CHAPTER 5

GENERAL CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

The decarbonation of barium carbonate occurs at reduced temperatures when silica, alumina and ferric oxide are present in the mix. In addition, the decomposition temperature of barium carbonate appears to be affected by the quantities of these oxides in the mix. These findings suggest that a lower BSF value should reduce the kiln temperature required for the manufacture of barium-type cements.

Thermogravimetric studies of the binary systems BaO-SiO$_2$, BaO-Al$_2$O$_3$, BaO-Fe$_2$O$_3$ and ternary systems BaO-SiO$_2$-Al$_2$O$_3$, BaO-Al$_2$O$_3$-Fe$_2$O$_3$ and BaO-SiO$_2$-Fe$_2$O$_3$ should be useful to determine the individual and combined effects of silica, alumina and ferric oxide on the decarbonation of barium carbonate. In addition, X-ray diffraction analysis at various stages of the heating process should be useful to determine the order of formation of the various phases. In this regard, in the ternary system BaO-Al$_2$O$_3$-Fe$_2$O$_3$, it appears that barium oxide is preferentially consumed by ferric oxide.

Unlike uncombined calcium oxide in Portland cement, uncombined barium oxide reacts extremely quickly when exposed to air and could not be detected in any of the prepared samples. When barium oxide is exposed to air, it appears that barium hydroxide forms first and then the carbonate is formed. Determination of the total barium carbonate and barium hydroxide content should therefore be useful to estimate the completeness of the reactions.

In the quaternary samples a variety of barium hydroxides were detected. The number of different hydroxides detected, as well as the extent of hydration of the hydroxides, appeared to depend somehow on the heating time, heating temperature and BSF value of the samples. Factors that affect the formation of the different barium hydroxides need to be investigated further.

Mainly dibarium silicate forms in the quaternary system BaO-SiO_2-Al_2O_3-Fe_2O_3, with a BSF value between 86 and 102 %, at heating temperatures of up to 1400 °C and heating times of up to 120 minutes. Small quantities of monobarium silicate, barium aluminosilicate, monobarium aluminate and tribarium aluminate also form. It is likely that ferric oxide is taken up as an impurity in some of the other phases that form, especially in dibarium silicate and tribarium aluminate.

In the binary system BaO-SiO_2, tribarium silicate forms in addition to dibarium silicate. On the other hand, no evidence could be found for the formation of tribarium silicate in the quaternary system BaO-SiO_2-Al_2O_3-Fe_2O_3 under the chosen reaction conditions. The prepared quaternary samples all contained significant quantities of unreacted barium carbonate, so that at least some tribarium silicate was expected to form. This observation agrees with the findings of Boikova et al. *[19]*, who doubted the existence and stability of tribarium silicate under normal clinkering conditions, but it contradicts the findings of Braniski *[23]*. According to Braniski, tribarium silicate forms in the quaternary system in the temperature range 1000 to 1400 °C (see Chapter 2).

The barium saturation factor (BSF) as described and defined in Chapter 2 cannot be employed like the lime saturation factor (LSF) in the manufacture of Portland cement. The LSF is a measure of the amount of CaO that can be combined (see Chapter 2). The BSF definition in Chapter 2 was based on the assumption that the phases formed in the system BaO-SiO_2-Al_2O_3-Fe_2O_3 will be analogous to that formed in the system CaO-SiO_2-Al_2O_3-Fe_2O_3. In particular, it was assumed that tribarium silicate does form and will exist at equilibrium in the quaternary system.

In the binary sample with BaO:SiO_2 in a 3:1 molar ratio, which were heated for 550 hours at a temperature of 1400 °C, a number of peaks in the diffractogram could not be resolved using the data sets from the 1995 Powder Diffraction File-2 (Set 45), release A6.

It is suspected that these peaks are due to the presence of a barium-rich silicate phase(s) with $BaO:SiO_2 > 3:1$ (see Chapter 3), but this needs to be investigated further.

Plots of the intensity ratio of the peaks at $2\theta = 29.585°$ and $2\theta = 23.901°$ in the diffractograms of the quaternary samples, with heating time and heating temperature for the different BSF values, proved to be useful to estimate the extent to which the reaction between barium carbonate and silica had proceeded to yield dibarium silicate. The heating time is very important at heating temperatures of up to 1200 °C, so that a longer heating time is required for the reaction to complete at these temperatures. At heating temperatures of 1300 °C and higher, the heating time is less important, so that a shorter heating time is required for the reaction to complete. It seems that the samples with the highest BSF values, especially the ones that are heated for longest, reach a maximum value for the intensity ratio at a heating temperature of 1300 °C. It is unclear why the ratio decreases again in some of the samples after reaching this maximum value and needs to be investigated further. Furthermore, in order to improve the accuracy of this intensity ratio, the total unreacted barium oxide, in the form of barium carbonate and barium hydroxide, should be determined and used to calculate new ratios. Any measures that can be taken to reduce any possible preferred orientation during X-ray diffraction analysis should also improve the accuracy of the ratio.

The raw materials used during this study did not contain impurities such as the alkali oxides and magnesium oxide often found in the raw materials used for the manufacture of Portland cement. The effects of these and other "impurities" on the formation and stability of the various barium-phases still need to be investigated.