Pergamon

Cement and Concrete Research, Vol. 26, No. 9, pp. 1399-1408, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in the USA. All rights reserved
0008-8846/96 $15.00 + .00

PII S0008-8846(96)00117-2

AUTOCLAVED CEMENT-QUARTZ PASTES: THE EFFECTS ON CHEMICAL AND PHYSICAL PROPERTIES WHEN USING GROUND QUARTZ WITH DIFFERENT SURFACE AREAS
PART I: QUARTZ OF WIDE PARTICLE SIZE DISTRIBUTION

Danielle S. Klimesch[a,b] **Abhi Ray**[b] **and Brian Sloane**[a]
[a]James Hardie & Coy Pty Limited, 1 Grand Avenue, Camellia, P.O. Box 219, Granville,
Sydney, NSW, 2142 (Australia)
[b]Department of Materials Science, University of Technology, Sydney, P.O. Box 123,
Broadway, Sydney, NSW, 2007 (Australia)

(Refereed)
(Received January 29, 1996; in final form June 19, 1996)

ABSTRACT

The effects of different surface area of ground quartz in 24 hour precured and autoclaved cement-quartz pastes, at C/S of 0.5, were investigated. Portlandite production and calcium silicate hydrate formation increased during precuring in the presence of ground quartz, while the compressive strength increased with increasing quartz surface area. Autoclaving for 8 hours at 177°C under saturated steam yielded calcium silicate hydrates, belonging to the tobermorite group, of decreasing crystallinity with increasing surface area of quartz. The drying shrinkage increased with increasing surface area of quartz corresponding with the decrease in crystallinity of the binder, while the compressive strength reached an optimum value at a quartz surface area comparable to that of the cement used.

Introduction

It is well known that many physical properties of cement and/or lime based products are enhanced by autoclaving (high pressure steam curing) and this has generally been attributed to the formation of more crystalline, low lime phases when compared to the presence of gel-like phases in products cured at ambient temperatures [1]. The benefits of autoclaving include a permanent high early strength equivalent to that of 28 day moist cured strength, lower moisture content after manufacture, a reduction in drying shrinkage and carbonation rate and consequently carbonation shrinkage [2-6]. Drying shrinkage is related to the crystallinity of the calcium silicate hydrate binder and is known to decrease with increasing crystallinity of the latter, while the compressive strength increases up to an optimum value [7]. Early experience in making autoclaved cement based materials showed that the presence of siliceous material of a sufficiently reactive nature was essential for satisfactory strength [8]. Autoclaving cement with finely ground quartz (quartz additions greater or equal to about 30% [9]) prevents the formation of portlandite, $Ca(OH)_2$, and results in the formation of "stable" calcium silicate hydrate C-S-H(I) [10], which is closely related to the natural mineral 11.3 Å tobermorite discovered by Heddle in 1880 [11]. In low-density autoclaved products, such as aerated concrete, tobermorite has been widely found to be the major constituent of the binder [12-15]. In denser materials, such as calcium silicate bricks, crystallisation of calcium silicate hydrates to give tobermorite is apparently minimal [16].

For moulded samples, the reaction between cement and quartz is mainly controlled by diffusion of silica through the product formed on the surfaces of the quartz particles [17,18]. For constant C/S and water/solids ratio and hydrothermal treatment, parameters which influence the kinetics are the particle size distribution of the silica, represented by the specific surface area, and the degree of crystallinity of the silica used [19]. It is known that the surfaces of silica gels and quartz are covered with acidic Si-OH groups [20]; in the presence of a strong base, such as $Ca(OH)_2$, their dissociation results in the formation, nucleation and precipitation of C-S-H phases, via a complex series of reactions. Greenberg [21] concluded that the rate determining step in the over-all lime/silica reaction was the rate of solution of silica and that this was proportional to the surface area of the latter, whereas other workers found evidence that the overall reaction was diffusion controlled [22]. Kennedy [23] concluded from his measurements in the hydrothermal temperature range that quartz is essentially insoluble at ambient temperature, whereas amorphous silica displays a sufficiently high dissolution rate. In a finely divided form, after ball mill grinding, for example, quartz is reactive because of a "disturbed" surface layer which has a thickness of approximately 0.11 to 0.15 microns [24], and even up to 2 microns [25]. A combination of cracks, dislocations and protruding edges seems to disturb the original quartz structure in such a way as to cause abnormally high dissolution rates of the quartz in water and alkaline solutions [20]. Various authors have come to similar conclusions [26-28].

