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# AUTOCLAVED CEMENT-QUARTZ PASTES: THE EFFECTS ON CHEMICAL AND PHYSICAL PROPERTIES WHEN USING GROUND QUARTZ WITH DIFFERENT SURFACE AREAS PART II: RESULTS OF ACCELERATED CARBONATION

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## ABSTRACT

Previously saturated and oven dried, autoclaved cement-quartz prisms, made with quartz of varying fineness,were exposed to carbon dioxide for 24 hours. The extent of carbonation and drying shrinkage, as well as the degree of cracking were found to increase with increasing surface area of quartz. The binder became progressively more like $SiO_2$-gel in character. Thermal analysis revealed both low- and high-temperature decarbonation steps, the mass loss increasing, in both decarbonation steps, with the surface area of quartz used. Difficulties encountered in interpreting the results, attributed to a multiplicity of factors involved, are highlighted. © *1997 Elsevier Science Ltd*

## Introduction

Atmospheric carbon dioxide ($CO_2$) is known to react with the hydration products of both air-cured and autoclaved materials (1). The kinetics of carbonation depend on the relative humidity (RH) of the environment, among other factors, with maximum carbonation occurring at RH of 40-80% (2). One of the main consequences of carbonation in air-cured concrete is the drop of pH of the pore solution, resulting in destabilization of the passive layer that usually covers and protects the reinforcing steel against corrosion (3). Reactions with $CO_2$ are not confined to calcium hydroxide [$Ca(OH)_2$] alone. Other hydration products are converted to hydrated silica, alumina and ferric hydroxide in addition to calcium carbonate ($CaCO_3$) (4). Well-autoclaved products, made from cement and ground quartz, for example, with bulk $CaO/SiO_2$ (C/S) ratios of about 0.5, do not contain $Ca(OH)_2$. The calcium silicate hydrates (C-S-H) present are nonetheless susceptible to carbonation. The C-S-H is decalcified, initially by lowering of its C/S ratio, and ultimately by conversion into a highly porous, hydrous form of silica ($SiO_2$-gel) (5). The presence of all polymorphs of $CaCO_3$, namely: calcite, vaterite and aragonite has been reported (6,7). It has been shown that 11 Å tobermorite, the principal binder of many cement-quartz or lime-quartz based products, can decompose through the action of $CO_2$ into vaterite and $SiO_2$-gel, the former being transformed

into the more stable calcite (8). Samples containing alpha-dicalcium silicate hydrate ($\alpha$-$C_2S$ hydrate) have been found to have lower drying shrinkages than those containing 11Å tobermorite (9). It has been shown that $\alpha$-$C_2S$ hydrate is more resistant to carbonation than 11Å tobermorite (8). Investigations of autoclaved aerated concrete have demonstrated that there exists a relationship between the crystallinity of the C-S-H binder, the carbonation rate and the generation of cracks (10).

In a previous paper (9), the effects of ground quartz fineness, in autoclaved cement-quartz pastes and prisms, on some physical and chemical properties were reported. In the present paper results after carbonation of these previously saturated and oven dried prisms are presented; difficulties encountered in interpreting the results are highlighted.

## Experimental

Sample preparation, curing conditions as well as % drying shrinkage determination have been described elsewhere (9). Briefly, the raw mixtures used were 47.5% OPC and 52.5% ground quartz, using a different grade for each mixture. The ground quartz grades were: 60G, 100G, 200G, 300G and 400G denoting increasing fineness. In addition 2 mixtures were made with cement only, one set was water cured for 28 days and the other autoclaved. Samples were autoclaved, after a 24 hour precuring period, for 12 hours of which 8 hours was at 177°C under saturated steam. Porosities were determined in conjunction with drying shrinkage measurements from the saturated, immersed and oven-dried masses of the prisms. Autoclaved and 28 day water cured prisms were subjected to carbonation after % drying shrinkage determination as follows: all prisms were conditioned in a specially-designed carbonation box for 7 days. A saturated solution of $Mg(NO_3)_2.6H_2O$ placed in the bottom of the box provided a RH of 50-65%. The RH, inside the carbonation box, was continuously monitored with a HOBO data logger, (HOBO relative humidity, 5-95% range non-condensing). The prisms were placed on perforated, perspex stands above the saturated salt solution. After the conditioning period $CO_2$ was injected into the box for 24 hours under dynamic conditions. $CO_2$ was passed through two water bubblers prior to entering the box, as previous experiments indicated a drop in RH when using "dry" $CO_2$ only. Carbonated prisms were then saturated in deionized water for 48 hours followed by oven drying and measurements as described previously (9). After the final length measurements, one prism was selected at random from each group, disc milled and the following tests conducted:

