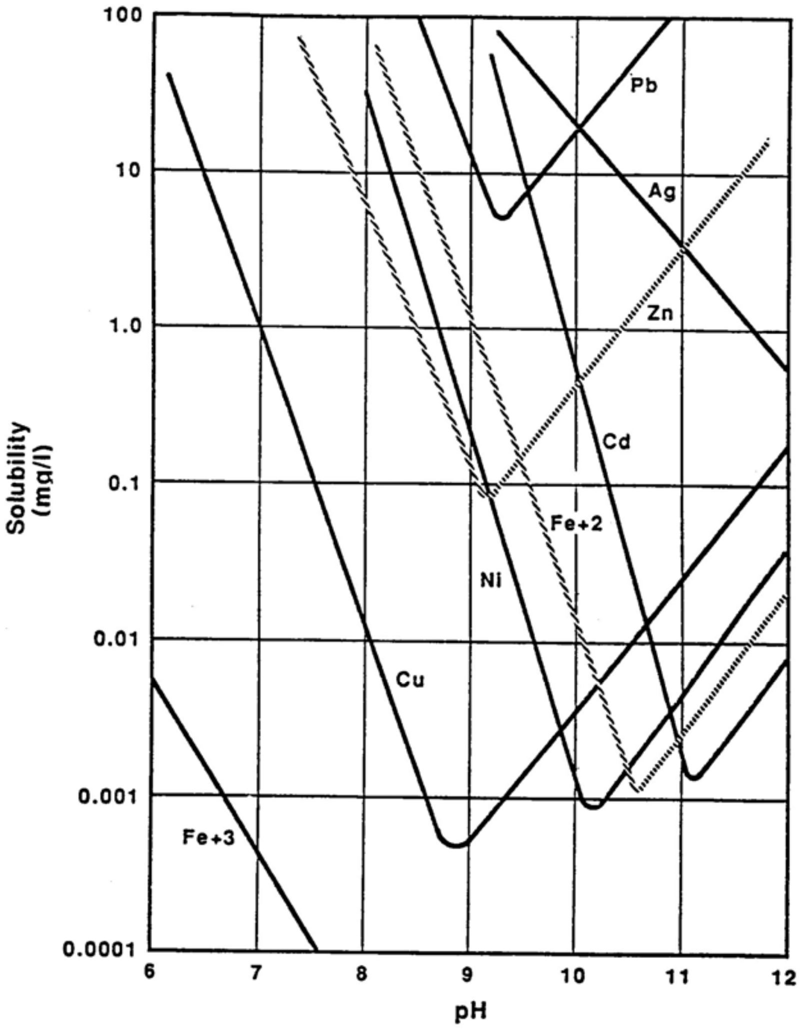


Fig. 24 Solubility of metal hydroxides as a function of pH (U.S. EPA, 1987)

4 USE OF AR IN PORTLAND CEMENT CLINKER PRODUCTION

4.1 Introduction

The focus of this chapter is the use of industrial wastes and by-products in the production of cement. Owing to the compositional compatibility of several of these wastes and by-products with the raw materials used in cement manufacture, their potential for reutilization is gaining ground. The degree of their usefulness as a substitute raw material, however, depends primarily on economic considerations as well as the chemical composition of the alternate material or materials that they replace.

In recent years, cement manufacturing has successfully made use of a number of wastes and by-products as supplementary raw materials. Typically these materials are lime-bearing carbonates, paper sludge, lime waste from water purification plants, sludge from sugar and fertilizer industries; slag from the iron, steel, and other metal industries; fly ash, bottom ash, and desulphurization sludge from power plants; red mud, mineral and ore tailings, catalyst fines, foundry sand; and sludge from sewage treatment plants. Several marginal raw materials have also been used as substitutes.

The prominent characteristics of the wastes and by-products and their compatibility with the cement raw feed, their degree of substitution, and the properties of clinker and cement produced, along with the derived material, economical, and environmental benefits to the cement industry are discussed in this chapter.

The principal raw materials in cement manufacturing are calcareous materials (containing calcium carbonates) such as limestone, chalk, marl, and marble; siliceous materials (containing silica) such as sand and sandstone; and argillaceous materials (containing alumina and silica) such as clay, shale, and slate. Other corrective materials such as bauxite and iron ore are frequently used to permit easy burnability. A carefully proportioned mixture of these materials is fired to produce clinker. Occasionally, though, fluxes and mineralizers have also been used to promote clinkering to further conserve thermal energy and improve production (see chapter 3.3).

It is critical that the composition of the waste or the by-product considered for use in the cement raw mix is compatible with that of the cement raw materials they replace or supplement. Based on this criterion, a number of wastes and by-product materials have been identified as partial or total substitutes for raw material in cement manufacture. Several marginal raw materials have also been used as substitutes.

In the following sections, the materials in question are classified according to their calcareous, siliceous, argillaceous, and other chemical characteristics. In many cases, some materials span over more than one of these categories. The best example is metallurgical slag that can be rich in lime, silica, and alumina. Although the focus of this chapter is on materials that are used as kiln feed, some materials can be interground with clinker or blended with cement (see chapter 3.4).

4.2 Alternative raw materials with calcareous main component

Calcareous materials are rich in lime (calcium oxide). They primarily replace, partially or fully, the calcareous component (limestone) of the cement raw feed based upon their chemical composition and compatibility with the replacing materials. Examples of their use in cement manufacture are given in the following sub-sections.

4.2.1 Marginal limestone

Gradual depletion of quality limestone for cement manufacture has prompted widespread use of marginal and lower grade limestone in recent years. Ahluwalia and Page (1992) have discussed an Indian experience on the use of a low-grade limestone high in magnesium and silica. They classified this limestone for use in cement raw feed according to the magnesia and silica contents (see Table 12). Note that the limit for MgO in the cement is set to ≤ 5 % in EN 197-1.

Table 12 Composition of marginal limestones

Limestone	Oxides (%)
High magnesia	6 - 12 MgO
High silica	14 - 21 SiO_2
High silica, low lime	$SiO_2 > 14$, $CaO < 44$
High silica, high magnesia	$SiO_2 > 14$, $MgO > 3.5$

In an earlier study, Ahluwalia et al. (1981) beneficiated low-grade limestones prior to their use and found them suitable for cement manufacturing. Out of the several beneficiation techniques employed, a flotation method proved most useful, despite higher energy consumption. The beneficiation involved size reduction by grinding and separation of the impurities by flotation to obtain a concentrate with increased calcium content. Other methods considered were differential grinding and sieving, electrostatic separation, photometric sorting, and bacterial leaching.

These limestones were regarded as more suitable to wet and semi-wet cement manufacturing processes, where they could be conveniently processed by flotation and used directly for raw feed preparation. Although more suitable for wet process, the upgraded limestone has also been successfully used in other cement manufacturing processes. One Indian cement plant used the beneficiated limestone in a kiln with two-stage preheater and calciner to produce 1,780 tons clinker per day (Purohit et al., 1987; Shrinkhande et al., 1991). The microstructure of this clinker featured well-formed alite and belite crystals distributed in interstitial phases. The estimated Bogue composition of the clinker was: 41 % C_3S, 48 % C_2S, 5 % C_4AF, and 6 % C_3A. The cement produced had normal strength, setting, and other physical properties.

A South African cement plant also used marginal limestones in raw mix for producing normal clinker and cements (Du Toit, 1996). In separate trials, two low-grade limestones (both high in silica) replaced 10 % and 14 % raw mix respectively; the balance was high-grade limestone, magnetite, and bottom ash. The composition of limestones used in the trials is shown in Table 13. The composition of the high-grade limestone used is also shown for comparison. Under identical burning conditions, the trial using 10 % low-grade limestone (and 80 % high grade, 8.5 % bottom ash, and 1 % magnetite) produced clinker and cement of acceptable quality. Phase distribution of alite and belite were normal for the clinker, and the cement showed comparable physical characteristics to that of normally produced cement.

Table 13 Composition (%) of selected limestones

Limestone	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	LOI[1]
Low grade 1	21.38	1.75	40.88	1.42	1.53	33.0
Low grade 2	20.62	2.92	40.73	1.83	1.43	32.3
High grade	11.84	1.21	46.21	0.95	1.41	36.5

[1] Loss on ignition when heated to 1,000°C, mostly CO_2 and water

Use of low-grade limestone together with high-grade limestone compensators is now becoming common in a number of U.S. cement plants for material as well as economical reasons. The cements produced are comparable to those produced with the typical limestones.

4.2.2 Cement kiln dust (CKD)

Cement kiln dust is generated from the cement plants as fine particulate material swept from the rotary kiln and collected in a bag house or electrostatic precipitator or frozen out in by-passes. Cement kiln dust (CKD) is often extremely rich in lime. Normally, all CKD that can be returned to the process is returned, except for cases where alkali considerations prohibit it. In wet kilns, it is injected through mid-kiln devices or even insufflated into the burning zone.

Typically, CKD is composed of partially calcined raw material, clinker particles, and alkali compounds swept out of the kiln with the exit gases. The reuse of CKD in kiln feed for vertical shaft kilns has been reported by Raina et al. (1997). Their results showed that although the alkalis and chloride contents in the CKD were high, the cement displayed good strength and met the soundness criterion.

It must, however, be kept in mind that since CKDs are so high in alkalis, their reuse in the raw feed has to be carefully controlled to avoid producing clinkers and cements with unacceptably high alkalis. For durability reasons (i.e. alkali aggregate reactions), low-alkali cements are more desirable for use in concrete than high-alkali cements. For this particular reason, attempts are made to separate alkali compounds from CKDs prior to their reutilization. Chlorides should also be kept low in order to avoid initiation of corrosion of steel reinforcement in concrete. Note that EN 197-1 states that the chloride level of cement should be ≤ 0.10 %, while the new Chinese standard under revision may have a limit of < 0.06 % Cl^-.

The practice of using CKD by mid-kiln injection in long wet kilns is typical. Since the addition of CKD to slurry in a wet process is counter-beneficial as it stiffens the slurry and requires high water demand to maintain slurry flow, CKD is injected at a mid-kiln location. The practice does not affect the thermal profile of the kiln as the CKD routinely becomes part of the kiln feed.

Fuller Company (1992) has beneficiated high-alkali and high-sulphate CKD by using a fluidized bed process. The clinker thus produced was separated from its alkali and sulphur and interground with normal clinker to produce ASTM C150 compatible cement. In addition, the alkali concentrate can be sold as a separate product. Young and Morrison (1991) developed Passamaquoddy scrubber technology for removing alkali compounds from CKD. The alkali compounds are separately marketed whereas the alkali-free CKD is reused as a component in cement raw feed.

4.2.3 Carbonate sludges

Use of a lime-rich sludge from the fertilizer industry in the raw meal of a wet process cement plant has also been referred to by Ahluwalia and Page (1992). In addition to the lime, the sludge contained elevated levels of sulphate (6 %), fluoride (1.2 %), and phosphate (1.8 %). These "impurities" restricted the use of sludge to 50 % of the kiln feed. The composition of the sludge is given in Table 14.

Table 14 Composition of carbonate sludge from fertilizer plant

Analysed	SiO_2	Al_2O_3	CaO	Fe_2O_3	K_2O	Na_2O	P_2O_5	SO_3	F^-	LOI
Mass %	6.0	0.3	46.5	0.3	0.13	0.04	1.8	6.0	1.2	37.5

The sludge partially replaced the high-grade limestone already used at the plant. Excessive use of sludge affected the strength and setting properties of cement, most likely due to the presence of phosphate and fluoride. However, the addition of sludge could be adjusted to overcome this problem.

The burnability of the raw feed was significantly improved at reduced temperatures, primarily because of the fluxing ability of fluoride present in the sludge. Burnability of the raw feed in terms of free-lime reduction and the degree of lime-combinability in the clinkers is shown in Table 15.

Table 15 Burnability of raw meal with carbonate sludge

Temperature	free lime, fCaO	Lime combinability
1,250°C	5.5 %	91.6 %
1,300°C	1.2 %	98.2 %
1,350°C	0.6 %	99.0 %

.

A 10 % use of phosphochalk, another lime-bearing sludge containing high contents of sulphate (9.9 %), phosphate (2.4 %), and fluoride (2.0 %), was also tested in a raw mix that contained limestone, marl, and sandstone (NCB Report, 1990). Addition of phosphochalk beyond 10 % was not considered because of the high phosphate and fluoride contents. Microscopic examination of the clinker showed well-formed C_3S (48 %) and C_2S (31 %), and low free lime.

4.2.4 Galvanic sludges

Chemical precipitation is the most popular process in treatment of wastewater from galvanic processes among the available heavy metal removal processes including ion exchange, adsorption, reverse osmosis, membrane filtration and chemical precipitation (Bryson and Dardis, 1980, Patterson, 1981, and Bailey et al., 1999). Generally, the heavy metals are precipitated in alkaline solutions to form metal hydroxide sludges. The solubility of various heavy metals as a function of pH is shown in Fig. 24. It is common to use slaked lime, and that is why these sludges often are rich in calcium. However, if pH is reduced by for instance carbonation on a land fill, the heavy metals may be released and leached to the environment. Although a number of technologies, including metal recovery and thermal processing, have been developed for treatment of the heavy-metal containing sludges (Smith and Amini, 2000, Brooks, 1993, Ramachandran and Kikukawa, 2002, and James et al., 2000), most of the treatment processes are either too expensive or not available at this stage. From an economic and ecological point of view, it is logical to use such sludges as alternative raw materials in cement production knowing that the calcination of calcium hydroxide at (dewatered at 450°C) requires lower energy than calcium carbonate /decomposing at 700-900°C). The influence of various heavy metals on clinkerization can be found in chapter 3.3. Although galvanic sludges may be rich in calcium, their content of heavy metals will limit the amount that can be used in the raw meal and it should maybe be placed in sub-chapter 4.5.1. However, it represents an excellent way of using a problem waste.

