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The use of DTA/TGA to study the effects of ground quartz with different surface areas in autoclaved cement : quartz pastes.

Part 1: A method for evaluating DTA/TGA results

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Abstract

A method is presented for consistent DTA/TGA evaluation using computer software for data analyses. DTA/TGA was used to study the effect of ground quartz addition to cement. Ground quartz was found to enhance portlandite production and calcium silicate hydrate phase formation in 24 hour precured cement:quartz pastes. Calcium silicate hydrate phases formed in autoclaved cement:quartz pastes belonged to the tobermorite group. XRD was found to be more sensitive than DTA in identifying differences in the phases formed after autoclaving.

Keywords: Ground quartz; Surface area; Cement; Precuring; Autoclaving

1. Introduction

In the fields of cement chemistry and building materials, including autoclaved building products, DTA/TGA has become an invaluable tool for studying hydration reactions [1,2], identifying phases formed [3,4] and studying the effects of pozzolanic additives [5,6], to name a few.

Since the classic studies by Kalousek [7,8,9] of autoclaved cement based materials, nearly every paper concerned with cement hydration reactions and related topics, has included DTA/TGA.

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The present paper is aimed at illustrating a method in which DTA/TGA data can be evaluated consistently, in particular for comparative studies, with the aid of computer software and appropriate choices for analysis parameters. Industrial autoclaved cement based building products, are usually made with cement:quartz ratios ranging from 70:30 to 30:70, (C/S = 1.0 to 0.25). Higher cement contents are undesirable as this usually results in the formation of α-C_2S hydrate which is detrimental to the strength [7]. The paper also presents preliminary results for 24 hour precured and subsequently autoclaved cement:quartz pastes using ground quartz of different surface area.

2. Experimental

In these studies C/S ratios of 1.0 to 0.25 are of interest, which cover the range of 70:30 to 30:70. The present paper presents preliminary results using a C/S ratio of 0.50. Water to total solids ratio was 0.35 for all mixes made. Ground quartzite 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. The major chemical and physical properties are listed in Table 1.

The pastes were made with deionised water in accordance with ASTM C 305-82 except that the final mixing was extended to 2 minutes. Pastes were cured for 24 hours in a moist cabinet, (23 ± 17°C, 95% relative humidity as per ASTM C 511-85), followed by demoulding, cutting and autoclaving under saturated steam for 12 hours of which 8 hours were at 177°C.

Thermal analyses were carried out on 24 hour precured and subsequently autoclaved cement:quartz pastes. Specimens were oven dried at 103°C for 24 hours followed by disc milling, drying and cooling over silica gel and soda lime in a desiccator.

Analyses were conducted using a TA-instruments SDT 2960 simultaneous DTA/TGA analyser at a heating rate of 10°C/min to 1100°C under flowing nitrogen (100 ml/min). Sample sizes were between 40 to 50 mg and were packed into a Pt-Rh crucible with 20 taps.

Table 1
Main physical and chemical properties of type A ordinary Portland cement and ground quartz of different surface areas used in this study

Ground quartz type	Blaine surface area (cm^2/g)	% SiO_2	Major oxides in cement (%)		Hypothetical 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_3O_3	4.60	C_4AF	14
400G	6750	99.0	SO_3	2.60		
cement	3550		MgO	1.14		

All DTA/TGA curves were evaluated using the TA instruments DTA-TGA data analysis software as set out below. X-ray diffraction (XRD) analysis was conducted on autoclaved specimens using a Siemens D5000 using copper $K_{\alpha 1}$ radiation from 5 to $50^\circ 2\theta$ at $0.02^\circ 2\theta$ per sec.

3. Results and discussion

Selection of instrumental parameters for data manipulation

Experiments were conducted to determine the most appropriate settings for data manipulation for subsequent quantitative analyses.

3.1. Selection of curves and 2 point rotation

Depending on whether peak temperature or mass loss determination were made the following curves were selected.

Peak temperature determination:	DTA and DDT (derivative difference in temperature, °C/°C).
Mass loss determination:	DTA, TGA and DTG (derivative mass, %/°C).

In either case a two point rotation was carried out for the DTA about the following X-Y coordinates; 103°C was chosen as all samples had been oven dried at this temperature:

X	103	1100
Y	1.0	1.0

Rotating the curve allows one to remove baseline slope from the data without running a reference thermal experiment [10]. Appropriate scale parameters were then chosen for the y-axes. The effect of such a rotation is depicted in Fig. 1 and 2.