These studies are part of an investigation to further elucidate the effects of surface area/ article size of ground quartz on various chemical and physical properties pertaining to autoclaved cement:quartz pastes, and relating these to the durability of commercially available autoclaved building products. The study presents the result of investigations on 24 hour precured and subsequently autoclaved cement:quartz pastes using ground quartz of different surface areas with a wide particle size distribution.

Experimental

Starting Materials. Ground quartz of various grades from Ballarat, Victoria, supplied by Commercial Minerals and type A Ordinary Portland cement from Blue Circle Southern Portland Cement, Berrima Works, NSW, were used in this study. Fig.1 depicts the particle size distribution by sedimentation, provided by the supplier. The major chemical and physical properties of the starting materials are listed in Table 1.

Sample Preparation. The raw mixtures used were 47.5% cement and 52.5% ground quartz, (C/S = 0.5), using a different grade for each mixture. Water to total solids ratio was 0.35 for all mixes, using deionised water. In addition 2 mixtures were made with cement only, one set of samples was water cured for 28 days and the other autoclaved as set out below. Mechanical mixing was conducted in accordance with ASTM C 305-82 except that the final mixing at medium speed was extended to 2 min. Pastes were cast into moulds and consolidated on a vibratory table, followed by a 24 hour curing period in a moist cabinet, (23 ± 1.7^{c} C, 95% relative humidity as per ASTM C 511-85). Demoulded samples were cut into ap-

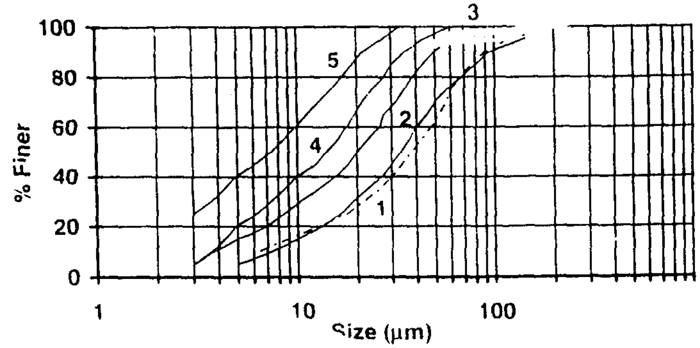

FIG. 1.
Particle size distribution by sedimentation for ground quartz used. 1 = 60G, 2 = 100G, 3 = 200G, 4 = 300G and 5 = 400G.

proximately 13 mm cubes and 90 mm long prisms, and were autoclaved for 12 hours of which 8 hours was at 177°C under saturated steam, followed by drying at 103°C for 24 hours. Samples for precure evaluation were also dried at 103°C for 24 hours.

Physical and Chemical Testing. Precured and subsequently autoclaved cement and cement-quartz pastes, were analysed using a TA-instruments SDT 2960 simultaneous DTA/TGA analyser at a heating rate of 10°C/min to 1100°C under flowing nitrogen (100ml/min). Details of the data analyses using computer software have been given elsewhere [29]. X-ray diffraction (XRD) analysis was conducted on autoclaved specimens using a Siemens D5000 using copper $K_{\alpha 1}$ radiation from 5 to 50° 2θ at 0.02° 2θ per sec. XRD patterns were smoothed, background corrected, $K_{\alpha 2}$ stripped and corrected for instrumental drift.

