CHAPTER 2

PREPARATION OF SAMPLES

2.1 Complete Replacement of Calcium with Barium in Portland Cement Clinker

A literature survey on the effects of complete replacement of calcium with barium in cement clinker revealed that very little research in this regard has been published. In 1968 Braniski *[23]* published a paper on the preparation of siliceous barium cements: barium cements were prepared by heating raw mixes consisting of either barium carbonate or barium sulphate, silica, alumina and ferric oxide for four hours at 1380 to 1430 °C when using barium carbonate, and at 1560 to 1620 °C when using barium sulphate in the raw mix. All samples were rapidly cooled in air. The major phases formed were analogous to the major calcium phases found in Portland cement. According to Braniski, the barium cements consisted mainly of the phases tribarium silicate, Ba_3SiO_5, dibarium silicate, Ba_2SiO_4, tribarium aluminate, $Ba_3Al_2O_6$, monobarium aluminate, $BaAl_2O_4$, tetrabarium alumino ferrite, $Ba_4Al_2Fe_2O_{10}$, and dibarium ferrite, $Ba_2Fe_2O_5$.

Tribarium silicate (B_3S) appeared to form at temperatures higher than 1200 °C in a mixture containing barium carbonate, silicon dioxide, alumina and ferric oxide. Dibarium silicate (B_2S) was said to form at temperatures higher than 775 °C. Monobarium aluminate (BA) was said to form at temperatures higher than 700 °C, while tribarium aluminate (B_3A) formed at temperatures higher than 1000 °C. The tetrabarium alumino ferrite phase (B_4AF) formed in the temperature range 950 to 1150 °C. Using optical microscopy, Braniski described the B_3S as colourless, B_2S as yellowish, and the ferrite phases as dark brown to grey black.

Braniski's findings on the properties of the different phases formed upon heating of a mixture containing barium carbonate, silica, alumina and ferric oxide are summarized in Table 2.1 *[23]*.

Table 2.1: Properties of siliceous barium cement phases

Phase	Formation Temperature (°C)	Density (g/cm^3)	Melting Point (°C)
$3BaO.SiO_2$	1000-1400	5.69	decompose
$2BaO.SiO_2$	775-1350	N/A	1820
$3BaO.Al_2O_3$	1000-1500	4.62	1750
$BaO.Al_2O_3$	700-1450	4.18	1830
$4BaO.Al_2O_3.Fe_2O_3$	925-1150	N/A	1450
$2BaO.Fe_2O_3$	900-1150	N/A	1410

However, more recently published studies seem to contradict some of Braniski's findings. Most importantly, there appears to be doubt about the formation and stability of the tribarium silicate phase under normal clinkering conditions *[19]*.

2.2 Selection of Suitable Compositions for the Quaternary Mixtures Containing $BaCO_3$, Al_2O_3, Fe_2O_3 and SiO_2

To calculate suitable compositions for raw mixes consisting of barium carbonate, silica, alumina and ferric oxide, it was assumed that the phases that would form during clinkering would be analogous to the calcium phases formed in Portland cement clinker. This assumption was based on the findings of Braniski *[23]* as discussed in Section 2.1. It was thus assumed that the main considerations in the proportioning of the raw materials for cement clinkering, i.e. the potential clinker composition, the percentage liquid phase and the burnability of the raw mix[1], will all be relevant and applicable to the proportioning of the raw materials for the preparation of barium clinker.