1. DTA-TGA using a TA-instruments SDT 2960 simultaneous analyzer at a heating rate of 10°C/min to 1000°C under flowing nitrogen ( 100mL/min).
2. X-ray diffraction (XRD) analysis using a Siemens D5000 using copper $K_{\alpha 1}$ radiation from 2 to 80° 2$\theta$ at 0.02° 2$\theta$ per sec.
3. Diffuse reflectance mid-infrared Fourier Transform spectroscopy (DRIFT) on powdered samples diluted with potassium bromide (KBr, FTIR grade) in a ratio of 1:20, using a Biorad FTS-7. A total of 100 scans were collected at a resolution of 4 cm-1. All spectra were baseline corrected.
4. The inorganic carbon content of autoclaved and 28 day water cured prisms, both before and after carbonation, was determined in triplicate with a LECO CR12 carbon determinator (LECO Australia Pty. Ltd. ). Calibration was carried out with standard carbon 12%. The bulk composition of autoclaved and 28 day water cured samples (before carbonation), was determined by X-ray fluorescence (XRF) using an ARL 8410 spec-

trometer. Samples were prepared as fused discs using 12-22 flux in a ratio of 1:10. The degree or percent of carbonation was determined using the following equations:

$$CaCO_3 = \%\, C_i \times \frac{M.W.\ CaCO_3}{M.W.\ C} \quad (1)$$

$$\text{Carbonation} = 100\,\% \times \{CaCO_3\} \times \frac{1}{\%\ CaO} \times \frac{M.W.\ CaO}{M.W.\ CaCO_3} \quad (2)$$

Substituting Equation 1 into Equation 2:

$$\text{Carbonation} = 100\,\% \times \frac{\%\, C_i}{\%\ CaO} \times \frac{M.W.\ CaO}{M.W.\ C} \quad (3)$$

where: $\%\, C_i$ = average inorganic carbon content
$\%\ CaO$ = total CaO in sample from XRF analysis
M.W. = molecular weight

## Results and Discussion

Carbonation, Drying Shrinkage and Cracking. The results for percent carbonation and drying shrinkage are shown in Fig. 1. The % carbonation was found to increase with increasing quartz fineness, with the exception of samples made with the finest quartz. The results do, however, clearly show that, both before and after carbonation, % drying shrinkage increased the finer the quartz used, suggesting that the shrinkage is not solely a consequence of carbonation. A correlation between % carbonation and % drying shrinkage is nonetheless evident.