The amount of acid-insoluble residue, AIR, of disc milled precured and autoclaved samples was used as a measure of the unreacted quartz content according to the method described by Crennan et al. [31]. Samples were analysed in triplicate. A minimum of 7 precured and autoclaved cubes were tested for compressive strength after cooling oven dried samples over silica gel and soda lime in a desiccator. The bulk density of each autoclaved cube was determined by weight and volume measurement prior to the compressive strength

TABLE 1
Main Physical and Chemical Properties of Type A Ordinary Portland Cement and Ground Quartz

Ground Quartz Type	Blaine Surface Area (cm^2/g)	% SiO_2	Major Oxides in Cement (%)		Potential Compound Composition (%)	
60G	2200	99.0	CaO	64.4	C_3S	60
100G	2600	99.0	SiO_2	21.1	C_2S	15
200G	3600	99.0	Al_2O_3	4.15	C_3A	3
300G	5200	99.0	Fe_2O_3	4.60	C_4AF	14
400G	6750	99.0	SO_3	2.60		
cement	3550		MgO	1.14		

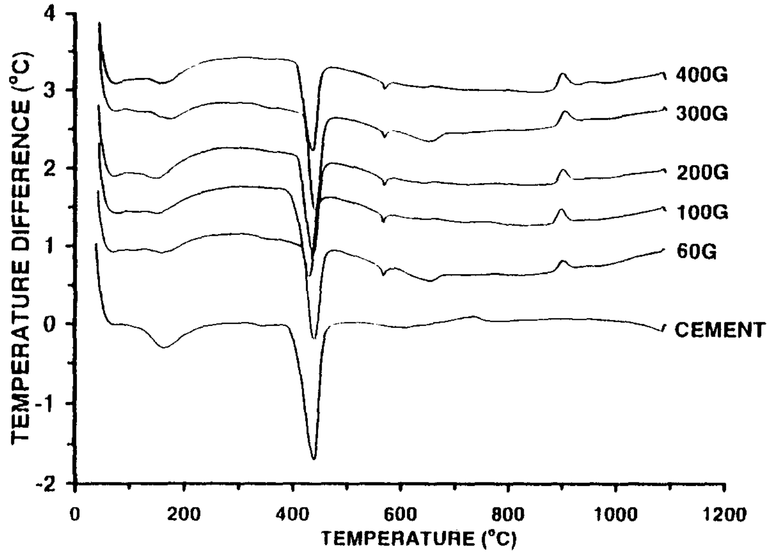

FIG. 2.
DTA curves for 24 hour precured cement and cement-ground quartz pastes.

tests. Drying shrinkage on autoclaved and water cured prisms was determined as per ASTM C 426-70 with modifications as follows: samples were dried at 103°C; a special jig was used to accommodate the prisms; length measurements were made using a Mitutoyo Digimatic Indicator measuring to 0.0001 inches.

Results and Discussion

Differential Thermal Analysis, XRD and Acid-Insoluble Residue. DTA curves for 24 hour precured cement and cement-quartz pastes are depicted in Fig. 2. The results show that after

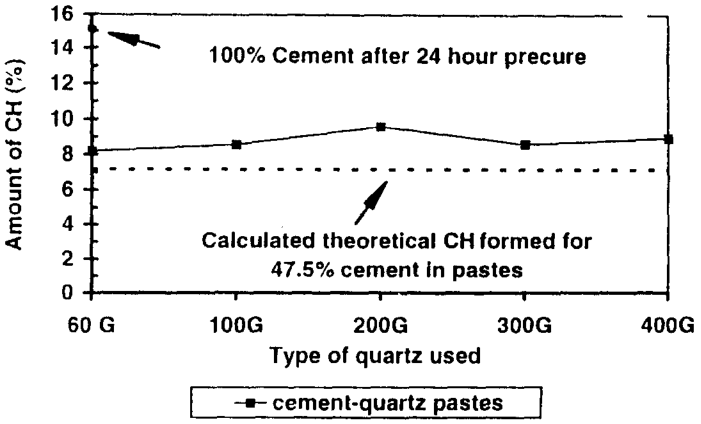

FIG. 3.
Amounts of CH formed in 24 hour precured cement-ground quartz pastes.