2.2.1 The Lime Saturation Factor

Lea and Parker *[24]* derived a formula to give the maximum acceptable calcium oxide content in a Portland cement raw mix. They showed that in order to have only tricalcium silicate and the liquid phase and no uncombined calcium oxide at equilibrium at normal clinkering temperatures, the maximum allowable calcium oxide content by mass could be expressed as

$$\%CaO_{max} = 2.80(\%SiO_2) + 1.18(\%Al_2O_3) + 0.65(\%Fe_2O_3) \qquad (2.1)$$

The lime saturation factor (LSF) of a raw mix can then be defined as

$$LSF = \%CaO \,/\, \%CaO_{max} \qquad (2.2)$$

Substituting Equation 2.1 into Equation 2.2, we get:

$$LSF = \frac{CaO}{2.8SiO_2 + 1.18Al_2O_3 + 0.65Fe_2O_3}, \qquad (2.3)$$

where the chemical formulae also denote mass percentages.

The LSF is therefore a measure of the amount of CaO that can be combined. From Equation 2.3 it can be seen that, theoretically, an LSF of 100 % would result in a clinker containing only tricalcium silicate and the ferrite solid solution. Although LSF values up to 102 % may be acceptable, values from 92 % to 98 % are frequently appropriate for reasonable burnability *[5]*. Lower LSF values will result

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[1] The burnability of a mix can be defined as the relative ease, in terms of temperature, time, and fuel requirements of combining the oxides into good quality clinker *[3]*.

in cements with higher dicalcium silicate and lower tricalcium silicate phase contents, so that slow hardening of the resultant cement can be expected. Furthermore, problems with dusting during the beta to gamma transformation of dicalcium silicate can be expected *[3]*. On the other hand, too high an LSF value could render the mix very difficult to burn and will result in clinker with unacceptable levels of uncombined calcium oxide (called free lime). Too high levels of free lime will lead to excessive expansion on hydration of the cement *[4, 5]*.

By adapting Equation 2.3 to incorporate Ba in the place of Ca, the barium oxide saturation factor (BSF) was defined as follows:

$$\mathrm{BSF} = \frac{\mathrm{BaO}}{7.65\mathrm{SiO_2} + 3.22\mathrm{Al_2O_3} + 1.78\mathrm{Fe_2O_3}}, \qquad (2.4)$$

where the chemical formulae also denote mass percentages.

A BSF value of 100 % would then indicate that only tribarium silicate and the liquid phase would exist at equilibrium. Values lower than 100 % would result in some dibarium silicate at equilibrium and values higher than 100 % would yield uncombined barium oxide. However, the BSF as defined in Equation 2.4 will only be valid if tribarium silicate does form and is stable under the clinkering conditions. Also, all phases formed must be analogous to the calcium phases.

2.2.2 The Silica and Alumina Moduli

Other parameters that are widely used in the cement industry for raw material proportioning are the silica modulus (M_S) and the alumina modulus (M_A) *[4, 5, 8]*. These are defined in Equations 2.5 and 2.6.

$$M_S = \frac{\mathrm{SiO_2}}{\mathrm{Al_2O_3} + \mathrm{Fe_2O_3}} \qquad (2.5)$$

$$M_A = \frac{Al_2O_3}{Fe_2O_3} \qquad (2.6)$$

For normal Portland cement clinkers, the M_S usually ranges between 1.9 and 3.2 *[5, 8]*. As the silicon is primarily bound in the solid phases tricalcium silicate and dicalcium silicate, while the aluminium and iron are contained in the melt, the silica modulus defines the solid:liquid ratio in the kiln. An increase in the M_S will lower the proportion of liquid at any given temperature and thus impede clinker formation *[8]*. Too high M_S values may ultimately result in slow setting and hardening of the cement *[8]*.

The M_A usually ranges between 1.0 and 4.0 *[5, 8]*. The M_A plays a role in the amount of liquid formed at lower temperatures and relates to the ratio of aluminate to ferrite phases that will form in the clinker *[4, 5]*. Increasing the value of M_A will result in more tricalcium aluminate and less of the ferrite phase forming. In general, if the alumina content is too high, too much of the liquid phase will form. This will prevent proper clinker formation in rotary kilns *[3]*. If the alumina content is too low, not enough of the liquid phase will form, so that higher temperatures will ultimately be needed for the reaction between calcium oxide and silica *[3]*.