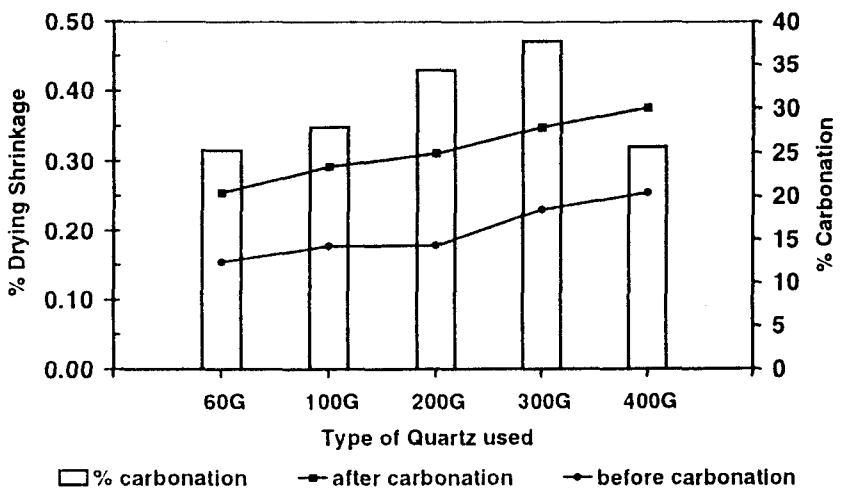


FIG. 1.
Percent carbonation and drying shrinkage, before and after carbonation, for autoclaved cement-quartz prisms.

Percent carbonation of autoclaved and 28 day water cured cement prisms, was found to be 12.7 and 13.6, respectively. The % drying shrinkage, both before and after carbonation, was lower for autoclaved cement prisms (0.14 and 0.19, respectively) and higher for 28 day water cured prisms (0.43 and 0.56, respectively) in comparison to autoclaved cement-quartz prisms. This is possibly due to lower porosities, and thus higher densities, compared to samples made with quartz: (~30% and ~36% porosity for autoclaved and 28 day water cured cement prisms, respectively, compared to ~40% porosity for autoclaved cement-quartz prisms). Samples containing $\alpha$-$C_2S$ hydrate, such as in autoclaved cement prisms, have been found to have lower drying shrinkages than those containing 11 Å tobermorite [9]. It has been shown that $\alpha$-$C_2S$ hydrate is more resistant to carbonation than 11 Å tobermorite [8]. For samples containing $Ca(OH)_2$, such as autoclaved and 28 day water cured cement prisms, the carbonation product ($CaCO_3$) is able to block all pores slowing further attack by $CO_2$, as the latter occupies ~17% more volume than $Ca(OH)_2$ (11).

The results for prisms made with the finest quartz, and indeed for all prisms tested, may be explained as follows:

1. Rapid carbonation of the prism surface may have resulted in deposition of carbonation products in the surface pores which may have hindered or slowed down further reactions with $CO_2$.
2. Carbonation is an exothermic process (12), the heat evolved is likely to reduce the moisture content. The absence of sufficient moisture required for carbonation may have hindered or slowed down further reactions with $CO_2$. This could have occurred for all the prisms, however, it may have been greatest for the ones made with the finest quartz.
3. Conditioning and carbonation were carried out on prisms which had previously been saturated in water followed by oven drying (103-105°C). This is quite a severe drying regime and would undoubtedly have affected both the pore structure (pore size distribution) and the calcium silicate hydrate binder.
4. The extent or rate of carbonation is affected by many factors including the moisture content of the specimen and the humidity of the environment. According to Moorehead (13), the reaction rate of carbonation is maximised when the moisture content is controlled so that about 50% of the pore volume is filled with water. The conditioning regime employed in these studies, both the RH of the environment and the duration of conditioning, may not have been sufficient to fulfill this requirement for all the prisms prior to carbonation. It has been suggested that measurement of the internal RH of each sample would be a useful indicator of the samples' readiness for carbonation (14).

After carbonation, the extent of cracking of all prisms was inspected using a stereomicroscope. Samples made with the coarser quartz (60G and 100G) displayed a small number of very fine cracks, most of which appeared unconnected with few areas displaying connectivity between cracks. Samples made with the finer quartz (300G and 400G) had many more cracks which were generally longer, wider and deeper; numerous cracks were observed in both axial and transverse directions. Samples made with 200G quartz displayed an intermediate cracking pattern. The extent or degree of cracking was thus found to increase the finer the quartz used. Samples made with coarser quartz underwent less % drying shrinkage, both before and after carbonation, and suffered less cracking, thus enhancing their durability properties.