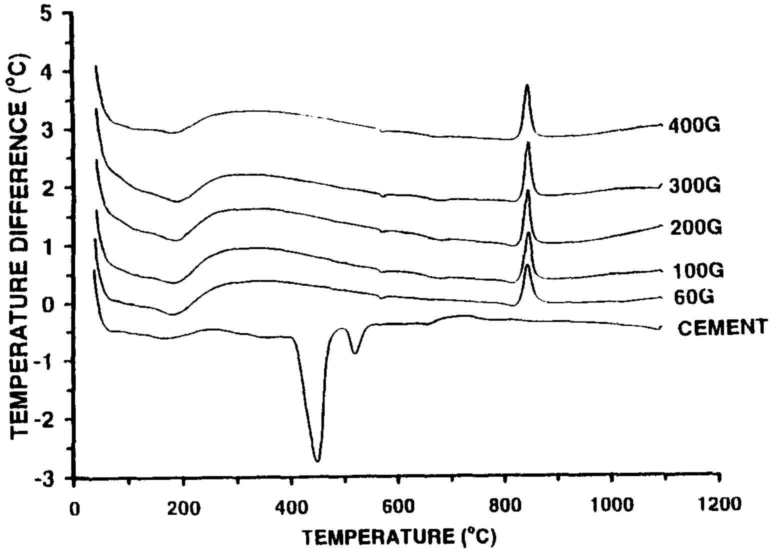

FIG. 4.

DTA curves for autoclaved cement and cement-ground quartz pastes.

the 24 hour precure, in the presence of ground quartz, both CH and C-S-H phase(s) had formed, indicated by an endotherm ~ 440°C and exotherm ~ 900°C, respectively. No such exotherm was apparent for the 100% cement paste. The small endotherm at 571°C is due to the α-β transition in quartz. The presence of C-S-H phase or gel in the cement paste, referred to as phase X in earlier studies [9], is manifested by the broad endotherm around 150°C. AFm and AFt phases may also contribute to this broad endotherm [9,30]. From TGA % weight loss determinations, 15.1 % CH was produced for cement paste, theoretically then 47.5% cement present in the mixtures should produce 7.2 % CH. The amounts of CH produced in the presence of ground quartz are depicted in Fig. 3. The results indicate that in the presence of ground quartz CH production and C-S-H phase formation were enhanced when compared to cement alone. These findings may be explained by considering the surfaces of the ground quartz particles as "nucleating agents", possessing cell-size domains of about the same size as that of the solid to be nucleated [2], here C-S-H phase(s) and CH.

Quartz surfaces may become a substrate on which nucleating points can form, as discussed by Moorehead et al. [22]. The number of nucleating points would then be proportional to the surface area of the ground quartz. Alternatively, the quartz may have "solubilised" during the precure which would then support the presence of a "disturbed" surface layer, i.e. an amorphous surface layer of lower stability and higher reactivity [32]. It must be noted, however, that in pastes the reactions between cement and ground quartz are mainly diffusion controlled [17,18]. The apparent drop in CH production with the 300G and 400G quartz compared with the 200G, as depicted in Fig. 3, may have been due to agglomeration in the raw materials, and could have resulted in a smaller total available surface area than indicated by the Blaine results. The quartz was not sieved prior to the paste making so that some agglomeration in the finer material was possible. Alternatively, the results may indicate that the 200G grade quartz was of optimum surface area, i.e. had the optimum particle size distribution, for enhancing CH production and C-S-H phase formation.

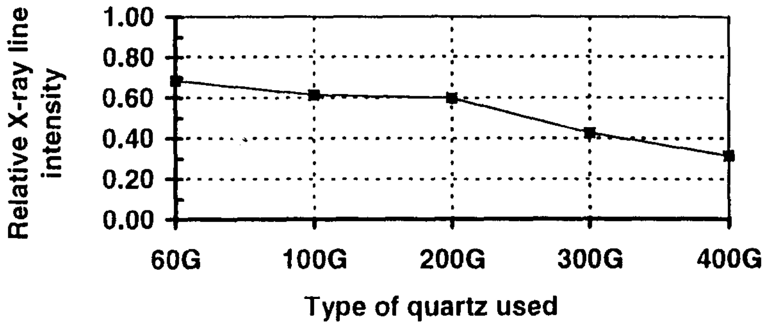

FIG. 5.