Shih et al. (2005) investigated the reuse of heavy metal containing sludges in cement production. The compositions of their surface finishing and electroplating sludges are given in Table 16. Note that the latter contain 17.5 % CaO. They claim that it was feasible to use up to 15 % of these sludges in the raw meal. 90 % of the lead evaporated during firing, but 90 % of the less volatile heavy metals (e.g. Cu, Cr and Ni) were fixed in the clinker. Leaching tests, even at low pH, showed that these heavy metals were retained in the clinker, even at low pH.

Espinosa and Tenório (2000) investigated a galvanic sludge from chroming electroplating industry as a potential alternative raw meal for the cement industry. The element composition of the sludge was 17.40 % Ca, 3.90 % Cr, 3.04 % Al, 0.51 % Mg, 0.16 % Fe, 0.15 % Na, 0.12 % Si, 0.03 % Zn, 0.02 % K, 90.9 ppm Cu and 46.2 ppm Pb. The addition of dry sludge up to 2.0 % of the charge did not affect the formation temperatures of C_3S, C_2S and liquid phase and was thus suitable for the clinkerization process. Leaching tests showed that total chromium and Cr^{6+} concentrations in the solutions were below the limits established by Brazilian Standards.

Table 16 Composition of surface finishing and electroplating sludges (Shih et al., 2005)

Parameter	Surface finishing	Electroplating
Water content (%)	39.8	62.9
Loss on ignition (%)	7.3	12.1
Ash (%)	52.9	25.0
CaO (% of dry)	4.1	17.5
SiO_2 (% of dry)	3.9	1.1
Al_2O_3 (% of dry)	0.2	0.2
Fe_2O_3 (% of dry)	65.4	1.1
MgO (% of dry)	0.7	4.3
Zn (ppm of dry)	237	360
Ni (ppm of dry)	714	104,616
Cu (ppm of dry)	50,190	22,541
Pb (ppm of dry)	51,748	22,811
Cd (ppm of dry)	14	< 2
Cr (ppm of dry)	109	41,585

Ract et al. (2003) studied the feasibility of using a galvanic sludge containing Cu and Ni as alternative raw material in cement clinkering due to its high content of calcium. The sludge analysis is shown in Table 17. They concluded that adding up to 2 % of the galvanic sludge containing 2.4 % Cu and 1.2 % Ni to the clinker raw material did not affect the clinkering reactions. However, it lowered the temperature for C_2S and melt formation. All of the nickel (Ni) and 99 % of the copper (Cu) were incorporated into the clinker during the burning process. Their leaching test was performed for a sample with the highest sludge addition (5 %). Brazilian law stipulates that the copper content in the leaching solution must not be higher than 250 ppm and the nickel content not higher than 0.25 ppm. However, leaching solution chemical analysis showed only 0.03 ppm Cu and 0.02 ppm Ni.

Table 17 Chemical analysis of galvanic sludge (Ract et al., 2003)

Element	Content (%)	Element	Content (%)
Ca	43.19	Sr	0.21
Si	9.02	Ti	0.15
Mg	2.77	Cr	0.14
Cu	2.41	P	0.13
Al	2.33	Sn	0.12
Fe	1.88	Mn	0.08
Ni	1.22	Zn	0.03
S	0.78	Zr	0.02
K	0.59	Cl	0.01

4.2.5 Carbide sludge

Lime-rich carbide sludge has also been used as partial limestone replacement in cement raw mix (NCB Report, 1987). Due to the high chloride content, and its effect on the flow properties of raw meal in a wet-process cement plant, the sludge could only be used for up to 30 % of the raw feed. The addition of sludge showed easy burning of the kiln feed, possibly due to better reactivity of the sludge, and the fact that at least some of the calcium is in the form of hydroxide, which requires lower calcination energy than $CaCO_3$. Clinker made from the raw feed with sludge showed well developed alite and belite crystals that produced cements with good performance characteristics.

4.2.6 Miscellaneous slags

Blast furnace slag is a by-product of iron smelting operations. Both crystallized and vitreous (glassy) slags are produced. The crystalline slag is allowed to cool slowly after it is discharged from the blast furnace, while the vitreous slag is quenched with water as it is discharged from the furnace. Studies have demonstrated that both crystallized and vitreous slags are suitable supplements for cement raw feed.

Texas Industries, Inc. (Young, 1996) patented the process of using blast furnace slag or basic oxygen furnace slag as feed stock components for cement clinker production in long rotary kilns. In their process, un-ground slag is added to the raw mix as it clinkers well without grinding. Up to 30 % slag has been used to produce clinker of acceptable chemical and phase composition. The composition of typical blast furnace slag used along with the processing parameters and phase composition of the resulting clinkers are shown in Tables 18 and 19. The process saves a significant amount of grinding energy.

Table 18 Typical composition of blastfurnace slag (Young, 1996)

Oxide	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	Na_2O	K_2O
Content (%)	40.01	35.76	9.42	0.63	2.70	8.55	0.32	0.57

Table 19 Slag addition, raw mix parameters and cement mineral estimates (Young, 1996)

Slag (%)	0	5	10	15	30
Silica ratio, S/(A+F)	2.42	2.33	2.32	2.32	2.06
Alumina ratio, A/F	1.35	1.44	1.44	1.44	1.21
C_3S (%)	63.33	63.76	63.39	63.09	60.37
C_2S (%)	14.66	13.20	13.25	13.21	12.75
C_3A (%)	7.22	8.00	8.00	7.98	7.92
C_4AF (%)	11.65	11.44	11.44	11.38	13.57

In another application, Puertas et al. (1988b) demonstrated the use of crystallized blast furnace slags in producing cement clinker. Being rich in CaO, SiO_2, and Al_2O_3 (Table 20), the slags replaced considerable amounts of limestone, silica, and clay in the raw mix. Tests were carried out using 37 % ground slag in a raw mix having a lime saturation factor of 0.98, a silica modulus of 2.18, and an alumina modulus of 2.2. The addition of slag altered the kinetics of clinker formation. Above 1,350°C the reactivity of the raw mix was good, and the clinker had normal formation and distribution of phases. Higher temperatures (1,450°C) and finer slag grains (90 µm) improved the burnability of the raw mix that produced clinker with normal mineralogical composition and a better distribution of clinker phases. Overall, the crystalline blast furnace slag was found more suitable than the glassy slag for cement manufacture, with a potential for improved operation and energy conservation.

Table 20 Composition (%) of different crystalline blastfurnace slags (Puertas et al., 1988b)

Slag	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO
A	37.57	39.37	12.57	0.31	1.21	8.14
B	38.03	39.17	11.68	2.25	1.92	7.16
C	40.69	37.66	10.04	0.37	2.26	10.90

Monshi and Asgarani (1999) made a combined use of blast furnace slag and converter steel slags as raw feed components. Compositions of the slags used are shown in Table 21.

Table 21 Composition (%) of blastfurnace and converter slag (Monshi and Asgarani, 1999)

Slags	CaO	SiO_2	Al_2O_3	Fe_2O_3	MnO	TiO_2	MgO
Blast furnace	37.2	36.2	8.0	0.7	0.9	4.7	10.3
Converter	56.4	10.4	2.0	21.0	2.5	3.1	1.7

Prior to their use, the undesired large iron pieces were magnetically removed from the slags. Several raw feeds were prepared by mixing the slags with calcined limestone. For the two best trial burns conducted, the additions of blast furnace slag and converter slag were 49 % and 8 %, and 42 % and 27 % by mass respectively; the remainder being the calcined lime. The properties of clinkers and cements produced from the mixes were comparable to those produced commercially. The compressive strength obtained for the cement exceeded the minimum required by the ASTM C 150 specifications. Their compositions suggest that the slags can be used in large portions provided the formulation of kiln feed meets the desired clinkering parameters.

Valkova and Dogandzhieva (1980) also used blast furnace slags (both crystallized and vitreous) as raw mix for producing cement clinker. These slags, however, contained higher contents of barium and manganese oxides. It was demonstrated that up to 20 % of these slags could be used in the raw mix. The slags enhanced the reactivity of the raw mix and improved the clinker formation. The presence of barium and manganese oxides modified the alite crystals and produced increased compressive strength.

Phosphorus furnace slag is a by-product of phosphate processing. Production of one ton of phosphorus generates about seven tons of slag. The slag is typically rich in calcium silicates, with phosphorus (2.5 %) and fluoride (1.5 %) as minor constituents. Singh and Bhattacharjee (1996) made use of 2.5 % granulated phosphorus furnace slag (GPFS) in the raw mix of vertical shaft kiln in cement manufacture. The use of GPFS improved the quality of the clinker and produced cement with better strengths than the control. To the extent that such slags can replace limestone, they have the potential to save calcination energy.

4.2.7 Oil shale residues

A Russian cement plant used lime-rich oil shale residues in the manufacture of cement (Freiman and Kougija, 1997). The residues contained 34.5-48.9 % CaO and 28-38.2 % SiO_2. The calcareous component used was waste limestone that contained 2-6 % organic substances. The kiln feed was prepared in a mixing chamber of the first stage of the cyclone preheater. Oil shale was added in the calciner or the riser duct at about 8 % of the raw mix. The residual fuel in the shale gave substantial energy savings and the clinker homogeneity, as examined by microscopy, was adequate. This study was a sequel to earlier work in Germany at Rohrbach's Dotternhausen plant (Rohrbach, 1969; Rechmeier, 1970), in which 8 % of the kiln feed was oil shale added directly to the calcining process, and oil shale ash was interground with clinker to create blended cements without the need for gypsum addition.

4.2.8 Other alternative raw materials rich in calcium

Aïtcin (2007) discussed the possibility of using slag, ASTM class C fly ash or even the mineral anorthite ($CaAl_2Si_2O_8$) as they contain a substantial amount of calcium as shown in his ternary phase diagram reproduced in Fig. 25. He claimed that using slag instead of clay could save 22 % CO_2 outlet, but he did not take into account that the alumina content may limit the use of these alternative raw materials since they might create an unacceptably high C_3A content in the clinker. Norway has by the way a good deposit of pure anorthite in Gudvangen should it be of interest.

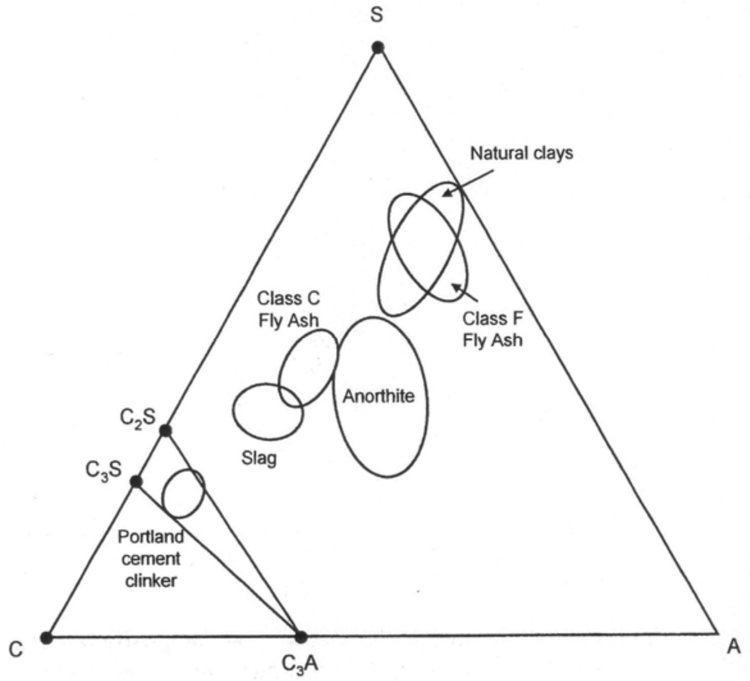


Fig. 25 A simplified ternary phase diagram of $CaO-Al_2O_3-SiO_2$ (C-A-S) comparing composition ranges of Portland cement clinker with those of clay, Class C and F fly ash, slag and anorthite after Aïtcin (2007).

Raupp-Pereira et al. (2007) describe the formulation of new cementitious materials starting from industrial wastes, such as sludges (generated in the cutting process of natural marble, in the Al-anodizing and surface coating industrial processes and potable water filtration/cleaning operations) and foundry sands (see also section 4.3.1). These materials are all classed as non-hazardous but are produced in high daily amounts. They were fully characterized and chemical/mineralogical predictions were made based on their location in the phase diagram of the $SiO_2-Al_2O_3-CaO$ ternary system as shown in Fig. 26, which are the major oxide constituents. They were able to make clinker with common minerals and behaviour using for instance a mixture of 60 % marble sludge (M-sludge), 15 % water cleaning sludge (W-sludge), 13 % aluminium anodizing sludge (A-sludge) and 12 % foundry sand (F-sand), showing the feasibility of this multi-component recycling alternative.

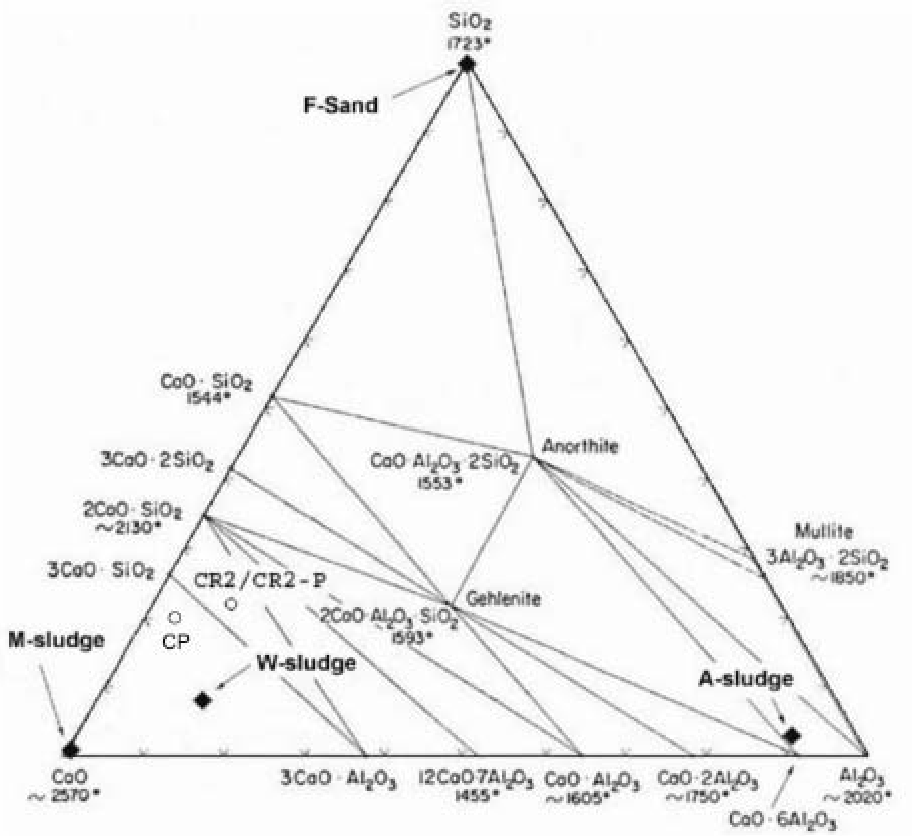


Fig. 26 Location of the wastes investigated by Raupp-Pereira et al. (2007), the combination they investigated (marked CR2/CR2-P), as well as reference clinker (marked CP), in the ternary phase diagram CaO- Al_2O_3- SiO_2.