2.3 Considerations in the Selection of Reaction Conditions

The conditions for the reactions were chosen to simulate to some extent the burning process in a cement kiln. As discussed in Chapter 1, during the manufacture of cement clinker the raw mix is fed into the cooler end of a rotary kiln and then slowly moves down to higher temperatures. The temperature at the cooler end of the kiln usually ranges between 400 and 900 °C, depending on a variety of factors, while the hotter end usually has a temperature in the range 1350 to 1500 °C *[1, 3]*. An oxidizing atmosphere usually exists in the kiln. As partial melting occurs when the material moves down the kiln to higher temperatures and as the kiln rotates slowly, rounded lumps (nodules) of clinker are normally formed. On moving down the kiln, it can take from forty minutes up to five hours for the mix to finally reach the hottest region where it normally spends up to twenty minutes *[1]*. Usually, the clinker formed in this way is then rapidly cooled in air.

As an additional aid in the selection of appropriate reaction conditions for the preparation of the samples, pure barium carbonate and selected sample mixtures were analysed thermogravimetrically. The thermogravimetric analyses were performed on a Netzsch STA 409 simultaneous TG/DSC analyser. The analyses were done in air and at a constant heating rate of 10 °C.min^{-1}. A platinum sample pan was used and temperature calibration was achieved using the ICTAC recommended DTA standards. The thermogravimetric curves of the analysed samples are shown in Figures 2.1 to 2.6.

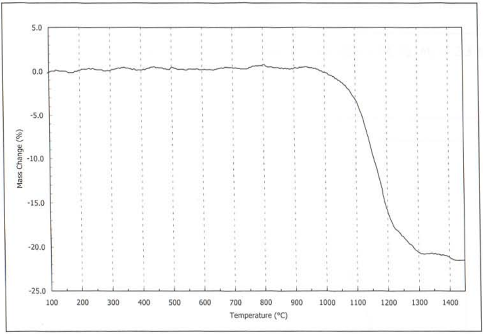

Figure 2.1: Thermogravimetric curve of barium carbonate (witherite)

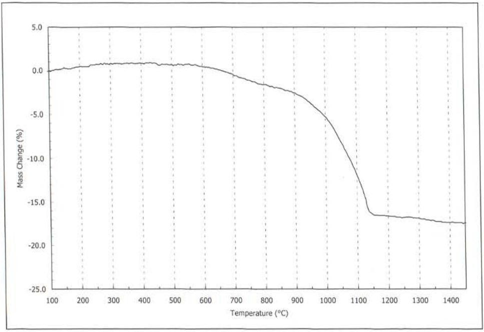

Figure 2.2: Thermogravimetric curve of mixture with BSF = 86 %, M_S = 2.3 and M_A = 1.5.

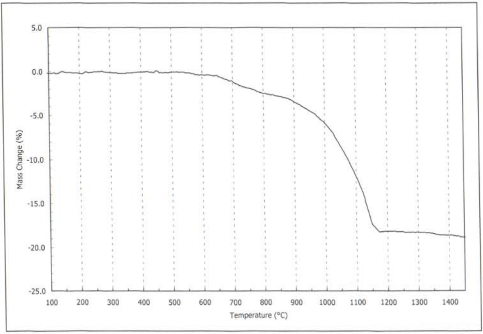

Figure 2.3: Thermogravimetric curve of mixture with BSF = 90 %, M_S = 2.3 and M_A = 1.5.

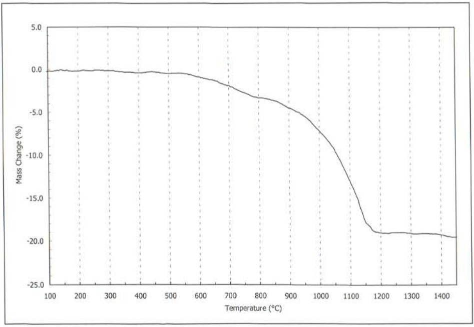

Figure 2.4: Thermogravimetric curve of mixture with BSF = 94 %, M_S = 2.3 and M_A = 1.5.