Autoclaved cement prisms displayed numerous, long cracks in both axial and transverse directions. 28 day water cured cement prisms displayed cracks all over each prism face in a

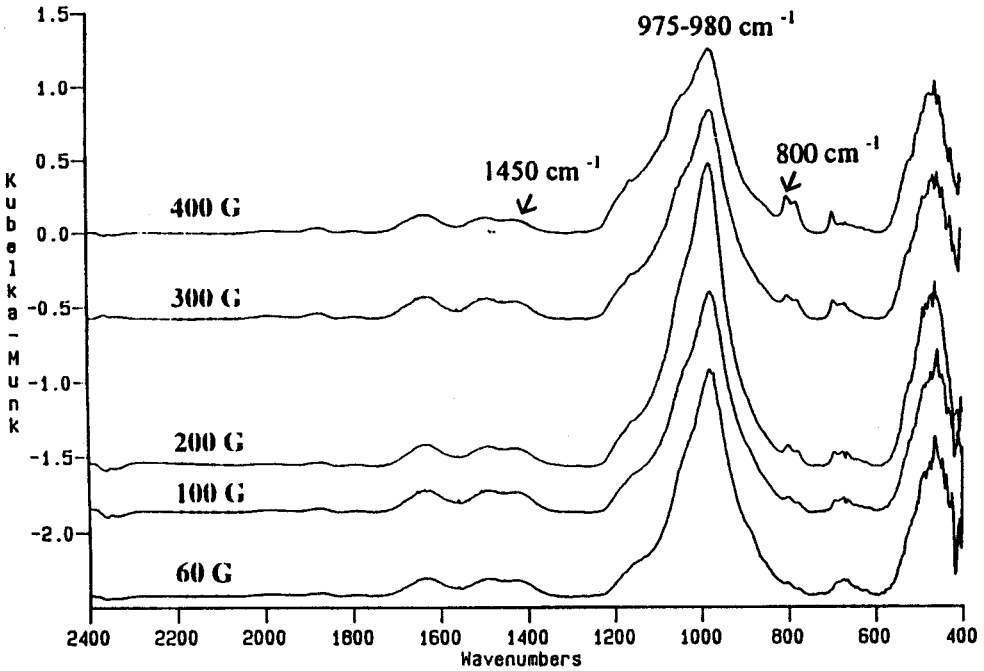


FIG. 2.
DRIFT traces of autoclaved cement-quartz prisms.

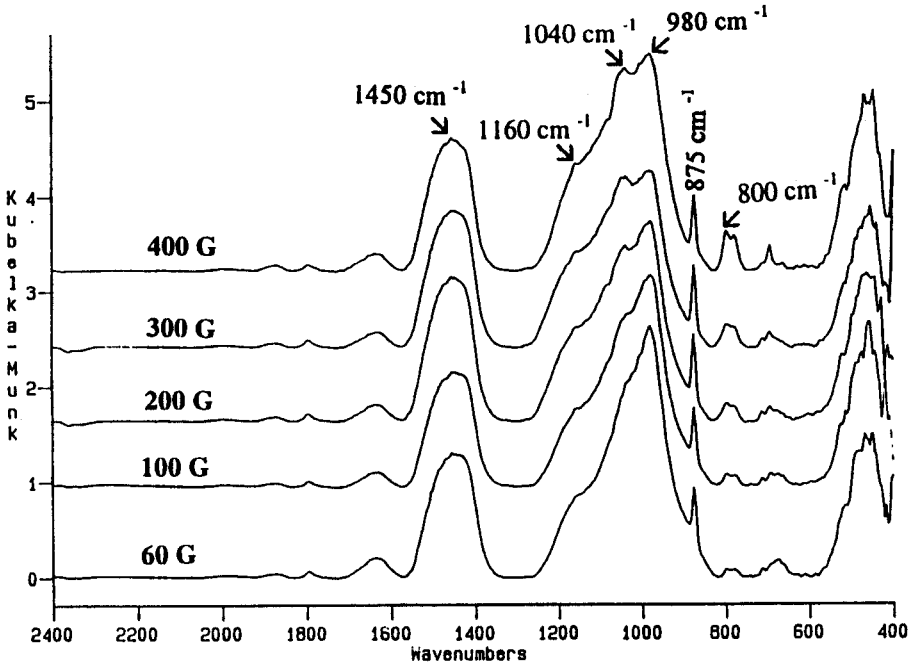


FIG. 3.
DRIFT traces of autoclaved cement-quartz prisms after carbonation.

pattern which could best be described as "mudcracking". Several prisms had broken in half upon handling, indicating increased brittleness.