4.3 Alternative raw materials with siliceous main component

This section focuses on wastes used for replacing siliceous components (containing silica) in clinker raw material feed.

4.3.1 Foundry sand

Foundry sand is a waste from metal processing foundries. It is used in making moulds for casting molten metal and alloys. Foundry sand is primarily rich in silica, with a small percentage of clay and molasses. Foundry sand has been used to replace silica in cement kiln raw feed; however, its use depends upon the composition of the foundry sand and the target kiln feed mix-design (Bhatty, 2002). A typical clay-bonded foundry sand composition is shown in Table 22.

Table 22 Composition of clay-bonded foundry sand (Bhatty, 2002)

Oxide	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO
Content (%)	93.0	2.8	0.2	0.7	0.3

Foundry sand was used to totally replace silica in the cement raw feed. The addition of foundry sand made the clinker somewhat harder to grind. The low grindability can be attributed to the presence of large alite and belite crystals formed due to coarse quartz in the foundry sand. The late strength of cement was better than that of control clinker. The 3, 7, and 28 day compressive strengths of cement produced from the foundry sand versus that of control cement were 20.5, 32.8 and 50.9 MPa vs. 21.3, 32.0 and 44.7 MPa, respectively (Bhatty, 2002).

4.3.2 Rice husk ash

Rice husk ash (RHA) is produced by incinerating rice paddies. The ash is rich in silica and it contains some unburned carbon. The ash has been successfully used as a kiln feed supplement to partially substitute high-ash coal in the dry kiln process with a suspension preheater (Ghosh et al., 1992). The composition of the ash used is shown in Table 23. At another cement plant, rice husk ash was used as an alternative to sandstone in a raw mix prepared with high-grade limestone. The use of RHA improved the kiln feed burnability and eased the strength and expansion problems in cement performance. In both cases the ash also contributed to fuel savings because of the unburned carbon.

Table 23 Chemical composition and heat value of rice husk ash (Gosh et al., 1992)

Parameter	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	LOI (%)	Calorific value (mJ/kg)
Value	88.2	3.1	2.1	0.6	4.2	15.7

Substitution of coal ash by 10 % RHA contributed 5 % to the fuel economy with no adverse effects to the clinker and cement properties. Additionally, the compressive strength of the resulting cement increased. A 20 % substitution of RHA contributed to about 10 % economy in fuel cost per ton of clinker. However, the clinker quality was adversely affected, at least in part because of a severe decrease in the amount of alite, and required blending with high quality clinker to produce cement with acceptable properties. The mix may not have been optimally proportioned, in view of the reduced alite content. The composition of clinker and selected properties of cement made from clinker with RHA substitution are given in Tables 24 and 25, respectively.

Table 24 Composition of clinker made with RHA as alternative raw material (Ghosh et al., 1992)

RHA (%)	C_3S (%)	C_2S (%)	C_3A (%)	C_4AF (%)	Free lime (%)
0	40	28	13	13	2-3.5
10	47	26	12	12	1.5-2
20	35	38	11	11	2-4

Table 25 Selected properties of cement based on clinker with RHA as AR (Ghosh et al., 1992)

RHA (%) as alternative raw material in clinker	Compressive strength (MPa) after			Setting time (min)	
	3 days	7 days	28 days	Initial	Final
0	21.0	30.5	41.0	100	225
10	26.5	35.5	42.5	70	160
20	19.5	27.5	36.0	140	290

Singh et al. (1997) also used RHA as a raw feed component in a vertical shaft kiln, and produced clinkers and cements of acceptable quality. An addition of 3 % RHA enhanced the kiln feed burnability, improved the production rate by 10 %, and gave noticeable fuel savings. Additionally, the presence of minor constituents like phosphate and sulphates in the RHA could increase the rate of clinkering by their mineralizing action, whereas the low magnesia content could help cement plants using high-magnesia limestone to mitigate problems related to soundness.

Ajiwe et al. (2000) used RHA to produce white cement. In one study, 24.5 % RHA was used with other raw materials, and the cement produced was evaluated for chemical as well as physical properties. The data confirmed that the cement produced from the RHA combination was similar to the commercially produced cement.

4.3.3 Ore rejects and mineral tailings

Tailings from ores and mineral processing plants are also rich in silica. One study has reported the use of copper-nickel and taconite (iron ore) tailings as replacements for silica in cement raw mix (Bhatty et al., 1985). The copper-nickel tailings were beneficiated prior to their addition to the raw mix. Their composition is shown in Table 26. The clinker produced from the raw mix was an ASTM Type I/II. It showed normal distribution of the major phases. The strength properties of the cement were better than those of a normal commercial ASTM Type I cement as shown in Table 27.

Table 26 Chemical composition (%) of mineral tailings (Bhatty et al., 1985)

Oxide	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO
Copper-Nickel tailings	56.96	27.57	8.80	0.62	0.16
Taconite tailings	58.54	0.64	0.22	27.40	3.10

Li et al. (2007) studied the utilization of Lead/Zinc mine tailings for production of moderate heat Portland cement. Lead/Zinc mine tailings, limestone, shale, and ironstone were mixed in six different compositions. The ground materials were burned at 1,350, 1,400 and 1,450°C for 30 min.

The clinkers were cooled, crushed, and ground. The contents of free CaO were measured and all of the samples contained less than 1.0% when burned at 1,450°C. X-ray diffraction and optical microscopy were applied to analyze the mineral compositions of the clinkers. The main phases determined in all clinkers were: alite, belite, cubic aluminate, and ferrite. The compressive strengths after 3, 7, and 28 days of the four clinkers with 5% gypsum were measured. The hydration heats of cements after 3, and 7 days were determined. It was concluded that Lead/Zinc mine tailings could be used to produce moderate heat Portland cement.

Table 27 Strength of tailing cement vs. normal ASTM type I cement (Bhatty et al, 1985)

Cement	Compressive strength (MPa) at			
	1 day	3 days	7 days	28 days
Tailings	6.9	22.1	32.4	48.3
ASTM type I	9.0	17.9	27.6	41.4

4.4 Alternative raw materials with argillaceous main component

This section discusses wastes and by-products that replace argillaceous components (alumina and silica) in the raw mix used in cement manufacturing. Materials discussed in this category include catalyst fines, fly ash, bottom ash, pond ash, red mud, basalt rock, et al.

4.4.1 Catalyst fines

Catalyst fines are traditionally rich in silica and alumina. A typical composition of catalyst fines had 50 % SiO_2 and 40 % Al_2O_3 (Bhatty, 2001). A 10 % addition of these fines was made to replace a large portion of silica and alumina (nearly 25 %) in a raw mix to produce cement clinker. The clinker showed phase distribution similar to that of the control (made without the catalytic fines). The addition of catalyst fines in the raw mix made clinker harder to grind, probably due to the formation of somewhat larger alite crystals. There appeared to be no change in the initial setting time of cement paste made with the catalyst fines clinker. The early strength was somewhat low (18.3 vs. 21.3 MPa), but the 7 and 28 day strengths were essentially equal to that of the control.

4.4.2 Fly ash

Fly ash is produced from coal-fired power plants. In 2003 well over 60 million tons fly ash were produced in USA. Only a portion of the ash is reused into marketable products, while the rest (over 40 million tons) is discarded. Being rich in silica and alumina, fly ash is regarded as a compatible component of cement raw feed largely replacing clay or shale. Typically, the composition of fly ash is similar to that of clay and shale except that it generally contains more alumina. However, in some cases, a high content of iron oxide in fly ashes can also be the sole source of iron required by the raw mix.

Several cement plants in USA have made use of fly ash as a component of raw feed. Plant types, use rate and mode of fly ash addition are given Table 28. In all these plants, the use of fly ash in raw kiln feed produced normal clinkers showing satisfactory amounts of C_3S, C_2S, C_3A, C_4AF, and liquid phases in the final clinker.

Table 28 Plant types, fly ash addition and mode of use in cement plants in USA

Plant type	Addition level	Mode of use
Dry	3 %	Blended with clay/sand and fed into raw mill
Wet	8 %	Added to clay at wash mill prior to feeding into raw mill
Wet	Varies	For ASTM type I/II cement; fly ash used as A source For ASTM type III cement; fly ash used as A, S and F source
Wet	1 %	Blended with raw mix
Dry	5.5 %	Fed into raw mill discharge riser duct and then blended with final kiln feed

At one of the largest cement plants in North America, the use of shale was completely eliminated by replacing with fly ash and iron ore tailings (Everett, 1995). The practice successfully reduced the generation of cement kiln dust (CKD). Prior to the switch over, the shale used at the plant was oil bearing and contained about 5 % sulphur that caused the plant to generate a large amount of CKD. By using the right proportions of fly ash (as a source of alumina) and iron ore (as a source of iron oxide) shale was replaced and CKD was reduced by at lest 50 % while producing a low-alkali cement. This was in addition to a significant reduction in both SO_2 and hydrocarbon emissions from the plant stacks.

Aalborg Portland cement plant in Rørdal, Denmark, introduced 10 % fly ash directly into the burning zone (Miller, 1980). The clinker was of good quality, showing normal phase distribution. Later in 1988, an improvement in the feeding system of fly ash in the raw kiln material and installation of a modern precalciner plant by Aalborg, allowed an increase in the proportion of fly ash in the clinker to 24 % without any detrimental effects to the quality of the clinker or to the environment (Borgholm and Nielsen, 1989). Reportedly, 2.3 million tons of fly ash have been processed, of which more than 50 % were consumed as a raw feed component in cement manufacture (Borgholm, 1992).

Two wet process plants in Belgium also used fly ash. Favourable change in slurry moisture, decreased dust loss, and reduced energy consumption were realized. Although the clinker showed an increased homogeneity of the major phases, it appeared overburned and hard to grind, causing grinding energy to increase. It is possible that the overburning was due in part to a failure to adequately compensate for the fuel value in the fly ash.

A Japanese cement plant used silica-rich fly ashes as a partial substitute for clay in the raw kiln feed (Mori, 1982). A treatment plant at the Takehara power station was installed to control the fly ash composition and create a sustainable supply. The chemical compositions of the two fly ashes (A and B) and the clay used in the raw mix are given in Table 29. The fly ash replaced 20 % to 40 % of the clay depending on the compositional compatibility.

Table 29 Composition of fly ashes and clay (Mori, 1992)

Material	SiO_2 (%)	Al_2O_3 (%)	CaO (%)	Fe_2O_3 (%)	MgO (%)	LOI (%)
Fly ash A	51.0	26.2	7.1	5.5	1.5	3.9
Fly ash B	51.3	27.0	6.8	5.4	1.5	4.1
Clay	62.4	17.2	1.5	6.3	2.2	7.4

Harada (1991) also reported a case study of recovery and utilization of fly ash and its major use in clinker manufacture. Fly ash replaced clay in the cement raw mix. No problem was encountered with the granularity or the presence of limited unburned carbon in the fly ash.

Mullick and Ahluwalia (1992) reported the use of fly ash in Indian cement manufacturing. The composition of the fly ashes used was close to that of clay, which was replaced fully or partially in the cement raw mix. Gore et al. (1992) replaced 6 % clay with fly ash in a wet process raw feed. The modification in the raw feed brought about by fly ash substitution gave several material, operational, and energy benefits. Lime combinability of the raw mix with and without the fly ash addition is shown in Fig. 28.

Kelly (1994) reported that control of the lime saturation factor, silica ratio, and alumina ratio for a target clinker was superior when raw mixes contained fly ash (3.2 %) as compared to an equivalent amount of shale. The addition of fly ash also enhanced the C_3A level of clinker, with equivalent C_3S and C_2S contents, as shown in Table 30. The early-age strength gain of cement prepared from these clinkers was superior to that of the control. In addition, an increased C_3A content allowed a larger scope for optimizing the early setting and strength properties of cement because gypsum could be added to the clinker over a wider range of concentrations during the finish grinding.