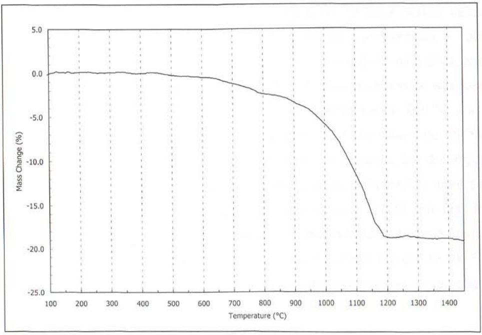

Figure 2.5: Thermogravimetric curve of mixture with BSF = 98 %, M_S = 2.3 and M_A = 1.5.

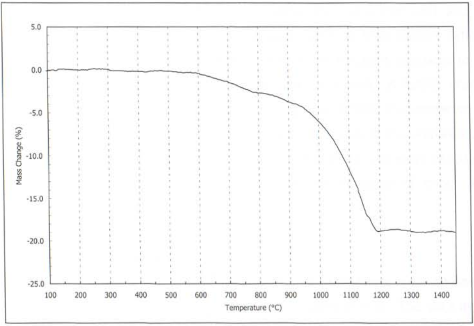

Figure 2.6: Thermogravimetric curve of mixture with BSF = 102 %, M_S = 2.3 and M_A = 1.5.

As can be seen from Figure 2.1, the decomposition of pure barium carbonate started at approximately 950 °C and was complete at a temperature > 1300 °C. From Figures 2.2 to 2.6, it can be seen that in the mixes containing silica, alumina and ferric oxide the decomposition temperature of barium carbonate was lowered. The decomposition in these mixes started at approximately 600 °C and was complete at approximately 1150 °C. It appeared that the lower the BSF of the mixes, the lower the decomposition temperature. In addition, the decomposition reaction took place over a bigger temperature range compared to pure barium carbonate. Furthermore, it can be seen from Figures 2.2 to 2.6 that in the presence of silica, alumina and ferric oxide, the decarbonation of barium carbonate appeared to occur in two stages. The first stage occurred from 600 to 800 °C and the second stage from 800 to 1150 °C. The decarbonation of barium carbonate will be discussed in Chapter 4.

2.4 The Preparative Procedures

The reagents chosen as raw materials for all preparations were laboratory grade barium carbonate (witherite), precipitated silica, alumina (corundum) and ferric oxide. Both the silica and the ferric oxide were shown by X-ray powder diffraction to be amorphous. This should increase the rate of the reactions compared to when the more ordered crystalline forms such as quartz are used. A further important benefit of using precipitated silica instead of quartz is that any unreacted silica should not interfere with the later X-ray diffraction analyses of the prepared clinker samples. Quartz has some very intense reflections, which can easily obscure less intense reflections from other phases, making the detection of minor phases difficult.

2.4.1 The Quaternary Mixes

For this study, the compositions of the quaternary raw mixes were chosen such that the BSF varied between 86 % and 102 % in steps of 4 %. The silica modulus and the alumina modulus were both kept constant in all mixes at 2.3 and 1.5, respectively. The chosen values for the silica and alumina moduli should ensure that a sufficient amount of liquid is formed for the solid state reactions to take place. The mixes with higher BSF values should favour the formation of more barium-rich phases (like tribarium silicate) as compared to the lower BSF mixes, which are expected to have relatively more dibarium silicate. The lower BSF mixes should also be relatively easy to burn and might reach equilibrium sooner.