Ratio of relative 2.97/3.07 Å X-ray line intensities of the binder in autoclaved cement-ground quartz pastes.

Wczelik [33], in his studies of the effect of active SiO_2 (Aerosil) in hydrating tricalcium silicate suspensions, found that the SiO_2 "stimulated" CH nucleation and growth, while Beradi et al. [34] demonstrated the positive influence of ground quartz on the degree of tricalcium silicate hydration during precuring and subsequent autoclave treatment. Results for autoclaved samples (Fig. 4) indicate the following:

- The main phases in the autoclaved cement pastes are CH and α-C_2S hydrate, represented by endotherms at 453°C and 523°C respectively.
- All autoclaved cement-quartz mixtures contain unreacted quartz (endotherm at 571°C).
- The dehydration of C-S-H phases is manifested by the broad endotherm between 100-300°C.
- The exotherm exhibited by all autoclaved cement-quartz samples at about 845°C, marking the crystallisation to wollastonite (β-CS) is due to C-S-H(I) of C/S ratio of 0.8-1.0 or aluminous tobermorite [2], or both. Pure C-S tobermorite does not show this exotherm [30].

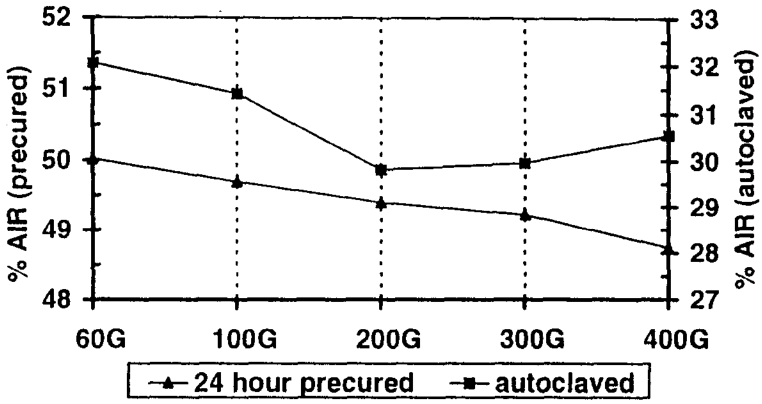

FIG. 6.

Percent acid-insoluble residue (AIR) for 24 hour precured and autoclaved cement-ground quartz pastes.

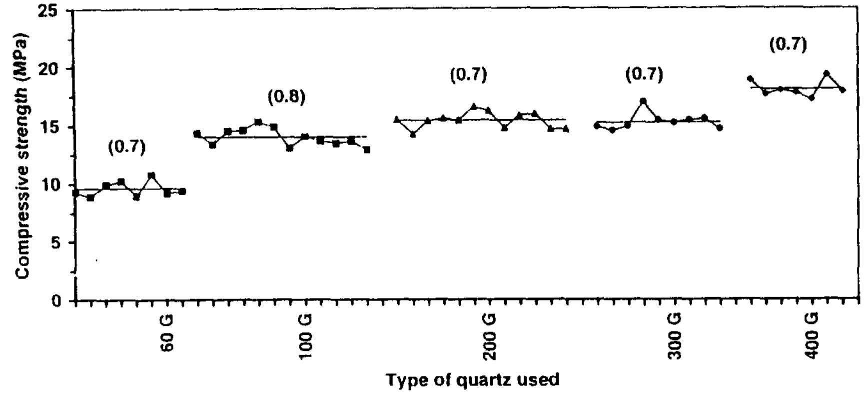

FIG. 7.
Compressive strength for 24 hour precured cement-quartz cubes.

Overall, DTA results indicate slight variations in peak height for the exotherms with no other "apparent" differences in the binder formed when using ground quartz of different surface area.