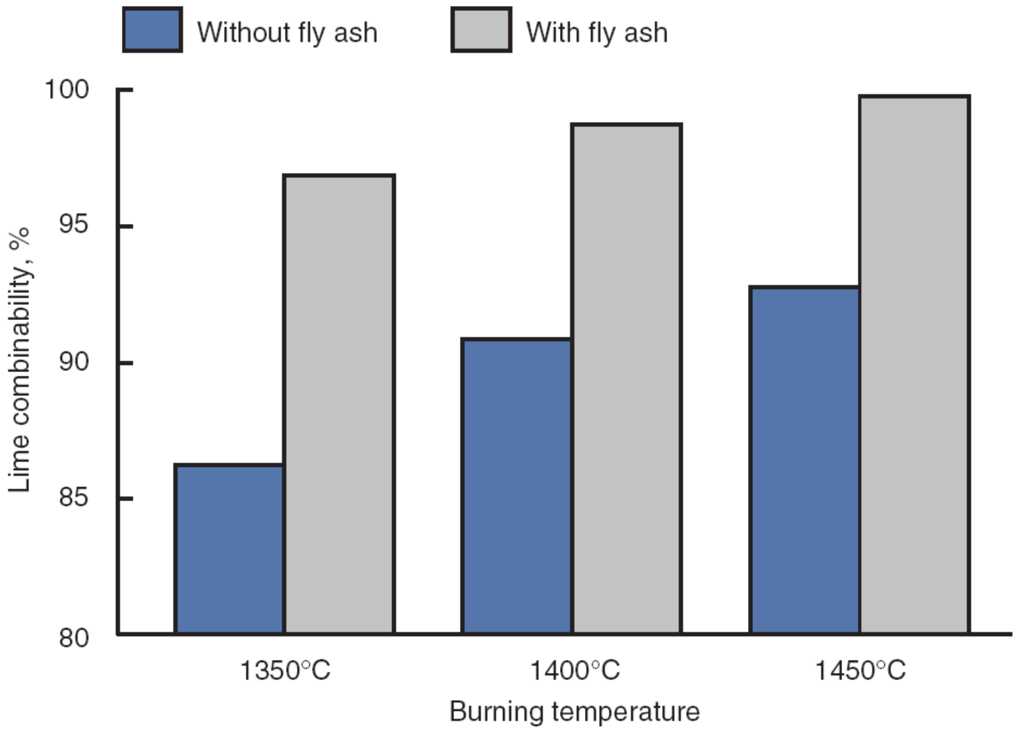


Fig. 28 Lime combinability of raw mix with and without fly ash addition (Gore et al., 1992)

Table 30 Raw mix parameters and clinker phases with and without fly ash additions (Kelly, 1994)

Raw mix	Silica modulus	Lime saturation factor	Alumina modulus	C_3S (%)	C_2S (%)	C_3A (%)
with fly ash	3.1	95.0	1.5	62.4	17.2	6.6
without fly ash	3.1	94.0	1.1	62.4	17.8	3.5

Komljenovic et al. (2007) studied fly ash from a coal fired power plant in Serbia as AR in cement kilns. Raw mixtures for Portland cement clinker synthesis were prepared with following cement module: LSF = 0.98. The sintering process was performed at 1,350 and 1,400°C. Chemical and mineralogical compositions of synthesized clinkers were compared with industrial ordinary Portland cement clinker. It was established that synthesized Portland cement clinkers based on fly ash had similar properties as the reference clinker.

In general, the following processing, operational, and product benefits have been observed from the use of fly ash as a component in cement raw kiln feed:

- Improved burnability, resulting in lower burning temperatures and a savings in fuel
- Increased clinker production
- No apparent deterioration in clinker quality
- Reduced SO_2, hydrocarbon, and NO_x emissions (in wet process) for some plants and fly ashes
- Reduced generation of cement kiln dust

Since fly ash is a free-flowing particulate material which is readily mixed and blended, additional benefits have also been realized as follows:

- Reduced material processing cost
- Reduced dusting due to reduced comminution of raw materials

However, some noteworthy adverse effects of using fly ash have also been pointed out. Some fly ashes cause reduced plasticity of the feed slurry in the wet process, while in a dry process plant, the fly ash resulted in an increased volatilization of alkalis that can cause blockages in preheaters.

4.4.3 High-carbon fly ash

With the installation of low-NOx burners and other emission-reducing measures at coal-fired power plants, large amounts of high-carbon fly ashes are expected to be generated. Although these ashes will pose difficulties for disposal, they will be capable of offering two major benefits if used in the cement manufacturing. First, the fly ash can partially replace raw materials such as shale and clay (as discussed above), and secondly, the carbon content of the fly ash can provide a fuel supplement during the clinker-firing process.

Bhatty et al. (2000 and 2001) demonstrated the use of a fly ash that contained approximately 20 % unburned carbon at a suspension preheater plant. The composition of the fly ash used in the trial run is shown in Table 31. The high-carbon fly ash was blended with the raw materials (crushed limestone and a small amount of shale) and ground into raw feed. The composition of the raw feed was targeted to the normal raw feed. The fly ash composition and that of other raw materials (limestone and shale) limited the fly ash substitution to 6 %. The total heat content (calorific value) of the ash was estimated to be > 740 kJ/kg that translated to an anticipated energy contribution from the fly ash of 67 kJ/kg of clinker.

Table 31 Composition of high carbon fly ash (Bhatty et al., 2000 and 2001)

Analyte	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O*	K_2O*	SO_3	TiO_2	LOI
Amount	42.95	15.46	7.1	4.47	1.3	1.88	2.5	0.49	1.08	20.8

*Composite contains 3.53 % Na_2O_{eq} and has a moisture content of 0.33 %.

During the demonstrations reported by Bhatty et al. (2000, 2001), the operation ran in a more efficient, stable, and predictable manner. Consequently, the cement plant incurred a fuel savings of nearly 4 %, and the clinker production increased by almost 10 %. Characteristics of clinker produced during the demonstration as determined by XRF, XRD, and free-lime tests are shown in Table 32. The XRF analysis indicates lower sulphates and alkalis in the fly ash clinker than in the control. Fig. 29 shows the major phase distribution in the clinker. Test results and ASTM C 150 standard physical requirements for cements presented in Table 33 indicate that the demonstration cement is comparable to the commercially produced cements.

Table 32 Composition of clinkers (Bhatty et al., 200 and 2001)

Parameter (%)	Without high carbon fly ash	With high carbon fly ash
SiO_2	20.07	21.57
Al_2O_3	5.45	5.98
Fe_2O_3	2.49	2.59
CaO	64.09	64.60
MgO	2.44	2.47
SO_3	2.43	0.59
Na_2O	0.40	0.39
K_2O	1.28	0.56
Na_2O_{eq}	1.24	0.76
LOI till 950°C	0.10	0.09
Free lime	2.98	0.44

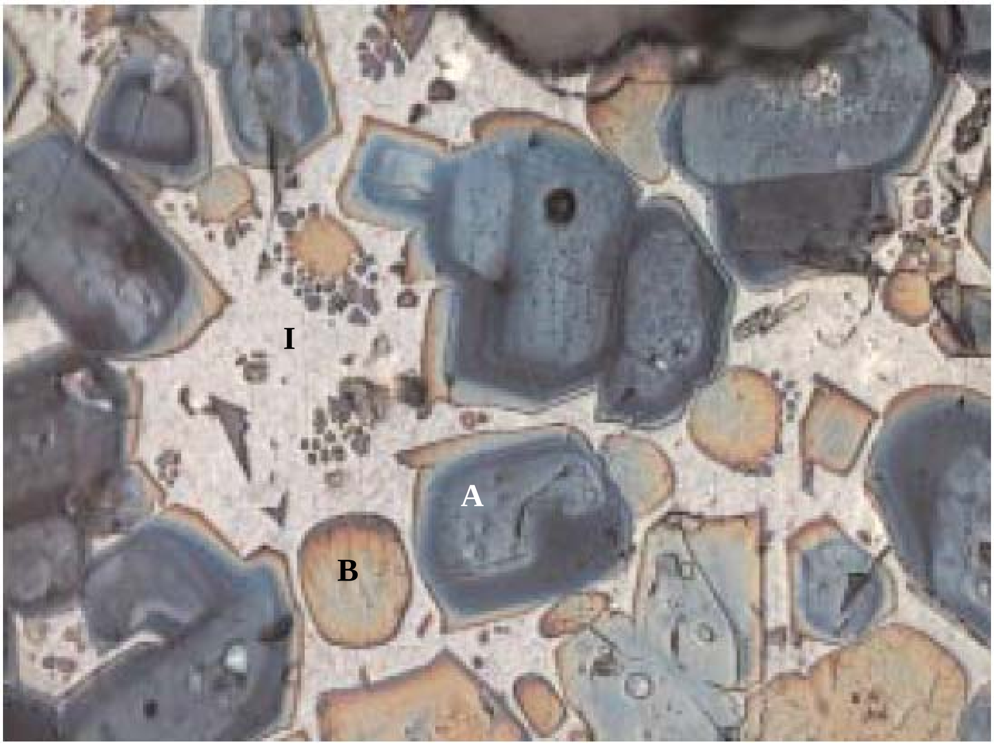


Fig. 29 Clinker produced from raw feed containing high carbon fly ash showing typical clinker minerals like alite (A), belite (B) and interstitials (I) after Bhatty et al. (2000, 2001)

Table 33 ASTM C 150 data for cements produced before and during high carbon fly ash feed

Cement	Compressive strength (MPa)			Air (vol %)	Setting time (min)		Autoclave expansion
	3 days	7 days	28 days		Initial	Final	
Before	25.9	31.0	40.5	7.8	85	180	0.12 %
During	25.2	28.9	41.9	8.1	105	210	0.07 %

Recently, Bhatty et al. (2007) claimed that more than half of the total fly ash produced in the US is land filled because its carbon content is too high for use in concrete. High carbon content in fly ash is either due to compliance with the emission regulations or operating older and less efficient plants. By virtue of its compositional similarity to shale/clay, high-carbon fly ash has been used in cement raw feed and has imparted many operational benefits. Several commercial demonstrations were carried out in which nearly 1,000 tons of fly ash with up to 20 % carbon replaced up to 6 % of cement plant raw mix. Bhatty et al. (2007) discussed selected demonstrations in which high-carbon fly ash from a Midwest station was used in a preheater process cement plant. Because of the additional heat derived from carbon, the use of fly ash essentially transformed the preheater process into a semi-precalciner process. During the demonstration several key operational parameters were improved; the kiln operation ran efficiently and smoothly; the plant realized a fuel savings of nearly 4 % and a 10 % increase in production. The resulting cement met the ASTM C 150 requirements. With this approach, large-scale reutilization of discarded fly ash is possible.

4.4.4 Bottom ash

Bottom ash is also a by-product from coal-fired power plants. Typically, a bottom ash is composed of partially fused coarse-sized particles. The ash is rich in silica, iron, and alumina and is suitable as a replacement for shale and clay, and iron (as corrective material) in cement raw feed. Compositions of select bottom ashes are shown in Table 34. In the long dry and preheater cement manufacturing processes bottom ash is generally blended with the raw mix prior to grinding. In the wet process, however, the bottom ash and clay are combined during the clay-wash process and added to the raw feed. Bottom ash is typically added as 2 % to 5 % of the raw feed, and produces clinkers showing satisfactory distribution of C_3S, C_2S, C_3A, C_4AF, and liquid phases; cements also display acceptable chemical and physical properties.

Table 34 Composition (%) of bottom ashes

Ash	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	LOI
A	41.5	16.8	28.9	3.8	0.9	0.7	4.3
B	42.8	18.3	24.6	5.0	0.9	0.7	4.4

4.4.5 Pond ash

Pond ash is generally a mixture of fly ash and bottom ash from coal-fired power plants. The material is generally sluiced and stored in ponds. Millions of tons of ash have been accumulated in the ponds over the past several years.

Singh et al. (1995) have made use of pond ash as a reactive component in the raw mix in a vertical shaft kiln. Use of 4 % pond ash gave optimum performance during the kiln operation. Composition of the pond ash used is shown in Table 35. The ash also contained a high carbon content. The raw feed mixture containing fly ash was nodulized prior to firing.

Table 35 Composition of pond ash (Singh et al., 1995)

Parameter	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	LOI
Content (%)	49.6	22.0	4.5	2.2	0.6	17.4

The clinker produced was of acceptable quality and was easier to grind, resulting in a savings in grinding energy. Since in a shaft kiln operation the fuel is incorporated into the raw feed, this practice was well suited for high-carbon pond ashes. The use of ash also realized an improvement in clinker quality, energy conservation, and cement production for the plant. Composition of the clinker produced with and without pond ash is shown in Table 36. As expected, the strength properties of cement made with pond ash clinkers were better than the control clinker because of higher C_3S content while the setting properties were comparable. Strength and setting data are shown in Table 37.

Table 36 Composition of clinkers from raw mixes with and without pond ash (Singh et al., 1995)

Clinker	Clinker minerals (%)				Free lime (%)
	C_3S	C_2S	C_3A	C_4AF	
With pond ash	48.7	20.6	9.9	14.6	1.6
Without pond ash	40.5	28.5	8.9	14.0	2.8

Table 37 Strength and setting times for cement based on raw mixes with and without pond ash (Singh et al., 1995)

Cement	Compressive strength (MPa)				Setting time (min)	
	1 day	3 days	7 days	28 days	Initial	final
with pond ash	19.0	30.5	40.0	48.5	140	235
without pond ash	18.0	26.0	34.2	45.0	135	230

4.4.6 Coal processing ash

Similar to high-carbon fly ash, coal processing plant wastes (also know as coal prep wastes) are being examined for use as a raw material in cement. These materials may be partly used as raw material replacement AR) and partial fuel substitute (AF). Because they are unburned and somewhat moist, these materials may affect emissions, limiting their use to particular types of cement manufacturing operations. Several million tons of coal prep wastes are generated every year, most of which are discarded. Reutilization of coal prep waste in cement manufacturing can result in high volume use with significant material and environmental benefits.

4.4.7 Municipal waste incineration ash

The processing problem of the significant amount of municipal solid waste incineration (MSWI) ash transported to landfills occurs in Tokyo in Japan. Therefore, cement making household waste a raw material was manufactured by the cement industry. Eco-cement that is made of municipal waste incineration ash and sewage sludge for at least half of the raw materials was developed and a Japanese Industrial Standard (JIS) about such cements was enacted in 2002. Concrete structures made by eco-cement are few (Kurumisawa et al., 2007) in spite of the standardization. Eco-cement does not provide so much long-term strength development of concrete, but the initial strength development is larger than for OPC. The reason for this was investigated by Kurumisawa et al., 2007). They clarified that different hydration products were produced in eco-cement and OPC by back-scatter electron imaging (BEI) in SEM and EDAX measurements. They confirmed that an increase in strength was not seen at later age although the strength development of eco-cement in early age is large. This is thought to be because eco-cement does not contain so much belite, but rather a lot of aluminate. A needle shape product was observed in the hydrated eco-cement paste, and it was shown that the structure was not particular dense even after 28 days curing.