The quaternary mixes were prepared by carefully weighing off the appropriate amount of each of the reagents and then thoroughly mixing the dry powders to ensure a homogeneous mixture. Before weighing, all raw materials were ground to a suitable fineness to ensure rapid reaction. After grinding more than 85 % of each raw material passed a 90-µm sieve. This agrees well with the fineness requirements for raw meal in the manufacture of Portland cement *[6]*.

After dry mixing, a small amount of water was added to each mix to form a thick moist paste, which was further homogenized using an agate mortar and pestle. An agate mortar and pestle was used, as agate is hard and unlikely to contaminate the mix; it also had a smooth, non-porous surface that was easy to clean. Nodules of approximately 15 mm in diameter of each of the mixes were then made by hand and dried at 100 °C.

After drying, all nodules prepared were placed in platinum boats and burnt at 900 °C for one hour in the homogeneous temperature zone of a tube furnace and then cooled in air. Platinum has a high melting point of ± 1700 °C, which made it suitable as a container for the reactions. Initial burning at a temperature of 900 °C was considered sufficiently high for the decarbonation of barium carbonate to start to take place, but still low enough to prevent too violent decarbonation and possible cracking of the nodules.

After burning at 900 °C, the nodules for each mix were thereafter divided into twenty-one roughly equal parts. These equally divided parts were then burnt at 1000, 1100, 1200, 1300 or 1400 °C for a further 15, 30, 60, or 120 minutes and then rapidly cooled in air. One part was kept aside and not heated further. The method used for the preparation of the nodules is similar to the method used by Johansen and Christensen *[25]*. A schematic diagram of the preparative procedures followed in obtaining the barium clinker samples is given in Figure 2.7.

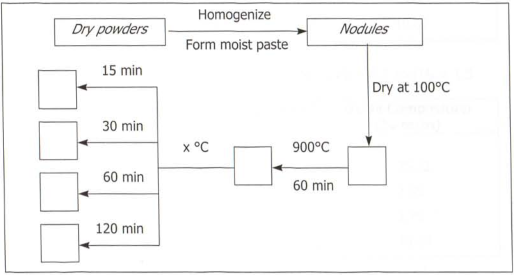

Figure 2.7: Preparation of barium clinker samples; x = 1000, 1100, 1200, 1300 or 1400 °C

The compositions of each of the quaternary raw mixes used in the preparation of the barium clinker samples are given in Tables 2.2 to 2.6.

Table 2.2: Composition of raw mix with BSF = 86 %, M_S = 2.3 and M_A = 1.5

Component	Component Composition (% m/m)	Oxide Composition (% m/m)
$BaCO_3$	87.17	-
BaO	-	84.06
Al_2O_3	2.33	2.90
Fe_2O_3	1.56	1.93
SiO_2	8.95	11.11

Table 2.3: Composition of raw mix with BSF = 90 %, M_S = 2.3 and M_A = 1.5

Component	Component Composition (% m/m)	Oxide Composition (% m/m)
$BaCO_3$	87.67	-
BaO	-	84.66
Al_2O_3	2.24	2.79
Fe_2O_3	1.50	1.86
SiO_2	8.60	10.69

Table 2.4: Composition of raw mix with BSF = 94 %, M_S = 2.3 and M_A = 1.5

Component	Component Composition (% m/m)	Oxide Composition (% m/m)
$BaCO_3$	88.13	-
BaO	-	85.22
Al_2O_3	2.16	2.69
Fe_2O_3	1.44	1.79
SiO_2	8.27	10.30

Table 2.5: Composition of raw mix with BSF = 98 %, M_S = 2.3 and M_A = 1.5

Component	Component Composition (% m/m)	Oxide Composition (% m/m)
$BaCO_3$	88.56	-
BaO	-	85.74
Al_2O_3	2.08	2.59
Fe_2O_3	1.39	1.73
SiO_2	7.98	9.94