From XRD analysis, the main phases in all the specimens were found to belong to the tobermorite group of calcium silicate hydrates, C-S-H's. The d-spacing for the low-angle tobermorite was present in all samples, however, for the sample made with 400G quartz it was hardly discernible. According to Kalousek [2] the ratio of intensities of the 2.97/3.07Å lines can be used to differentiate between Taylor's C-S-H(I), (intensity ratio = 0), and tobermorite (ratio = 0.7-0.8). He also noted that partial transformation of the latter into xonotlite causes a drop of this ratio to 0.5 or less; as no xonotlite was found in any of the samples, the ratios of relative intensities are depicted in Fig. 5. The findings suggest that with increased quartz surface area the binder became less crystalline and more C-S-H(I)-like in character, for autoclaving conditions employed in these studies. These results are in accordance with the findings of Isu et al. [36] in their studies of autoclaved aerated concrete

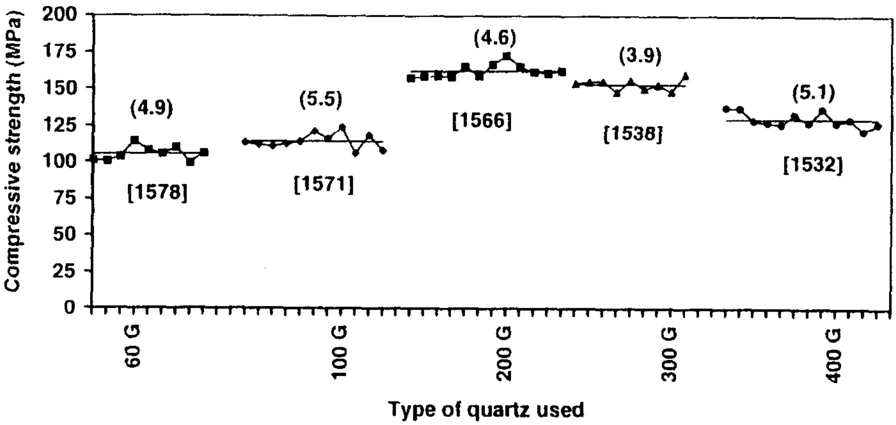

FIG. 8.
Compressive strength for autoclaved cement-quartz cubes.

using quartz of different particle sizes. The tobermorite formed using the finer quartz was of lower crystallinity than that using the coarser quartz, based on crystallite size determinations.

Fig. 6 depicts the results for the acid-insoluble residue (AIR) determinations for precured and autoclaved samples. The AIR for precured specimens was found to decrease slightly with increasing quartz surface area suggesting that more became solubilised during precuring, thus a greater reaction conversion of quartz to produce primary reaction products. The assumption that the reagents used to determine the uncombined or acid-insoluble residue attack the C-S-H phases and not the quartz may not be strictly true but is unlikely to be grossly in error [37]. For autoclaved samples the trend was found to be different, decreasing slightly and increasing again for the finer quartz used. The lowest AIR corresponded to the quartz surface area which also yielded the highest compressive strength. The slight increase in the AIR, when the finer quartz was used, suggests that the degree of reaction was lower during autoclaving possibly due to more primary product having formed during precuring, and retarding the subsequent diffusion controlled reactions during autoclaving. Isu et al. [36] had come to similar conclusions.

Compressive Strength, Bulk Density and Drying Shrinkage. Results for the compressive strength for 24 hour precured and autoclaved samples are depicted in Figs. 7 and 8, respectively. The numbers in brackets ( ) and [ ], correspond to standard deviations and average bulk densities respectively.

The results show increasing strength with increasing quartz surface area for the precured samples, suggesting enhanced cement hydration and thus more "primary" product formation, as indicated by TG results and AIR determinations. Increased formation of CH and C-S-H phase(s) are accompanied by a reduction in unreacted quartz, suggesting increased reaction conversion of quartz during precuring.