Taiheio cement has made a special process where the MSWI ash is washed to remove alkali and chlorides while soluble heavy metals are precipitated by hydroxides or sulphides. The concentrate is then sold to the metal industry according to Hirao et al. (2006). The processed ash is used as AR in their eco-cement making.

The feasibility of municipal solid waste incineration (MSWI) ash utilized as the replacement of raw mix in cement production was investigated by Shih et al. (2003). Their results showed that sieving, self-grinding, and magnet separation processes are necessary to remove the debris, salt, and metallic contents that existed in the MSWI ash. By using the pre-treated MSWI ashes, the produced cement specimens were in compliance with the unconfined compression strength (UCS) standard in Taiwan at small replacement dosages (< 5 %). At larger ash replacement percentage (> 10 %), the strength development of specimens would be hindered due to the deficient formation of calcium silicate. Calculation of lime saturation factor (LSF) also shows a descending trend in with increasing replacement percentage. Thus, compositional effects should be taken into consideration for promoting the calcium silicate formation in the case of large ash replacement. Shih et al. (2003) adjusted the chemical composition by adding 183 g calcium oxide per kilogram of cement raw mixture with 15 % ash replacement. After adjustment, the produced cement could develop seven- and fivefold increase on UCS compared with those without calcium oxide supplement at 3 and 7 days of curing, respectively. Results concluded that the MSWI ash was suitable in reuse for cement production under a well-conditioned situation.

Kikuchi (2001) reported a technology for producing cement from incineration ash of municipal solid waste, incineration ash of sewage sludge and other wastes such as aluminium dross and copper slag. As incineration ash of municipal solid waste contains chlorine, special attention should be paid to fixing the chlorine within the cement. It was verified that proper treatment (formation of calcium-chloroaluminate) is capable of fixing the chlorine. In order to confirm the efficacy of this technology before it is used on an industrial scale, a pilot-scale test (50 tons/day) was conducted. The quality of the resulting cement was sufficient to enable the cement to be put to practical use. Furthermore, the tested process did not cause secondary pollution. Consequently, 50 % of raw materials for cement production can be obtained from incineration ash of municipal solid waste.

Singh et al. (2007) got around the high alumina and chloride content of incineration ash by producing Alinite cement. Alinite based cements have attracted a great deal of attention because these can be produced at considerable energy savings. Alinite has an additional ability to incorporate in its structure various impurity ions and can thus be made using a number of industrial and mining wastes, but in this study incinerator ashes were in focus. They showed that Alinite cements having strengths comparable to ordinary Portland cement can be successfully prepared by controlling the composition and firing schedule. For the records, the composition of Alinite corresponds to the formula $3[(CaO)_{0.875}\cdot(MgO)_{0.070}\cdot(CaCl_2)_{0.055}]\cdot[(SiO_2)_{0.885}\cdot(Al_2O_3)_{0.115}]$ according to Mazzaza and Gilioli (1983).

Krammart and Tangtermsirikul (2004) replaced cement raw materials by either MSWI bottom ash or calcium carbide waste (CCW) at levels of 5 and 10 %. They concluded that all MSWI ash and CCW cements showed slightly longer setting times compared to control cement. The compressive strength of mortars with CCW cement was not much different from the control cement, but the MSWI cement gave lower strength (especially for the highest dosage). The expansion of mortars based on cements with MSWI and CCW in sodium sulphate solutions were lower than that of OPC, with the lowest expansion for the MSWI cement.

Sikalidis et al. (2002) studied the utilization of municipal solid waste for mortar production, but not incineration ash as AR in cement production. They used the waste in a special two-stage rotary kiln together with a mixture of minerals to make cement after separating the waste in a light part for fuel and a heavy part for minerals. The process is patented.

4.4.8 Red mud

Red mud is a waste generated when alumina is recovered from bauxite during the Bayer process. Red mud is especially rich in Fe_2O_3 and $A1_2O_3$ and also contains SiO_2. Being rich in iron, it appears red in color, hence the name. Satisfactory use of red mud as an iron source in cement raw feed has been reported by Laxmi and Parashar (1985). Oxide compositions of two red muds used at different cement facilities are shown in Table 38. The amounts of red mud used in cement raw mix are also shown in the far right column of the table. Case 1 used 2.5 % red mud as replacement for iron ore in the raw mix. Cement produced from the raw mix showed acceptable setting behaviour and significant improvement in the early strengths. The later strengths were also comparable to cement produced without red mud substitution (see Table 39). The red mud substitution also helped address the problem of sulphur build-up in the kiln system of the cement plant. Case 2 used 8 % red mud in the raw mix and produced clinker of good quality. The clinker showed well-developed major clinker phases of alite and belite. It may be noted that excessive titanium content can have an adverse effect on the formation of the melt phase, and can restrict the addition of red mud in the raw mix.

Table 38 Composition and use (%) of different red muds (Laxmi and Parashar, 1985)

Red mud	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	TiO_2	LOI	amount used
Case 1	9.20	22.84	46.40	2.70	4.81	-	13.50	2.5
Case 2	9.60	18.60	26.65	15.44	3.09	12.03	13.45	8.0

Table 39 Strength and setting times for cement based on raw mixes with and without red mud (Laxmi and Parashar, 1985)

Cement	Compressive strength (MPa)				Setting time (min)	
	1 day	3 days	7 days	28 days	Initial	final
Control	14.5	30.0	44.0	54.0	135	200
Case 1	24.0	34.5	42.5	54.5	130	190

Red mud from HINDALCO (Hindustan Aluminium Corporation) Industries Limited, Renukoot, India, contains significant quantities of alumina, iron oxide and silica. Presence of these constituents makes it a suitable ingredient for the preparation of special cements according to Singh et al. (1996). Preparation of three varieties of cements was investigated, namely:
(a) aluminoferrite (C_4AF)-belite (β-C_2S) using lime + red mud + fly ash
(b) aluminoferrite-ferrite (C_2F)-aluminates (C_3A and $C_{12}A_7$) utilizing lime + red mud + bauxite
(c) sulphoaluminate ($C_4A_3\bar{S}$)-aluminoferrite-ferrite using lime + red mud + bauxite + gypsum

The effects of composition (proportions of lime, red mud, fly ash, bauxite and gypsum), firing temperature and duration on the properties of cements produced were studied in detail. Cements made from lime + red mud + bauxite or lime + red mud + bauxite + gypsum exhibited strengths comparable or superior to ordinary Portland cement (OPC). On the other hand, those prepared using lime + red mud + fly ash did not have sufficient strength. Moreover, it was not possible to replace bauxite by fly ash (as a source of alumina) in any significant quantity.

4.4.9 Basalt rock

Basalt rocks are volcanic in nature, and can be reactive to promote lime combinability in cement kiln feed. Basalt is rich in silica and alumina, with other significant components being lime, iron, and magnesium. The bulk of silica in basalt is in the form of silicates; iron is present as magnetite and ilmenite; and almost all magnesia is in the form of magnesium ferrosilicate. A range of typical basalt compositions is shown in Table 40.

Table 40 Chemical compositions (%) of basalt rocks

Oxide	Basalt rock				
	A	B	C	D	E
SiO_2	50.83	46.56	43.76	46.23	51.31
Al_2O_3	14.07	10.44	8.98	18.59	18.60
Fe_2O_3	2.88	1.87	2.88	2.71	2.91
FeO	9.06	10.19	9.57	8.17	5.81
CaO	10.42	8.32	7.91	11.21	10.30
MgO	6.34	18.28	22.43	6.23	5.95
Na_2O	2.23	1.49	1.48	2.80	2.93
K_2O	0.82	0.34	0.50	0.84	0.74
TiO_2	2.03	1.92	1.82	2.20	0.88
SUM	98.68	99.41	99.33	98.98	99.43

Promising test results on the use of basalt as a corrective material in the raw feed for Portland cement manufacture have been reported by Khadilkar et al. (1989). Improvement in the raw mix reactivity was studied by firing raw feed containing basalt. The raw feed was prepared with 2 % basalt as the corrective material by replacing bauxite and iron ore in the feed. The material was pelletized and fired from 800°C to 1,450°C for 20 minutes. The fired pellets were tested for free lime and also for any expansion or shrinkage while their mineralogical characteristics were determined by XRD analyses.

The raw mix containing basalt underwent more expansion than the mix without basalt up to 1,100°C, suggesting higher rates of solid-solid reactions to form calcium silicates and aluminates. Higher shrinkage of basalt raw mix above 1,300°C suggests higher liquid formation and C_3S formation. Significant reduction in free lime content for the basalt-containing mix also indicates improved lime combinability with basalt. The XRD analysis confirm the formation of C_3S at around 1,300°C for basalt-containing raw feed as compared to the raw mix without basalt which showed the C_3S peak at a much higher temperature according to Khadilkar et al. (1989). The microstructure of clinker produced from basalt raw feed exhibited well-developed C_3S and C_2S crystals. Stabilized polymorphs of belite were observed with higher hydraulic activity. Consequently the cement produced from basalt clinker gave higher compressive strength.

Hassan (2001) suggested basalt rock as an alternative raw material for Portland cement clinker as replacement of clay.

4.4.10 Slags from miscellaneous metallurgical industry

Pandey et al. (2007) studied waste slag from a melting lead zinc plant as AR replacing ferrous and siliceous material in clinker production. The composition of the slag was 39.0 % Fe_2O_3, 17.5 % SiO_2, 14.9 % CaO, 12.4 % ZnO, 8.7 % Al_2O_3, 1.3 % PbO and 0.9 % MgO as well as 4.1 % loss on ignition (LOI) giving a sum of 98.8 %. XRD revealed the mineralogy to be predominantly amorphous material along with crystalline Hematite (Fe_2O_3), iron (II) oxide (FeO), Gehlenite ($Ca_2Al_2SiO_7$), Hercynite ($FeAl_2O_4$) and Zincite (ZnO). The oxide and mineralogical compositions of the slag confirmed that it was suitable as a corrective raw mix ingredient. Clinkers were made using 2 and 5 % slag relative to impure limestone. The rate of hydration for cement made from clinker containing this slag was considerably slower than the reference. Leaching tests on the other hand showed that both Zn and Pb were rigorously bound in the hydrated phases.

4.5 Other alternative raw materials

4.5.1 Wastes with fluxing and mineralizing potentials

Wastes from the fluoride and fertilizer industries contain components with mineralizing and fluxing capabilities. The principal component in these wastes is calcium fluoride or its compounds which have been used advantageously in the cement industry. Use of waste from zinc, molybdenum, barium, and phosphogypsum industries has also been reported. The wastes have been added to the raw mix to promote reactivity at reduced clinkering temperature. When used as a mineraliser, zinc waste improved the burnability of the cement raw mix. Fig. 30 shows free lime as a function of ZnO in the waste added to the raw mix. Zinc-containing waste was also an effective mineraliser for the raw mix in the vertical shaft kiln process since it activated the formation of alite in clinker and improved the cement early strength (Jinyu et al., 1989).

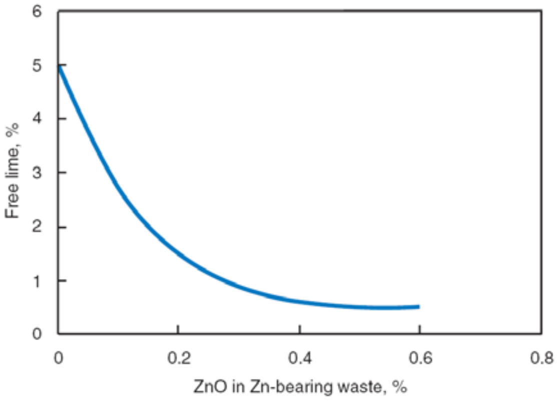


Fig. 30 Free lime as a function of ZnO in the waste added to the raw mix (Jinyu et al., 1989).

Molybdenum-iron ore tailings as studied by Zhou (1992) also imparted a mineralizing effect on the clinkering of cement raw feed. It promoted clinker formation by reducing the melt viscosity and helped accelerate C_3S formation. When used in the plant, the tailings produced clinker and cement with excellent properties. Free lime in clinker decreased, and the early age and ultimate strength of cement increased significantly. It markedly increased the kiln output by greater than 13 %, and improved fuel saving by over 5 %.

Caponero and Tenório (2000) studied the feasibility of co-processing phosphate coating sludge in the clinker process. The sludge contained basically water, ferrous and zinc phosphate and traces of other elements as shown by the chemical analysis in Table 41.

Table 41 Phosphate coating sludge analysis (Caponero and Tenório, 2000)

Component	Content (%)	Element	Content (ppm)
Ash[1]	75.7	Ca	230
Mass loss[1]	24.3	Si	500
Fe	7.00	Mg	31
Na	1.95	Al	186
P	5.85	Pb	45
Zn	8.30		

[1] Sample heated to 1,000°C to obtain mass loss and remaining ash.

Caponero and Tenório (2000) showed that up to 7 % phosphate coating sludge could be used without damage to the clinkerization process and no atypical phases were observed for dosages up to 5 %. The major element of the sludge, zinc (Zn) showed an incorporation of 75 % in the clinker.

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 in the un-spiked reference sample. In Fig. 31 it can be seen that the burnability increases with increasing WAM 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 Fig. 31 and it is referred to as the fCaO determined at temperatures in the region of 1,100-1,450°C. The DTA analysis upon heating of the raw mix samples indicated no influence on the decarbonation mechanism (700-900°C) by the addition of WAM. However, the melt formation temperature 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. This study is an 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.

