

**X-Ray diffraction study of high temperature reaction products in the
barium oxide-silica-alumina-ferric oxide system**

by

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SUMMARY

**X-Ray diffraction study of high temperature reaction products in the
barium oxide-silica-alumina-ferric oxide system**

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Chemistry Department of the University of Pretoria

Submitted in partial fulfilment of the requirements for the degree

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The ever-increasing environmental pollution and the fast depletion of fossil fuels have contributed to the need to find suitable ways to reduce the energy consumption in the manufacture of Portland cement. Substantial savings in this regard in the manufacturing process can be achieved if more belite and less alite are necessary to produce a cement of good quality. To allow for more belite and less alite in the cement, the reactivity of the belite phase has to be increased. The addition of small quantities of barium to the raw mix is said to increase the reactivity of the belite phase. This study was initiated to obtain a better understanding of the reaction products that can be expected in systems containing combinations of barium oxide, silica, alumina and ferric oxide under similar reaction conditions as used in the manufacture of normal Portland cement.

After careful consideration, binary, ternary and quaternary samples were prepared containing different proportions of barium carbonate, silica, alumina and ferric oxide. In the case of the quaternary samples, the silica modulus and alumina modulus were kept constant at 2.3 and 1.5, respectively, while the "barium oxide saturation factor" was chosen to be 86, 90, 94, 98 or 102 %. The quaternary samples were burnt in air under varying conditions of heating time and temperature to simulate the clinkering process in the manufacture of Portland cement.

The crystalline phases that formed under various conditions in the samples were determined by means of XRD analysis. XRD analysis proved to be a useful tool to determine the effects of heating temperature, heating time and mix composition on the formation of some of the phases. Some of the contradictory statements found in the literature were discussed as well as the trends observed in the ratio of dibarium silicate to barium carbonate in the samples. The hydration and carbonation of barium oxide were also discussed with the aid of the diffractograms.

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Voorgeleë ter vermelding van 'n deel van die vereistes vir die graad

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Die toenemende omgewingsbesoedeling en uitputting van bronne van die byvoegingsmiddels om variëte te vind om die energieverbruik tydens die vervaardiging van Portlandsement te verminder. Aansienlike besparings in hitte verbruik wat bereik word indien meer dikalsiumsilikaat en minder trikalsiumsilikaat benut word om 'n sement van goeie gehalte te vervaardig. Om vir 'n groter hoeveelheid dikalsiumsilikaat voorsiening te maak, is dit nodig om die reaktiwiteit van hierdie fase te verhoog. Daar is aanduidings dat die byvoeging van klein hoeveelhede barium tot die grondstofmengsel van die sement die reaktiwiteit van die dikalsiumsilikaatfase verhoog. Hierdie studie het ontstaan uit die behoefte om 'n beter begrip te verkry van die reaksieprodukte wat verwag kan word in sisteme wat bariumoksied, silika, aluminiumoksied en ysteroksied bevat, onder reaksietoestande soortgelyk aan wat gebruik word tydens die vervaardiging van gewone Portlandsement.

Na droëlike oorweging, is twee-, drie- en vierledige monsters met verskillende hoeveelhede van bariumkarbonaat, silika, aluminiumoksied en yster(III)oksied voorberei. In die geval van die vierledige monsters was die sliken modulus en die aluminiumoksiedmodulus konstant gehou op 2,3 en 1,5, onderskeidelik, terwyl die bariumversadigingsfaktor 86, 90, 94, 98 of 102 % was. Die vierledige monsters is verhit

SAMEVATTING

X-straaldiffraksiestudie van die hoë-temperatuurreaksieprodukte in die bariumoksied-silika-aluminiumoksied-ysteroksiedsisteem

Heinrich Schmidt

Studieleier: Professor CA Strydom

Departement Chemie van die Universiteit van Pretoria

Voorgelê ter vervulling van 'n deel van die vereistes vir die graad
Philosophiae Doctor

Die toenemende omgewingsbesoedeling en uitputting van brandstowwe dra by tot die behoefte om maniere te vind om die energieverbruik tydens die vervaardiging van Portlandsement te verminder. Aansienlike besparings in hierdie verband kan teweeggebring word indien meer dikalsiumsilikaat en minder trikalsiumsilikaat benodig sou word om 'n sement van goeie gehalte te vervaardig. Om vir 'n groter hoeveelheid dikalsiumsilikaat voorsiening te maak, is dit nodig om die reaktiwiteit van hierdie fase te verhoog. Daar is aanduidings dat die byvoeging van klein hoeveelhede barium tot die grondstofmengsel van die sement die reaktiwiteit van die dikalsiumsilikaatfase verhoog. Hierdie studie het ontstaan uit die behoefte om 'n beter begrip te verkry van die reaksieprodukte wat verwag kan word in sisteme wat bariumoksied, silika, aluminiumoksied en ysteroksied bevat, onder reaksietoestande soortgelyk aan wat gebruik word tydens die vervaardiging van gewone Portlandsement.

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onder wisselende toestande van verhitings temperatuur en -tydsduur om die klinkeringsproses tydens die vervaardiging van Portlandsement na te boots.

CHAPTER 1

Die kristallyne fases wat onder verskillende omstandighede in die monsters gevorm het is by wyse van X-straaldiffraksie-analise bepaal. X-straaldiffraksie-analise was nuttig om die invloed van verhitings temperatuur, -tyd en monstersamestelling op die vorming van sommige van die fases te bepaal. Sommige van die teenstrydige stellings wat in die literatuur voorkom is bepreek, asook die verhouding van dibariumsilikaat tot bariumkarbonaat in die monsters. Die hidrasie en karbonasie van bariumoksied is ook bespreek met behulp van die diffraktogramme.

1.2 Considerations on the Reactivities of Clinker Phases

1.3 Stabilization of High Temperature Polymorphs of Dicalcium Silicate

1.4 Barium in Portland Cement

1.5 Objectives of this Study

1.1 Background on Portland Cement

1.1.1 Definition and History of Cement

The name cement dates back to the Romans, who called concrete-like mixtures made from stones and a burnt lime binder "opus caementitium". Later additions such as ground bricks and volcanic ash, which were mixed with burnt lime to form a hydraulic binder, were given the names cementum, cement, caement, and cement. The term cement is used today to designate many different types of substances that are used as binders or adhesives.

Portland cement is a hydraulic cement, i.e. when mixed with water, it sets and hardens by hydration. After hardening, it does not disintegrate in water. Modern Portland cement originated in Britain in the nineteenth century, when high temperatures were first used in the preparation of cements. The name derives from the similarity in colour and appearance to Portland stone, found on the channel coast of the Portland peninsula in Dorsetshire, England (1, 2). Portland cement is the cement produced in the greatest volume and is most widely used in