FTIR, XRD and DTA-TGA. DRIFT traces before and after carbonation, are shown in Figs. 2 and 3, respectively. Prior to carbonation all samples are characterized by a band at ~975-980 $cm^{-1}$ attributed to C-S-H (15). A small amount of carbonates is indicated by the band at ~1450 $cm^{-1}$, the carbonation being ~2-3% as determined by the carbon determinator. The band at ~800 $cm^{-1}$ was found to increase the finer the quartz used. After carbonation, bands due to carbonated products have become very intense at ~1450 $cm^{-1}$ and ~875 $cm^{-1}$. Changes in the C-S-H binder are also apparent. For samples made with the three finest quartz fractions, the band at ~975 $cm^{-1}$ had broadened and shifted to higher wavenumbers, with additional peaks (unresolved) and shoulders appearing, indicating that the C-S-H binder became more like $SiO_2$-gel in character. The Si-O band at ~800 $cm^{-1}$ was found to increase further the finer the quartz used, its gradual increase with increasing quartz fineness, and the Si-O bands at ~1040 $cm^{-1}$ and ~1160 $cm^{-1}$ are typical of a $SiO_2$-gel type material, suggesting that there are fewer Ca-O-Si bonds in the structure (16). The increasing "diffuseness" of the peaks, the finer the quartz used, suggests poorer crystallinity (17). Carbonation promotes the polymerization of silica in C-S-H type materials, resulting in higher molecular weights and a different mode of organization (15). The Si-O vibrations have a tendency to shift to higher wavenumbers with increasing degree of condensation. This trend is clearly seen in Fig. 3, indicating that samples made with coarser quartz were more resistant to this change than those made with finer quartz.

From XRD calcite, vaterite and in some cases aragonite, were found to be present in the autoclaved samples prior to carbonation. The reflections for aragonite were very weak and diffuse indicating that this phase was present as a trace only and/or was not well crystallised. It is possible that some scawtite may have been present, although reflections at 3.02 Å, 2.99 Å and 3.20 Å, (PDF card number 31-0261), were not well resolved. The presence of scawtite in autoclaved cement-quartz pastes is to be expected, however, unless precautions are taken to eliminate atmospheric $CO_2$, both during the precure and autoclaving (18). It has been

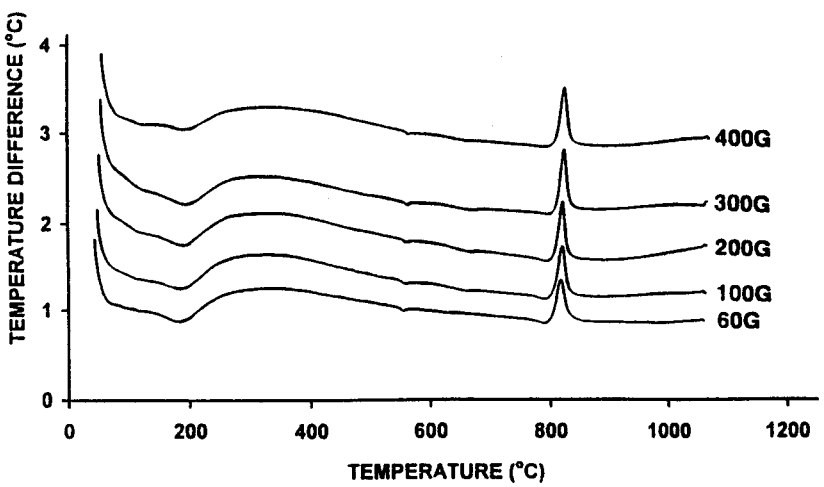


FIG. 4.
DTA curves of autoclaved cement-quartz prisms.

reported that the best conditions of scawtite formation exist when quartz as silica source is used (19). After carbonation calcite and vaterite were present in all samples with traces of aragonite. The presence of scawtite is also possible.