Table 2.6: Composition of raw mix with BSF = 102 %, M_S = 2.3 and M_A = 1.5

Component	Component Composition (% m/m)	Oxide Composition (% m/m)
$BaCO_3$	88.96	-
BaO	-	86.22
Al_2O_3	2.01	2.51
Fe_2O_3	1.34	1.67
SiO_2	7.70	9.61

2.4.2 The Binary and Ternary Mixtures

To investigate the reaction products in binary and ternary mixtures containing barium carbonate and alumina and/or ferric oxide or silica, additional sample mixtures were prepared containing these compounds in fixed molar ratios. The molar ratios were chosen to correspond to the molar ratios of each of the barium phases expected to be formed in the quaternary mixtures, based on the findings of Braniski *[23]* as discussed in Section 2.1.

Stoichiometric amounts of barium carbonate, silica, alumina and ferric oxide were weighed off, dry mixed and heated in a platinum boat for two to six hours at 900 °C. The samples were cooled in air, crushed and remixed. The samples were then further heated at higher temperatures as shown in Table 2.7. The samples were intermittently cooled, ground and remixed. Each mix was repeatedly heated until X-ray diffraction showed the mix to contain only one phase. In cases where a mixture of phases persisted even after repeated heating, the heating was stopped after about 500 hours.

Table 2.7: Heat treatment of binary and ternary sample mixtures

Component 1	Component 2	Component 3	Molar Ratio	Temperature (°C)	Time (hours)
$BaCO_3$	SiO_2	-	1:1	1400	120
$BaCO_3$	SiO_2	-	2:1	1400	480
$BaCO_3$	SiO_2	-	3:1	1400	550
$BaCO_3$	Al_2O_3	-	1:1	1200	18
$BaCO_3$	Al_2O_3	-	3:1	1400	40
$BaCO_3$	Fe_2O_3	-	2:1	1000	16
$BaCO_3$	Al_2O_3.	Fe_2O_3	4:1:1	1100	500

2.5 Properties of the Prepared Samples

2.5.1 The Quaternary Mixes

In general, the quaternary raw mixes produced clinker that became gradually darker with an increase in burning time, burning temperature and/or BSF of the mix. The clinker changed from an original light brownish pink colour to a light grey colour after heating at 900 °C for one hour. On further heating, the colour of the clinker gradually varied from a light greyish green to a dark olive-green colour with increase in oven temperature, burning time and BSF of the mix. At a burning temperature of 1200 °C and a burning time of 120 minutes, the clinker samples with BSF values of 94 % or higher acquired almost black colours. All raw mixes produced almost black clinker when burnt for 120 minutes at a temperature of 1300 °C or when burnt for 60 minutes or longer at 1400 °C.

The clinker samples were ground to a suitable fineness for later X-ray diffraction analysis using an agate planetary mill (Fritsch Pulverisette). The time of grinding differed from sample to sample, as the darker samples appeared to be harder than the lighter coloured ones. After grinding the clinker samples the final colours of all the samples were much more similar. The colours varied from a light greyish green colour to a light olive-green colour.

2.5.2 The Binary and Ternary Mixtures

The binary and ternary samples, in general, formed powders that varied in colour. Only the sample mixture with a $BaCO_3$:SiO_2 ratio of 1:1 produced a solid melt that had to be crushed before X-ray diffraction analysis. The appearances of these prepared samples are given in Table 2.8.

Table 2.8: Appearance of binary and ternary samples

Component 1	Component 2	Component 3	Molar Ratio	Appearance
$BaCO_3$	SiO_2	-	1:1	Light grey solid
$BaCO_3$	SiO_2	-	2:1	Light green powder
$BaCO_3$	SiO_2	-	3:1	Brown powder
$BaCO_3$	Al_2O_3	-	1:1	White powder
$BaCO_3$	Al_2O_3	-	3:1	Beige powder
$BaCO_3$	Fe_2O_3	-	2:1	Black powder
$BaCO_3$	Al_2O_3.	Fe_2O_3	4:1:1	Brown-black powder