For autoclaved mixtures, the compressive strength was found to be highest for the 200G quartz and compares well with earlier findings that for each degree of fineness of quartz, there exists a certain C/S ratio which will produce optimum strength [38]. In these studies the optimum surface area of ground quartz was 3600 cm^2/g at a C/S = 0.5 and was comparable to that of the cement used, i.e. 3550 cm^2/g. Autoclaved cement was found to be of lower

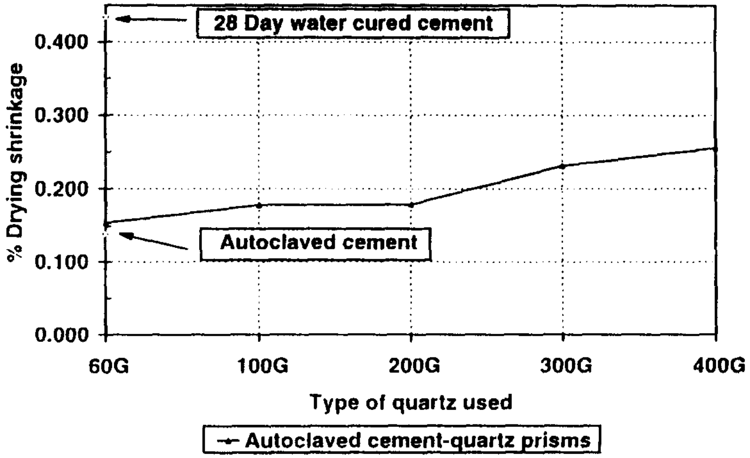

FIG. 9.
Percent drying shrinkage for autoclaved cement-quartz prisms.

strength (99 MPa) than any of the cement-quartz mixtures. Bulk densities decreased the finer the ground quartz used and agree with the findings by Crennan et al. [31]. The results for the drying shrinkage are shown in Fig. 9.

The drying shrinkage was found to increase with the fineness of the ground quartz. Comparing these results with the ratio of relative X-ray intensities of the 2.97/3.07Å lines, clearly demonstrates the relationship between the crystallinity of the binder and the drying shrinkage, more "C-S-H(I)-like in character" meaning less crystalline. The less crystalline the binding material the more it tends to shrink. The results are in accordance with the findings of Alexanderson [7]. It is interesting to note that the drying shrinkage was found to be lowest for the autoclaved cement paste; this may perhaps be explained by the presence of α-C_2S hydrate. Taylor [37] noted that products containing xonotlite or α-C_2S hydrate were found to have lower drying shrinkages than those containing 11 Å tobermorite. The drying shrinkage for 28 day water cured prisms was found to be almost double that for autoclaved mixtures, highlighting the advantages of autoclaving over curing at ambient temperature.

Conclusions

From this study we conclude:

1. The presence of ground quartz in cement paste enhanced CH production and C-S-H phase formation during 24 hours of precuring, possibly by acting as a nucleating agent and/or by having "solubilised" during the precure.
2. The strength of 24 hour precured cement-ground quartz mixtures was found to increase with increasing surface area of ground quartz.
3. The main phases in autoclaved cement-ground quartz mixtures belonged to the tobermorite group of calcium silicate hydrates with the binder being less crystalline with increasing surface area of ground quartz used. The present results show tobermorite in a dense material.
4. XRD was found to be more sensitive than DTA in identifying differences between the phases formed.
5. Drying shrinkage of cement-ground quartz mixtures was found to increase with increasing surface area of quartz. This correlated with the decrease in crystallinity of the binder with increasing surface area of the ground quartz.
6. Compressive strength of autoclaved cement-ground quartz mixtures increased up to an optimum value and then decreased. The optimum strength corresponded to a ground quartz surface area comparable to that of the cement at a C/S ratio of 0.5.

The determination of carbonation shrinkage for all autoclaved and water cured prisms is currently being carried out. Current studies are also conducted using ground quartz of narrow size distribution, to eliminate possible opposing factors of surface area and particle size distribution, and to further elucidate the effects of ground quartz during precuring and autoclaving in cement-ground quartz pastes.

Acknowledgments

We thank James Hardie & Coy Pty. Ltd. of Australia for their financial support to D.S. Klimesch during her postgraduate studies.