Samples made with the three finest quartz fractions displayed an "amorphous-type" hump in the XRD background (10-16 °2θ region), indicating $SiO_2$-gel type material. Similar observations were made by Sauman (2) and Baozhen et al. (10). 11 Å tobermorite was detected in all samples, except the one made with the finest quartz. There was no clear evidence of the existence of other crystalline products. Diffraction lines in the ~3.00-3.15 Å region can be difficult to interpret as several calcium silicate hydrates, as well as calcium silicate carbonate compounds and calcite, have reflections in this range. There is thus a possibility of more than one line overlapping in this region. The presence of an amorphous calcium silicate hydrocarbonate is also possible, as suggested by Goto et al. (6).

DTA curves of autoclaved cement-quartz samples, before and after carbonation, are shown in Figs. 4. and 5, respectively. For the carbonated samples slight differences are apparent in the size of the dehydration endotherm (~200°C), decreasing slightly with quartz fineness. All carbonated samples display a similar pattern at higher temperatures. A broad endothermic deflection ranging from ~500-750°C is the most prominent feature and includes the crystalline inversion at ~571°C, due to unreacted quartz, which is also present in uncarbonated samples (Fig. 4). A further notable feature of this broad endotherm, is a smaller endotherm at ~680-750°C, which has increased in size when compared with those of uncarbonated samples.

Fig. 6 shows DTG results for samples after carbonation. The region between ~500-750°C displays a series of 2 to 3 peak maxima, indicating that the mass loss is due to different phenomena. Additional mass loss, due to well crystallized calcite (20), is indicated at ~800°C, which is also detected in uncarbonated samples. It was possible to resolve all DTG peaks between 100-1000°C, for carbonated and uncarbonated samples, by employing a semi-isothermal heating regime. Details of the analyses and results have been reported else-

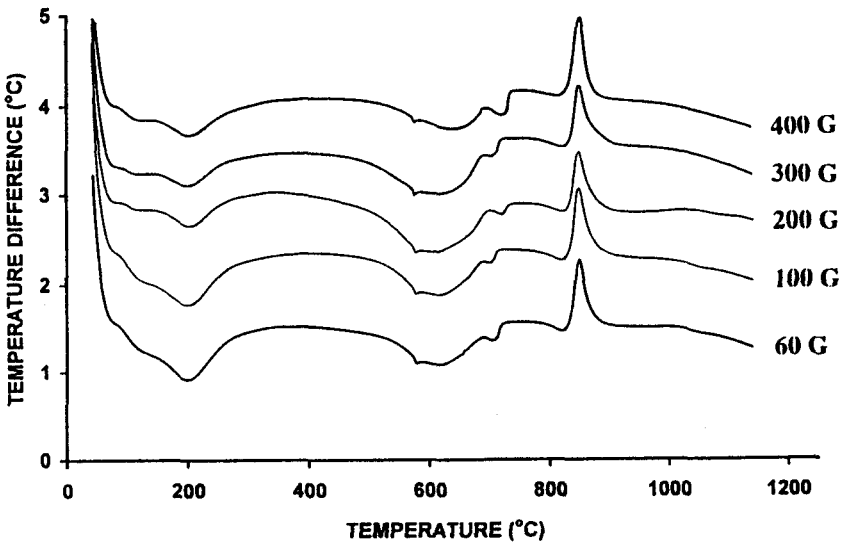


FIG. 5.
DTA curves of autoclaved cement-quartz prisms after carbonation.