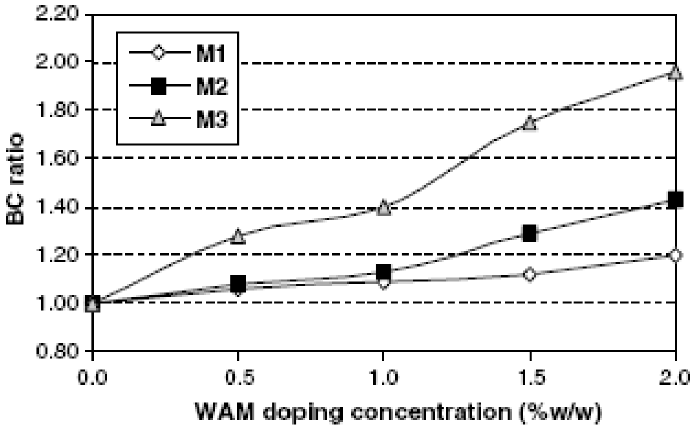


Fig. 31 Burnability Capacity (BC) ratio for the three different mix samples (M1-M3) as function of the WAM doping concentrations (0-2 %) from Kolovos (2006).

In Kacimi et al.(2006) the by-product phosphogypsum (PG) from the fertiliser industry was used as a mineraliser. It mainly contains gypsum with smaller amounts (~ 3 %) of sodium fluorosilicate (Na_2SiF_6), alkalis (1-2 %) and P_2O_5 (~ 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 Fig. 32 where 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 increases 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°C. The overall amount of amorphous phases was found to decrease and porosity increased, resulting in increased grindability.

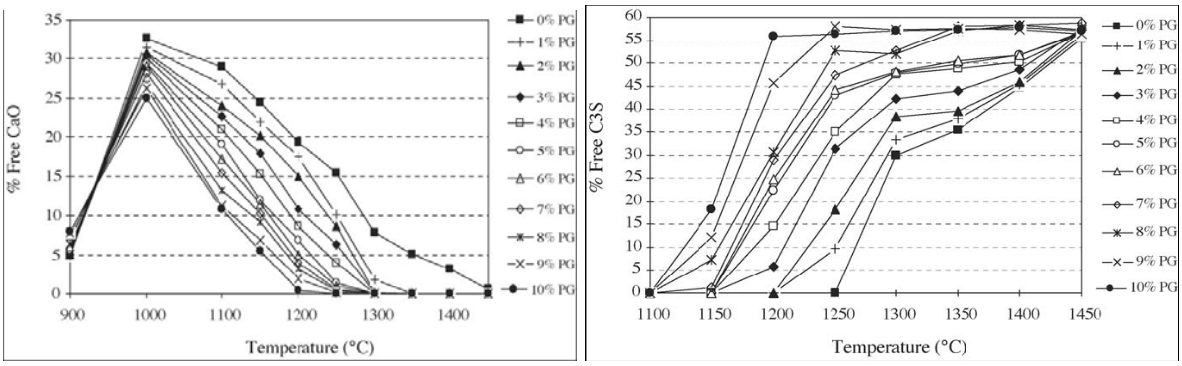


Fig. 32 Free CaO contents (left diagram) and C_3S formation (right diagram) as function of temperature and different quantities of phosphogypsum additions (Kacimi et al. 2006).

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 were not influenced, which indicates dissolution in the molten phase. Significant reduction in fCaO was achieved by 0.5 % addition of the ore material. Helmy (2003) studied the mineralizing effects of adding as much 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 mineraliser.

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 sulphoaluminate clinker. This precipitate originates from a hydro metallurgic process which treats low-grade nickel oxide ore. The original physical properties of the cement were maintained, but .increased content of C_4AF and $C_4A_3\bar{S}$ was determined in the clinker.

Dominguez et al. (2007) presented preliminary results on clinkerization reactions using industrial by-products as raw materials. Different concentrations of anhydrite, fly ash and treated electric arc furnace dust (EAFD) together with diverse amounts of $CaCO_3/CaF_2$ were mixed and sintered. High temperature reactions were characterized using powder X-ray diffraction and thermal analysis together with scanning electron microscopy. Thermal and X-ray results indicated that the clinkering temperature required for satisfactory combination may be reduced by as much as 200°C when CaF_2 was incorporated in the raw materials. Finally, it was observed that after hydration of the cement clinker, the mechanical properties were dependent on the amount of CaF_2 in the mix. A mean compressive strength of 40 MPa after curing samples for 7 days at 30°C indicated equivalent properties to those of conventional Portland cement.

4.5.2 Contaminated soil

Volcanic soil can be used to remove metals from waste waters. Once used, it is usually disposed in landfills. However, Navia et al. (2006) studied the possibility of utilizing spent volcanic soil as AR in cement clinker production using life cycle assessment (LCA) methodology and it came out favourably.

Occasionally soil is polluted with organic, industrial waste, such as tar etc. Beijing cement, being a part of this Sino-Norwegian project (Karstensen and Justnes, 2007) is to burn soil contaminated with dioxins. The destruction efficiency of dioxins and other organics in cement kilns is known to be excellent, and the inorganic part of such soil will of course become an integral part of the clinker. The most important inorganic oxides probably being Al_2O_3 and Fe_2O_3, at least if the soil is rich in clay.

4.5.3 Flue gas desulphurization sludge and waste gypsum

Flue gas desulphurization (FGD) sludge is collected from the scrubbers of power plants that use high sulphur coal. Lime is made to react with the SO_2 released from the coal to form calcium sulphite or calcium sulphate sludge that is collected by the scrubbers. FGD sludge is a fine material collected from the filtration units. Typical FGD sludge is mainly calcium sulphite ($CaSO_3 \cdot \frac{1}{2}H_2O$). Some power plants have additional equipment to oxidize the FGD sludge so that the calcium sulphite is converted to the more marketable calcium sulphate (gypsum).

Since, the oxidized FGD sludge consists of 99 % gypsum; it can conveniently be used as a gypsum substitute in the finish milling of clinker. The sludge is also a finely divided material that provides energy relief during finish milling. It also saves energy otherwise required to crush gypsum prior to the finish milling. Handling issues, however, need to be addressed before successful implementation at a plant. The sludge is often available in moist condition. Adequate drying of the sludge frequently results in excessive powder flowability which can be a problem, in addition to concerns relative to outside storage.

No adverse effects on the setting or the strength properties of cement have been reported from cements made with oxidized FGD sludge. These cements meet the ASTM C150 standard specifications for both physical and chemical requirements.

Singh and Garg (2000) studied the utilization of phosphogypsum produced as the waste of phosphoric acid manufacture for use in gypsum cement formulations (not Portland cement). Phosphogypsum is a fine powder with high calcium sulphate content. The phosphatic and fluoride impurities present in phosphogypsum cannot be removed completely neither by washing nor chemical treatments. However, phosphogypsum, when heated at elevated temperature, produced an anhydrite with inert impurities. The formation of anhydrite cement was examined by microscopy and X-ray diffraction. Data showed that a stable anhydrite can be produced by heating phosphogypsum at 1,000°C. The effects of different chemicals on setting and hardening of anhydrite cement and its hydration characteristics were studied. Results show that with the use of sodium sulphate and ferrous sulphate activators, maximum attainment of strength can be achieved. A correlation was established between hydration and chemically combined water. Microscopic studies revealed that formation of euhedral prismatic and rhombic shaped gypsum crystals govern high strength development in the anhydrite cement. Manufacture of anhydrite cement from phosphogypsum is recommended because of its lower energy requirements than the traditional building materials.

4.6 Alternative fuels with important ash components

4.6.1 Animal meal, bone meal and expired animal feed

Nastac et al. (2007) studied the influence of using meat and bone meal as an alternative fuel on the formation and properties of Portland cement clinker. From their investigations they concluded that: 1) Introduction of phosphorus in the clinkering process resulted in higher free lime content, up to 2 %, 2) the a belite phase was stabilized and no changes in alite polymorphism were observed with increasing P_2O_5 content and 3) the presence of P_2O_5 in alite and belite affects the hydration behaviour favourably, with higher degrees of hydration being observed with increasing amount of P_2O_5. However, their maximum P_2O_5 content in the clinker was 0.6 %.

Moudilou et al. (2007) investigated two commercial cent clinkers with 0.14 and 0.70 % P_2O_5. The aim of their study was to check the distribution of phosphorus and to evaluate its effect on mechanical properties development at 20°C and 60°C. All the analytical techniques (EDAX, SEM, TEM and XRF) confirmed that phosphorus is mainly distributed into belite grains without any structural modifications. Mechanical strength tests of the two clinkers exhibit a very different behaviour at 20°C and 60°C: at 60°C the higher the P_2O_5 content, the lower is the mechanical strength whereas it is the reverse at 20°C. As an explanation to this difference, Moudilou et al. (2007) suggested that thermal activation of belite dissolution at 60°C boosts the release of P_2O_5 which precipitates as hydroxyapatite in substitution of a part of Portlandite (3.0 % of CH in low P_2O_5 clinker sample and 2.4 % of CH in high P_2O_5 clinker sample, after heat-curing cycle). This reaction may reduce CSH growth and amount. Consequently, mechanical strength development after heat-curing cycle for P_2O_5 rich clinkers may be affected.

Note that some expired animal feed; e.g. for cat, dog (used as AF in Vietnam) and fish (used as AF in Norway), is composed of meat and bone containing phosphorous that will end up in the clinker.

Generally 1% P_2O_5 in clinker is considered the maximum value where clinker is not affected, but the recommendation is < 0.5 % to be on the safe side. More details on how phosphorous may affect clinker can be found in section 3.3.7.

A special kind of animal residue comes from the tannery industry. According to Trezza and Scian (2007), the tannery industry in Argentina processes 12 millions of bovine hides every year and generates an average of 50,400 t of scraps and shavings having a calorific value between 6,700 and 7,000 J/g. The concern was not so much any phosphorous, but rather the chromium content. Trezza and Scian (2007) clinkered different raw materials with shavings as AFR containing 2 % Cr_2O_3. Although the shavings contain largely trivalent chromium, it would at least partly oxidize to hexavalent in a commercial cement kiln. They found that the chromium changed the cell parameters of the main minerals and accelerated the hydration the first 48 h (see also section 3.3.3.1). The cement produced from the clinker showed retention of chromium giving leaching values below the regulatory limits.

4.6.2 Spent car tyres

The European Commission's Landfill Directive 1999/31 will ban the disposal of whole tyres to landfill by 2003, and shredded tyres by 2006. Furthermore, The European Directive 2000/53, "End of Life Vehicle", requires that 80 % in weight of an end life vehicle is reused or recycled by 2006, and the processes concerned with scrap tyres play an important role in achieving this target.

Corti and Lombardi (2004) compared different end life treatments of spent tyres by means of an life cycle analysis (LCA) and showed that tyres as AF in cement production was favourable mainly due to the avoided use of conventional fuels.

Prisciandaro et al. (2003) showed how some statistical tools can be applied in the process analysis of real cement plant data, e.g. in the clinker production process by using AF (shredded tyres and waste oils) in 2 different plants. Statistical Student's t-test, stepwise linear regression models and factor analyses were employed in the data analyses to evaluate the effect on the atmospheric stack emission of these AFs. They found that if less than 20 % regular fuel is replaced by AF, the clinker characteristics were not altered. However, in the case of tyres the stack emissions of NO_x, SO_2 and CO were slightly increased, but still below the regulatory limits. In the case of waste oil, pollutant gas emissions were even decreased.

Sheinbaum and Ozawa (2003) analysed the use of AF in the cement industry of Mexico to reduce CO_2 emission and energy consumption. They acknowledged the importance of spent tyres in this respect.

Note that tyres also will give a beneficiary supply of zinc (see section 3.3.3.2) while the content of sulphur also can give local reducing conditions keeping a larger fraction of chromium as harmless trivalent (see section 3.3.3.1).

However, it is not allowed to use spent tyres as AF in China, as it is more valuable for recycling of rubber and even thermal decomposed to low grade oils etc.

4.6.3 Waste oils

See the section on Prisciandaro et al. (2003) in 4.6.2 for statistical analysis of effect of waste oil as alternative fuel (AF).

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 1,000°C. The results showed no influence on the fCaO (free lime) 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. The study of ash impact indicated that the waste oil can substitute up to 30 % fuel in the cement kiln.

4.6.4 Paint sludges

Paint sludges can contain in particular titanium oxide as pigment (white), but also a number of other transition metals.

Potgieter and Potgieter-Vermaak (2007) used paint sludge from car manufacturer as AFR in clinker production. The ash from the paint sludge was high in titanium (see also section 3.3.3.1) and phosphorous (see also section 3.3.7); 55.1 % TiO_2, 17.4 % Al_2O_3, 12.6 % P_2O_5, 8.2 % SiO_2, 2.5 % Fe_2O_3, 1.5 % CaO, 1.2 % Na_2O, 0.7 % MgO, 0.2 % Mn_2O_3, 0.2 % SO_3 and 0.1 % K_2O yielding a sum of 99.7 %. It was demonstrated that an OPC clinker could be produced that incorporated 1-4 % of this paint sludge ash without compromising the burnability and microstructure of the baseline clinker made from the production raw mix. Potgieter and Smith (2007) tested cement based on clinker with the above paint sludge ash on a number of concrete key-parameters, but found no difference to ordinary Portland cement.

4.6.5 Sewage sludge

At present most of the sludge from wastewater treatment plants (WWTP) is applied directly or indirectly to the agriculture land or disposed by land filling (Corbitt, 1998, and Tchobanoglous, 1991). According to the European directive EU 99/13/EC it is obligatory to reduce the amount of biodegradable waste deposits to landfills by the end of 2010 to 75 % of the production in the year 1995. Another requirement of the European Union (EU) is to build WWTP for municipality for over 2,000 equivalent inhabitants. As a result one can assume that the quantity of cleaned waste water and sludge production will increase within EU in the years to come. It is likely that the amount of sludge used in agriculture will decrease to approximately 50-55 % of total production in near future, and that the pressure will increase for reducing the share of dewatered sludge from WWTP to landfills (European Commission, 2001a). Thus thermal utilization of burning dried sludge is a promising, convenient and efficient approach to reduce its volume, in particular when the sludge composition do not comply with the legislated requirements for agricultural use (BUWAL, 2005).