References

1. G.L. Kalousek, Proc.3rd Int. Symp. Chem. Cement, London, 334 (1952).
2. G.L. Kalousek, 5th Int. Symp. Chem. Cement, Tokyo, 3, 523 (1968).
3. G.W. Washa, ACI Journal, August 869 (1965).
4. L.R. Baker and E.L. Jessop, Int. J. Concrete Masonry Construction, 2, 75 (1982).
5. S. Baozhen and S. Erda, Chem. Abs., 102, 136737c (1985).
6. F.H. Wittmann, Autoclaved Aerated Concrete, Moisture and Properties, p. 209, Elsevier, Amsterdam (1983).
7. J. Alexanderson, Cem. Concr. Res., 9, 507 (1979).
8. H.F.W. Taylor, Cement Chemistry, p. 367, Academic Press Inc., New York (1990).
9. G.L. Kalousek and M. Adams, ACI Journal, 77 (1951).
10. E.R. Cantrill, M.G. Stevens, A. Ray and L. Aldridge, Thermochim. Acta, 224, 241 (1993).
11. M.F. Heddle, Mineral. Mag., 4, 119 (1880).
12. T. Mitsuda, K. Sasaki and H. Ishida, J. Am. Ceram. Soc., 75, 1858 (1992).
13. T. Mitsuda, T. Kiribayashi, K. Sasaki and H. Ishida, Advances in Autoclaved Aerated Concrete, p. 11, edited by F.H. Wittmann. Balkema, Rotterdam, Netherlands (1992).
14. T. Mitsuda, K. Sasaki and H. Ishida, see Ref. 13, p. 19.
15. N. Isu, S. Teramura, K. Ido and T. Mitsuda, see Ref. 13, p. 27.
16. H.F.W. Taylor, see Ref. 8, p. 367.
17. R. Kondo, Autoclaved Calcium Silicate Building Products, p. 92, Society of Chemical Industry, London, England (1967).
18. S.O. Oyefesobi and D.M. Roy, Cem. Concr. Res., 7, 95 (1977).
19. H. Mörtel, abstract for MICRO '76, p.12.
20. J.A. van Lier, P.L. deBruyn and J.Th.G. Overbeek, J. Phys. Chem., 64, 1675 (1960).
21. S.A. Greenberg, J. Phys. Chem.,65, 12 (1961).
22. D.R. Moorehead and E.R. McCartney, J. Am. Ceram. Soc., 48, 565 (1965).
23. G.C. Kennedy, Econ. Geol., 45, 629 (1950).
24. K.M. Alexander, ACI Journal, 557 (1960).
25. R.K. Iler, The Chemistry of Silica, p. 30, John Wiley & Sons, New York (1979).
26. P.B. Dempster and P.D. Ritchie, Nature, London, 169, 538 (1952).
27. P.B. Dempster and P.D. Ritchie, J. Appl. Chem., 3, 182 (1955).
28. D.W. Clelland, W.M. Cumming and P.D. Ritchie, J. Appl. Chem., 2, 31 (1952).
29. D.S. Klimesch and A.Ray to be published in Thermochim. Acta.
30. H.F.W. Taylor, see Ref. 8, p. 176, 207.
31. J.M. Crennan, S.A.S. El-Hemaly and H.F.W. Taylor, Cem. Concr. Res., 7, 493 (1977).
32. R. Kondo and M. Daimon, J. Am. Ceram. Soc., 52, 503 (1969).
33. W.N. Wczelik, Thermochim. Acta, 93, 565 (1985).
34. M.C. Beradi, G. Chiocchio and M. Collepardi, Cem. Concr. Res., 5, 481 (1975).
35. G.L. Kalousek, J. Am. Ceram. Soc., 40, 74 (1957).
36. N. Isu, H. Ishida and T. Mitsuda, Cem. Concr. Res., 25, 243 (1995).
37. H.F.W. Taylor, Autoclaved Calcium Silicate Building Products, p.200, Society of Chemical Industry, London, England (1967).
38. W.H. Taylor and D.R. Moorehead, Mag. Concr. Res., 8, 145 (1956).