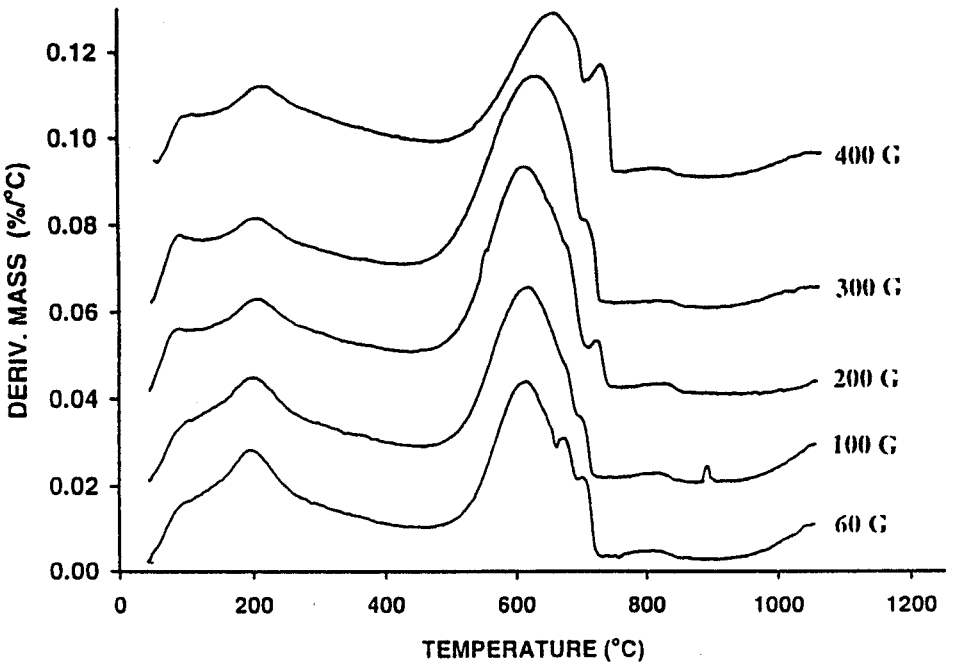


FIG. 6.
DTG curves of autoclaved cement-quartz prisms after carbonation.

where (21). Mass losses were determined both before and after carbonation (semi-isothermal method) and are shown in Fig. 7.

The results reveal mass losses in three steps:

1. Dehydration ~103-220°C, (TG1).
2. Low-temperature decarbonation ~220-600°C, (TG2).
3. High-temperature decarbonation ~600-1000°C, (TG3).

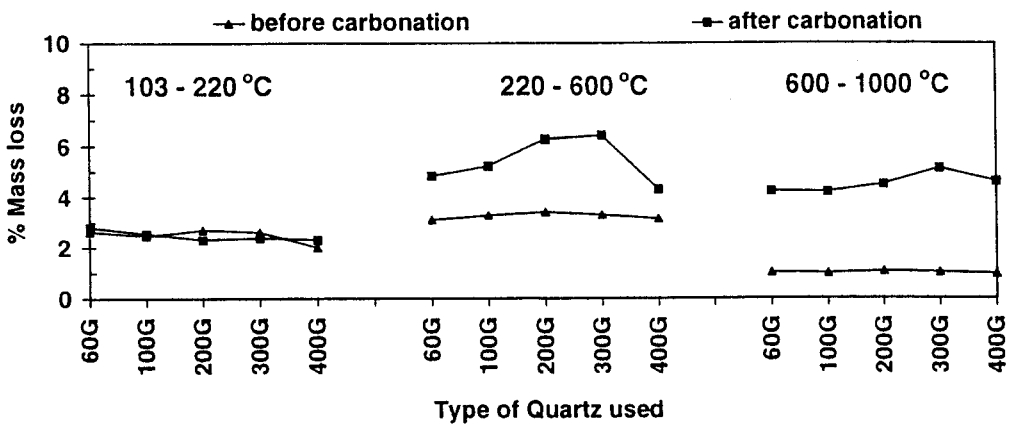


FIG. 7.
Mass loss of autoclaved cement-quartz prisms before and after carbonation.