Stasta et al. (2006) evaluated the feasibility of co-processing sewage sludge in cement plants as AFR. They found that part of the fuel can be substituted (European Commission, 2001b, Association of Swiss Cement Plants, 2003) and that the ash can save raw material. Stasta et al. (2006) claimed that one ton sewage sludge can substitute 1/3 ton raw material. The chemical element composition of digested sludge is typically 67 % C, 5 % H, 25 % O, 2.2 % N and 0.8 % S. Dried, digested sludge has similar composition as brown coal, but the heating value is lower (8-12 vs. 21 MJ/kg). The recommended sewage sludge feed rate should not be more than 5 % of the clinker production capacity of the cement plant (Wether and Ogada, 1999). Heavy metals in sewage sludge can be a problem, and Stasta et al. (2006) concluded that 1) the content of mercury and cadmium is much higher than in both the raw meal and fuel for the kiln, but that the clinker is able to fixate at least a part of this, 2) the content of nickel, chromium and arsenic are comparable to the usual feed and 3) the content of zinc, copper and lead in the sludge is higher than in the usual feed, but the clinker fixate these elements very well. The overall conclusion by Stasta et al. (2006) was that co-processing sewage sludge in cement works utilizing the excess heat can be considered from energetical, economical and environmental points of view, as one of the most appropriate solutions of sludge treatment both for WWTPs and cement works.

Zabaniotou and Theofilou (2006) studied the utilization of sewage sludge as an alternative fuel (AF) at cement kilns, covering all processes, health and safety and environmental matters. Trials were performed at the Vassiliko cement plant at Cyprus on how to treat and utilize wet sewage sludge with 65-70 % moisture content as AF. Environmental gas emission measurements were performed, in particular regarding mercury (Hg). 22,000 m^3 of wet sewage sludge was treated at this cement plant during the years of 2003 and 2004. The recommended technology is to mix sewage sludge with petcoke and then incinerate the mixture at high temperatures. There were then no emissions of dioxins harmful to human health.

4.6.6 Shredder residue (SR)

Metal recycling from automobiles, appliances and scrap steel occurs at dedicated metal shredding operations. Shredder residue (SR) consists of glass, rubber, plastics, fibres, dirt and fines that remain after ferrous and nonferrous metals have been removed. The over 3 Mt of SR generated in USA each year are managed by land filling. Material recovery or energy recovery alternatives to land filling can be beneficial because of conservation of non-renewable resources and reduction of waste disposal.

Boughton and Horvath (2006) studied the human health and environmental impacts of land filling and three recovery operations; AFR for cement manufacturing, hydrolysis to light fuel oil and material recovery for recycling, These options were quantified and characterized using a life cycle assessment (LCA) approach. Comparisons were carried out after characterization of emissions relative to potential impact categories of global warming, fresh water aquatic toxicity, acidification, eutrophication, human toxicity, photochemical oxidant creation and terrestrial ecotoxicity. SR recovery in cement manufacturing could result in 1 Mt of coal conservation each year for USA alone. Compared to land filling, recovery of the fuel and mineral value of SR in cement making provided net benefits for all environmental impact characteristics considered primarily due to avoided coal mining amid land filling impacts. As much as 750,000 t of recyclable materials could be recovered from SR. Material recovery system impact results were very sensitive to process energy requirements as well as the assumptions of percent recovery and the specific material types recovered. Hydrolysis of SR could produce 250 million gallons (about 1 billion litres) of light fuel oil equivalent per year. The hydrolysis process requires a significant amount of electricity, which are somewhat offset by the avoided impacts of producing fuels from crude oil resources. Primarily due to high electricity consumption, both the hydrolysis and material recovery scenarios yielded trade-offs (some net benefits and some net higher impacts) compared to land filling. The result of their end-of-life impact assessment showed that the supplement for cement manufacturing option was environmentally beneficial to the current practice of land filling and appeared better in comparison to the other management methods studied.

A similar LCA as performed for SR by Boughton and Horvath (2006) could be interesting to perform on spent tyres in China to see if the decision of recycling or light oil production is more beneficial than using them as AF in cement kilns (see section 4.6.2).

5 EMISSION OF HEAVY METALS FROM CEMENT AND CONCRETE

This chapter discusses the emission of heavy metals with the stack gas and dust during cement clinker making, as well as leaching of heavy metals from the finished concrete and recycled concrete.

5.1 Acceptance limits and emission of heavy metals during clinker production

Cement kilns may discharge heavy metals in AFR through 3 different waste streams. These include emissions from the kiln through the exhaust stacks, incorporation into the cement kiln dust (CKD) or incorporation into the clinker. The two latter solids are continuously withdrawn from the kiln, but a portion of the CKD may be recycled back to the kiln. The major concern about heavy metals are air pollution through stack emissions, groundwater pollution from deposits of CKD and leaching into drinking water conveyance systems made or lined by cement made with AFR.

The high alkali content in cement kilns and the scrubbing action of the high solids content favour the retention of metal compounds in the clinker and collected particular matter (including CKD). Emissions of refractory metals (such as As, Be and Cr) are generally below 0.1 % of the input feed rates, and emissions of semi-volatile metals (such as Cd and Pb) are generally below 0.5 % according to Sarofim et al. (1994).

In Europe recovery operations in cement plants are in compliance with the provision of both Directive 1996/61/EC –concerning IPPC- and the Directive 2000/76/EC on the incineration of waste. The emission limit values for the cement plants under the "co-incineration" source category define three groups of metals, and also the units and the conversions before they are reported:

1) $(Cd + Tl) \leq 0.05$
2) $Hg \leq 0.05$
3) $(Sb + As + Pb + Cr + Co + Cu + Mn + Ni + V) \leq 0.5$

were all values are in mg/m^3 at temperature 273 K, pressure 101.3 kPa, 10 % oxygen, and dry gas. Fine particular matter (PM) from co-incineration sources could be considered as indirectly regulated, through emission limit values for pollutants, such as heavy metals (HMs) that occur in this size range (DEFRA, 2000).

Note that the emission limit of for instance Hg is much higher (50,000x) than for dioxins/furans with a maximum allowed concentration of 0.1 ng/Nm^3 as a weighted sum of 17 different species.

Exposure to particulate matter (PM) is associated with a number of health issues including shortened life expectancy, cardiovascular and lung disease. However, no mechanism has been proposed yet which can fully explain this relationship in terms of the chemical composition of the aerosol (Pope, 2000). The fraction of metal-rich PM is small and highly variable, and the concentrations of metallic species are generally very low. Spatial and temporal variability of both amounts and physical and chemical properties causes a large uncertainty in aerosol climate forcing calculations (Seinfeld et al., 2004). The discussion on PM2.5 (particle matter ≤ 2.5 μm in size) regulation in ambient air is currently going on. Unlike standards for gaseous compounds, the particle limit values are based on a condensed-phase metric (particulate mass or number) according to Ylatalo and Hautanen (1998) and Guiterrez-Canas et al. (2002) without regard to chemical composition. Controlling PM2.5 means more stringent performance requirements on precursors and primary particles emitted from industrial processes. The lower the current value of the mass emission is the harder and more costly to reduce them further. The particle formation and trace element behaviour during combustion of solid fuels have been studied since almost 20 years (Markowski and Filby, 1985, Kauppinen and Pakkanen, 1990, Clarke and Sloss, 1992, and Linak et al., 1995) and could be considered fairly good described. In clinker processes, there are three central issues: the release into the gas phase - kiln and preheater -, the chemical transformations as function of the local environment, and the subsequent aerosol dynamics. Either from thermodynamic predictions or experimental approaches to combustion systems (Markowski and Filby, 1985, Kauppinen and Pakkanen, 1990, Clarke and Sloss, 1992, and Linak et al., 1995), it is expected that metal-rich particles will occur mostly in the submicron regime of bimodal distributions. Heavy metal emission from combustion sources (Linak and Wendt, 1993, Eldabbagh et al., 2005, and Ferge et al., 2004) is described as originated by the release of metals into the vapour phase, with the particle dynamics of a nucleating, condensing, and coagulating aerosol that may be subsequently formed (Friedlander et al., 1991), and with the reactive scavenging of metals. Published data for fine particle and size resolved HMs have been obtained from combustion and incineration sources. Some recent examples are: Lind et al. (1999, 2003), Strand et al. (2002), Seames et al. (2002), Yao and Naruse (2005). Studies for other pyro-processing sources are very sparse with the exception of Ahn and Leeb (2006) and Davis and Wendt (2000). Aerosols are affected by other dynamic processes as they evolve with time and temperature along the preheater and the conditioning tower of the cement plant. Larrión et al. (2007) studied the allocating emissions signatures and enrichment of heavy metals in PM2.5 when alternative raw materials were used in a cement plant.

Guo and Eckert (1996) analyzed measured data on heavy metals output from a kiln equilibration test from a kiln co-fired with hazardous waste fuels. Metal outputs from stack emissions, cement kiln dust and cement clinker were considered. Equations were derived for predicting all three metal outputs at any hazardous waste feed rate under steady state conditions. Through analysis of two steady state conditions, at the beginning and at the end off the equilibration test, essentially the same ratios of metal feed rates were found to be distributed to the kiln dust at either high or low metal feed rates. Applying the same distribution ratios in the derive equations, metal concentrations could be predicted when the kiln was not using hazardous waste fuels. Measured concentrations of As, Be, Cd, Cr and Pb in wasted kiln dust, at the highest intended hazardous waste feed rates to the kiln, were 68, 10, 72, 18 and 68 times, respectively, to those predicted for feed rates with no hazardous waste. In addition, the intermediate, non-steady state segment of the equilibration test was analysed. If metals were assumed not to accumulate in the kiln, the intermediate metal concentrations in cement clinker were predicted to be substantially higher than those at the final steady state.

Su et al. (2007) studied emissions of heavy metals during cement calcinations by utilizing waste materials. Emission pollution of Pb, Cd, Zn, Cu and Hg during cement calcinations was investigated by means of atomic absorption spectroscopy (AAS). The samples of raw materials, clinker and soil were collected from several cement plants utilizing waste materials such as Pb-Zn tailings, Pb-Zn smelter slag and electronic arc furnace dust (EAFD). The emission rate of Hg during cement calcinations is very high, in the range 89-96 %; the emission rates of Pb and Cd are in the range 63-90 %; those of Zn and Cu are in the range 29-47 %, all in percentage of feed rates. The emitted Pb, Cd and Hg polluted the soil nearby during the cement production facility utilizing the waste materials. The contents of Pb, Cd and Hg in the soil 500 m leeward were 2-3 times of those in the soil 2,000 m leeward and 1,000 m windward. The fluorite mineraliser promoted the emission of Pb, Cd, Zn and Cu.

Maringolo et al. (2003) published a thorough study of the emission of a number of metals from a Brazilian cement plant burning a waste derived fuel processed from paints, thinners, resins, greases, wash-up solvents and waste oils. They did not detect Te, Pd and Be, but Cd, Hg, Pb, Ta, Se, Pt and Ag concentrated preferentially in the electrostatic precipitator dust. Higher degrees of incorporation into the Portland clinker structure was seen for the transition elements Co, V, Mn, Ni, Cr, Cu, Zn, Ba and Sn. Composite cements prepared exclusively with this waste derived fuel did not leach detectable amounts of As, Be, Ag and Tl, while Sb, Cd, Hg, Ni and Se were found in extremely low concentrations. Slightly higher, but still 91, 88 and 84% lower than the corresponding standard leaching limits were Ba, Pb and Cr, respectively.

5.2 Leaching of heavy metals from cementitious products and recycled concrete

5.2.1 Standards and methods relevant for leaching tests

European standards for leaching from construction products, recycled materials and waste are under development by several technical committees (TCs) under the European Committee for Standardization (CEN). Some of the most important TCs in this respect are

- CEN/TC 164 Water Supply/WG3 Materials effect on drinking water
- CEN/TC 292 Characterization of waste
- CEN/TC 154 Aggregates (including recycled aggregates)
- CEN/TC 351 Assessment of release of dangerous substances

CEN/TC 351 will influence all other product related TCs as it will harmonize the test methods so that the products comply with ER3 (Essential Requirement 3; health, hygiene and environment, one of 6 ERs to be fulfilled for a product to be CE marked) in the construction product directorate (CPD). Their mandate is M366, which means that emission (common term for de-gassing, evaporation and leaching) from products to indoor air, soil and ground water shall be quantified by standardized methods. The new philosophy is a "horizontal" standardization of methods, meaning that the test methods will apply to several product TCs. The work in TC 351 is in progress and the positioning of which methods will be fundamental is already a fact. TC 351 is not necessarily developing new methods, but may choose from existing methods. There will not be one horizontal standard for all products, but most likely several horizontal standards for different product groups. Products that evidently do not constitute a health risk can be classified under the categories "without testing" (WT) or "without further testing" (WFT). The details for placing products within these categories are not ready yet, but the general guidelines are that documentation must be available either as historical data or fundamental emission data. The decision of placing a product within the WT/WFT is made at the European commission level.