It is possible that dehydration reactions contributed to the mass loss in the low-temperature decarbonation step; the larger mass loss, for samples before carbonation, in the TG2 region compared to the TG3 region seems to support this notion. The identity of the various mass losses could be confirmed by employing gas-phase mass spectrometry.

It is evident that upon carbonation both TG2 and TG3 increased in magnitude. TG2 was found to increase the finer the quartz used with the exception for samples made with the finest quartz, the reasons of which cannot be fully explained. TG3 displayed a similar trend, the differences between samples being smaller than for TG2. The increase in mass loss from before-to-after carbonation was greater for TG3 than for TG2.

The evolution of $CO_2$ is complex, because $CO_2$ and $H_2O$ are evolved simultaneously; most of the $CO_2$ comes from the decomposition of calcium carbonate but peaks associated with other processes are observed at temperatures lower than the calcium carbonate decomposition temperature. Cole and Kroone (7) concluded that the $CO_2$ is chemically bound as calcium carbonate largely in the form of poorly crystallized vaterite, aragonite and calcite. Gaze and Robertson (22) suggested that the $CO_2$ was absorbed into the 2-dimensional lattice to give an interstitial compound which slowly released $CO_2$ on heating, while well-crystallized calcite decomposes at ~800°C (20). It has been noted that the type of calcium carbonate product formed depends on the nature of the calcium silicate hydrate present initially (23).

Butt et al. (24) noted that less crystallized calcium silicate hydrates are characterized by forming a great number of loose calcium carbonates with small binding powers while the more crystallized calcium silicate hydrates are characterised by forming stable calcium carbonate crystal adhesions. The increased mass loss in the TG2 and TG3 regions upon carbonation, increasing with quartz fineness, can in part, be explained by these observations and our previous findings of decreasing binder crystallinity with increased quartz fineness. Additionally, the nature of the silica source has been shown to produce structurally different C-S-H precursors at room temperature, which affect subsequent tobermorite formation during autoclaving (25).

## Conclusions

From these studies we consider that the superposition or multiplicity of factors involved, both chemical and physical in nature, makes it difficult to conclude with certainty which ones in particular were the main causes for the differences in both drying shrinkage and degree of carbonation as observed in these studies.

The results do however indicate the following:

1. The degree of carbonation increased with increasing surface area of quartz, with the exception of samples made with the finest quartz.
2. The drying shrinkage of autoclaved cement-quartz prisms, both before and after carbonation, increased the finer the quartz used, suggesting that factors other than carbonation were contributing.
3. The extent of cracking, observed after carbonation followed by water saturation and oven drying, was found to increase the finer the quartz used.
4. The binder became more like $SiO_2$-gel in character after carbonation the finer the quartz used, indicating that samples made with the coarser quartz were more resistant to this transformation.

5. Points 1-4 above demonstrate that samples made with coarser quartz have better durability properties than those made with finer quartz.
6. Mass loss before and after accelerated carbonation consisted of one dehydration step and a low- and a high-temperature decarbonation step.
7. Mass loss for the low-and high-temperature decarbonation steps increased upon carbonation, the mass increase for the high-temperature decarbonation being greater than for the low-temperature decarbonation.
8. DTG curves were found to be more sensitive than DTA curves in identifying differences between samples after accelerated carbonation.
9. DRIFT spectroscopy was found to be a useful technique in identifying differences between carbonated and uncarbonated samples.

Properties such as the pore size distribution, the relative amounts and types of calcium silicate hydrates present, their crystallinity and surface characteristics, as well as the particle size distribution of the unreacted quartz are additional factors that must be considered to fully understand observations made as described in these studies. It would be worthwhile to continue these investigations using mercury intrusion porosimetry (MIP) and solid-state nuclear magnetic resonance (NMR) to follow changes in the pore size distribution and the state of polymerisation of the calcium silicate hydrate binders, respectively, after the various treatments and measurements described.

$N_2$ adsorption-desorption isotherms of these types of samples, both before and after carbonation, may also prove useful in evaluating the behaviour of the calcium silicate hydrates and to monitor changes in surface area.

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