CEN/TC 164/WG 3 has worked with the development of an European Acceptance Scheme (EAS) for nearly10 years. The mandate is M136. The methods developed and finalized in this committee will be evaluated by TC 351. Materials in contact with drinking water will be subject to both the construction product directive (CPD) and the drinking water directive (DWD) with CPD as the most important. This means that the emission limits (DWD parameters) are determined in this work (unlike the work of TC 351). Another fact is that the drinking water is a defined, closed system unlike the many other scenarios in TC 351. EAS is different from other corresponding acceptance schemes, for instance in USA, Australia and Japan. Important standards from CEN TC 164 with respect to drinking water are;

- EN 12873 part 1:
    - Influence of materials on water intended for human consumption - Influence due to migration - Part 1: Test method for non-metallic and non-cementitious factory made products

- EN 12873 part 2:
    - Influence of materials on water intended for human consumption - Influence due to migration - Part 2: Test method for non-metallic and non-cementitious site-applied materials

- EN 12873 part 3:
    - Influence of materials on water intended for human consumption - Influence due to migration - Part 3: Test method for ion exchange and adsorbent resins

- EN 12873 part 4:
    - Influence of materials on water intended for human consumption - Influence due to migration - Part 4: Test method for water treatment membranes

- EN 14944-1:2006:
    - Influence of cementitious products on water intended for human consumption - Test methods - Part 1: Influence of factory made cementitious products on organoleptic parameters

- prEN 14944-3
    - Influence of cementitious products on water intended for human consumption - Test methods - Part 3: Migration of substances from factory-made cementitious products

- EN 12901:1999:
    - Products used for treatment of water intended for human consumption - Inorganic supporting and filtering materials – Definitions
    - Followed by EN 12902-12915 for different materials as active carbon, silica, barite, garnet etc.
    - In addition EN 14368 and EN 14369 for manganese oxide and alumina

- EN 14395-1:2004
    - Influence of organic materials on water intended for human consumption - Organoleptic assessment of water in storage systems - Part 1: Test method

- EN 14718:2006
    - Influence of organic materials on water intended for human consumption - Determination of the chlorine demand - Test method

- prEN 15664-1
    - Influence of metallic materials on water intended for human consumption - Dynamic rig test for assessment of metal release - Part 1: Design and operation

Methods for characterization of waste are developed by CEN/TC 292. The methods from TC 292 will be central for the work in TC 351. The methods for leaching are divided into basic characterization test and compliance tests, since the waste is classified according to different categories (inert waste, waste, special waste etc). The methods developed by TC 292 are often used for both waste and "ordinary" materials since they also have set emission limits from disposal sites. However, this emission limits can not be directly transferred to other emission scenarios. In Norway, a comprehensive work has been done in developing general leaching limits from recycled materials used as road base lead by the Norwegian Road Directorate (Petkovic et al., 2004). Important standards developed by CEN/TC 292, but important for leaching in TC 351, are;

- CEN/TS 14429:2005
    - Characterization of waste - Leaching behaviour tests - Influence of pH on leaching with initial acid/base addition
    - The results are suitable for geochemical modelling

- CEN/TS 14997:2006
    - Characterization of waste - Leaching behaviour tests - Influence of pH on leaching with continuous pH-control
    - The results are suitable for geochemical modelling

- CEN/TS 14405:2004
    - Characterization of waste - Leaching behaviour tests - Up-flow percolation test (under specified conditions)
    - The results are suitable for geochemical modelling

- EN 12457-1:2002
    - Characterisation of waste - Leaching - Compliance test for leaching of granular waste materials and sludges - Part 1: One stage batch test at a liquid to solid ratio of 2 l/kg for materials with high solid content and particle size below 4 mm (without or with size reduction)

- EN 12457-2:2002
    - Characterisation of waste - Leaching - Compliance test for leaching of granular waste materials and sludges - Part 2: One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 4 mm (without or with size reduction)

- EN 12457-3:2002
    - Characterisation of waste - Leaching - Compliance test for leaching of granular waste materials and sludges - Part 3: Two stage batch test at a liquid to solid ratio of 2 l/kg and 8 l/kg for materials with high solid content and particle size below 4 mm (without or with size reduction)

- EN 12457-4:2002
    - Characterisation of waste - Leaching - Compliance test for leaching of granular waste materials and sludges - Part 4: One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 10 mm (without or with size reduction)

CEN/TC 154 developed a leaching method covering both new and recycled aggregate that became much debated (too be revised). The discussion evolved around the lack of consideration of pH influence, particle size and whether equilibrium is achieved or not. These are parameters that have been worked on a lot and which TC 292 has taken into account. TC 154 has also argued that new and recycled aggregates are products and should be classified as such and also that the methods should reflect conditions closer to reality.

The continued work in CEN on establishing the emission properties of a material will focus on a more stepwise characterization starting with the basic characterization where fundamental properties is laid down. The leaching mechanisms are often described by geochemical modelling. Several relevant studies (Dijkstra et al, 2004 and 2006, Engelsen et al., 2007ab, van der Sloot et al., 2006) have been performed on various materials. Such a basic characterization can be useful to establish already today using available standards and can be compared with existing data in commercial available European leaching databases (www.leachxs.net). After a basic characterization, a compliance test will be necessary with respect to existing emission limits. These emission limits will be scenario specific and together with the data from the basic characterization and the compliance testing, a comparison can be made with an acceptable risk. This is not a new principle, as it is applied in the disposal site directive and other earlier suggestions for waste handling (Kosson et al., 2002).

SINTEF is participating actively in the national reference groups and in CEN TC 164 and 351 (earlier also 292), and is holding a central position in the European Organization for Technical Approval (EOTA) PT 9 (regulated substances).

Some important standards for leaching from concrete are;

- CEN/TC 51 N 614
    - Study of the characteristic leaching behaviour of hardened concrete for use in the natural environment

- prCEN/TR 15678
    - Concrete - Release of regulated dangerous substances into soil, groundwater and surface water - Test method for new or unapproved constituents of concrete and for production concretes

- NEN 7345
    - Dutch diffusion tank leaching test

Schneider and Spanka (2003) published a thorough discussion of the European legislation for construction products compared to the German legislation. They also discussed the content of trace elements and organic substances in cement and cementitious materials and their emission behaviour being controlled by

1) Incorporation in the crystal lattice of the hydrate phases
2) Chemical binding to the surface of the hydrate phases
3) Sorption on to the surface of the hydrated phases
4) Formation of insoluble salts

Schneider and Spanka (2003) concluded that the leaching behaviour of trace elements from cementitious materials is controlled by the degree of binding of these substances to the hardened cement paste and the pore size distribution of the cementitious matrix. The long-term leaching behaviour of substances from cementitious materials follows diffusion controlled transport mechanisms with low diffusion rates. This is especially true for properly manufactured concrete. Therefore the most important engineering tool to minimize leaching from cementitious materials like concrete is to reduce the capillary porosity of the hardened cement paste matrix.

Hohberg et al. (2000) developed a procedure for leaching testing of hardened concrete. The development of a short term test was difficult since they realized that leaching is diffusion controlled. This means that leaching is slow and will be slower the lower the porosity is. Thus a concrete made with a low water-to-cement ratio (w/c) will leach slower than a concrete with higher w/c.

5.2.2 Leaching of heavy metals from cementitious materials

Serclérat et al. (2000) studied the retention mechanism in mortars of the trace metals contained in Portland cement clinkers made with natural raw materials, fossil fuels or waste derived fuels. Industrial cements were studied along with laboratory samples enriched with lead, zinc and chromium. Zinc appeared to be insoluble in the pH range 7-13, while lead was only released in alkaline medium above pH 12.5. Chromium was retained in the hydrated paste. The role of Ettringite in this matter was discussed.

Marion et al. (2005) investigated leaching of heavy metals from sidewalk concrete and found that only 1 % of the total amount of heavy metals in the concrete did leach out. They also stated that typical heavy metal levels in CEM I cements (values in mg/kg = ppm) are for arsenic (As) 7-11, cadmium (Cd) 0.5-1.5, chromium (Cr) 74-121, copper (Cu) 22-60, mercury (Hg) 0.7-3.5, manganese (Mn) 234-465, nickel (Ni) 56-84, lead (Pb) 12-145, antimony (Sb) 4.4-9.4, zinc (Zn) 91-514, selenium (Se) 4-10, silver (Ag) 0.5-0.6 and barium (Ba) 205-577.

Since a large fraction of heavy metals may be bound in slowly reacting clinker minerals like C_4AF, it is of interest if the hydration products of faster reacting minerals like C_3S and C_3A actually will bind these heavy metals. This can be investigated by adding heavy metals solutions to already hydrated cement (e.g. Coleman et al., 2005). Cheeseman et al. (1998) mixed synthetic metal hydroxide waste containing Zn and Pb with partly hydrated cement and uni-axially pressed them. They found that leaching of Zn and Pb from the pressed samples was primarily determined by pH.

Another topic is stabilization/solidification (S/S) of heavy metal solutions added to cement and water (detailed information can be found in Connor, 1990) before the main cement minerals are properly hydrated. Qiao et al. (2007) added hydroxide of zinc, lead and copper individually to C_3S and C_3A paste and noted that only zinc retarded the hydration of C_3S strongly. A dynamic leach test was performed on the paste specimen. After 56 days curing the zinc leached was only 0.3 % of added amount, while leached amounts of lead and copper were below the detection limit.

5.2.3 Leaching of heavy metals from recycled concrete

The fixation of heavy metals in the cementitious binder of concrete is so strong that Coleman et al. (2005) claimed that the fines from crushed concrete could be used to remove copper, zinc and lead from contaminated waters. Crushed concrete with particle sizes 1-2 mm removed effectively the heavy metals from solutions with 35,000 ppm Cu^{2+}, 33,000 ppm Zn^{2+} and 37,000 ppm Pb^{2+}. Subsequent leaching revealed that only 1.9, 0.9 and 0.2 % of the bound metals copper, zinc and lead, respectively, could be leached out again.

Cements usually contain less than 0.02 % Cr (total). In a recent Norwegian 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. This acceptance limit was risk based and it was assumed that no more than 50 % Cr^{6+} of total chromium was present. Taking the latter into account and the fact that normal cement contents in concrete are 300-400 kg/m^2, the proposed acceptance limits for Cr will cover most of the cements used today. 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 road base scenario.

6 CONCLUSIONS

The report gives a short review of cement production and focus on the effect of different foreign elements in cement making, both when they are added deliberately as fluxing agents and mineralizers and when they are contaminants in raw meal and alternative raw materials (ARs). The different types of ARs are reviewed. Many foreign elements, and in particular some heavy metals (e.g. Cu and Zn) can have a positive influence on the burnability of clinker.

The high alkali content in clinker and scrubbing action of the high solids content favors retention of heavy metals in clinker and collected particular matter (e.g. CKD). Emission of refractory metals (As, Be, Cr) is found to be < 0.1 % of input feed rates (i.e. amount of element in feed), while semi-volatile metals (e.g. Cd, Pb) usually are < 0.5 % of feed. Compounds of Zn, Cd, Tl and Pb undergo cycling and can be deposited in pre-heaters.

In Europe recovery operations in cement plants are in compliance with the provision of both Directive 1996/61/EC –concerning IPPC- and the Directive 2000/76/EC on the incineration of waste. The emission limit values for the cement plants under the "co-incineration" source category define three groups of metals, and also the units and the conversions before they are reported:

1) $(Cd + Tl) \leq 0.05$
2) $Hg \leq 0.05$
3) $(Sb + As + Pb + Cr + Co + Cu + Mn + Ni + V) \leq 0.5$

where all values in mg/m^3 at temperature 273 K, pressure 101.3 kPa, 10 % oxygen, and dry gas.

The chemistry of cement hydration and cement classification are also reviewed. Too high concentrations of heavy metals, in particular zinc (Zn), can retard early hydration, but it is found that clinkers high in MgO can tolerate more zinc due to solid solution. In terms of cement properties, there are a few elements to be aware of when AR is used in clinker making;

1) Too much chloride may initiate corrosion of reinforcement in concrete. The Chinese cement standard is under revision and may set a limit of ≤ 0.06% Cl^- (no limit earlier).
2) Too much phosphorous can destabilize C_3S formation. Safe limit is < 0.5 % P_2O_5 of clinker.
3) Too much magnesium can give expansion during hardening. Cement must comply with the Le Chatelier soundness test (< 10 mm expansion). The limit of MgO is < 5 % of cement.
4) Too much zinc may retard setting, but contents < 1% ZnO in clinker seems safe.
5) Too much chromium can create contact eczema for concrete workers. < 2 ppm Cr^{6+} in water of fresh concrete is considered to be safe. Cement can be milled with reducing agents like ferrous sulphate to achieve this limit.
6) Too much alkali can cause problems for alkali-reactive aggregate in concrete. Cement is considered low alkali when Na and K recalculated to equivalent Na_2O is < 0.6 % of cement.

Most heavy metals in clinker is fixated and leaching of them to the environment is usually well below regulatory limits. The one element that sometimes can be problematic is hexavalent chromium.

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8 ABBREVIATIONS

A = Cement chemist short hand notation for aluminium oxide, Al_2O_3
AAS = Atomic Absorption Spectroscopy
AF = Alternative Fuels
AFR = Alternative Fuels and Raw materials
AR = Alternative Raw materials
BC = Burnability Capacity
BEI = Back-scattered Electron Imaging
C = Cement chemist short hand notation for calcium oxide, CaO
$\bar{C}$ = Cement chemist short hand notation for silicon dioxide, CO_2
CCW = Calcium Carbide Waste
CEN = European Committee for Standardization
CKD = Cement Kiln Dust
CPD = Construction Product Directive (European)
DWD = Drinking Water Directive
EAFD = Electric Arc Furnace Dust
EAS = European Acceptance Scheme
EDAX = Energy Dispersive Analysis of X-rays
EOTA = European Organization for Technical Approval
ER = Essential Requirement

EU = European Union
fCaO = free lime
F = Cement chemist short hand notation for ferric oxide, Fe_2O_3
FGD = Flue Gas Desulphurisation
GGBS = Ground Glassy Blastfurnace Slag
GPFS = Granulated Phosphorous Furnace Slag
H = Cement chemist short hand notation for water (hydrogen oxide), H_2O
HW = Heavy Metal
K = Cement chemist short hand notation for potassium oxide, K_2O
LSF = Lime Saturation Factor, a mass ratio of C to a weighed sum of S, A and F
M = Cement chemist short hand notation for magnesium oxide, MgO
MSWI = Municipal Solid Waste Incineration
N = Cement chemist short hand notation for sodium oxide, Na_2O
PG = Phospho-Gypsum
PM = Particular matter
PM2.5 = Particular matter with size ≤ 2.5 μm
S = Cement chemist short hand notation for silicon dioxide, SiO_2
$\bar{S}$ = Cement chemist short hand notation for sulphur trioxide, SO_3
SEM = Scanning Electron Microscopy
SR = shredder residue
S/S = Stabilization/Solidification
TC = Technical committee
UCS = Unconfined Compressive Strength
USA = United States of America
WAM = Waste Ammunition Material
W/C = water-to-cement ratio by mass
WFT = Without Further Testing
WG = Working Group
WT = Without Testing
WWTP= Waste Water Treatment Plant
Z = Cement chemist short hand notation for zinc oxide, ZnO