In some cases an additional one point shift along the y-axis was carried out for better curve separation. This is illustrated in Fig. 3.

3.2. Peak temperature using a linear baseline

The endotherm due to the dehydroxylation of portlandite, $Ca(OH)_2 \rightarrow CaO + H_2O$, is depicted in Fig. 4 in expanded view after the following analysis parameters were selected.

onset + step transition:	automatic
step transition midpoint:	1/2 height
step signal change between:	onset + end
baseline type:	linear

The software provides the choice of displaying peak height, peak area as well as peak onset temperature for the DTA endo- or exotherm based on the criteria selected above.

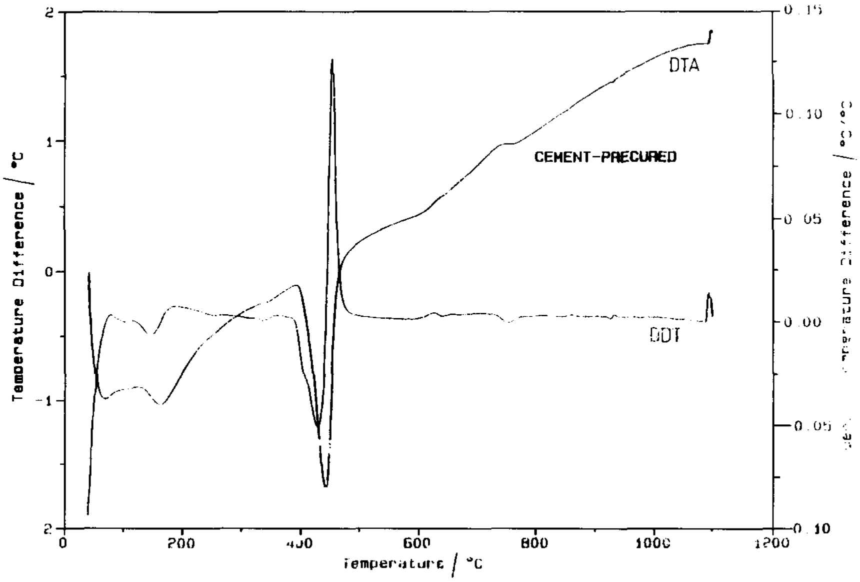

Fig. 1. Example of DTA for 24 hours precured cement paste and corresponding DDT.

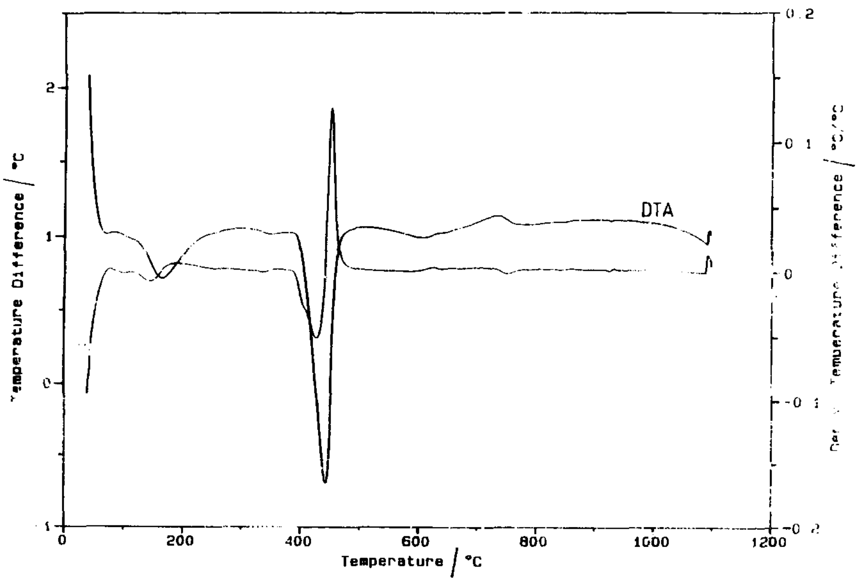

Fig. 2. Effect of a two point rotation about (103, 1.0) and (1100, 1.0) coordinates.

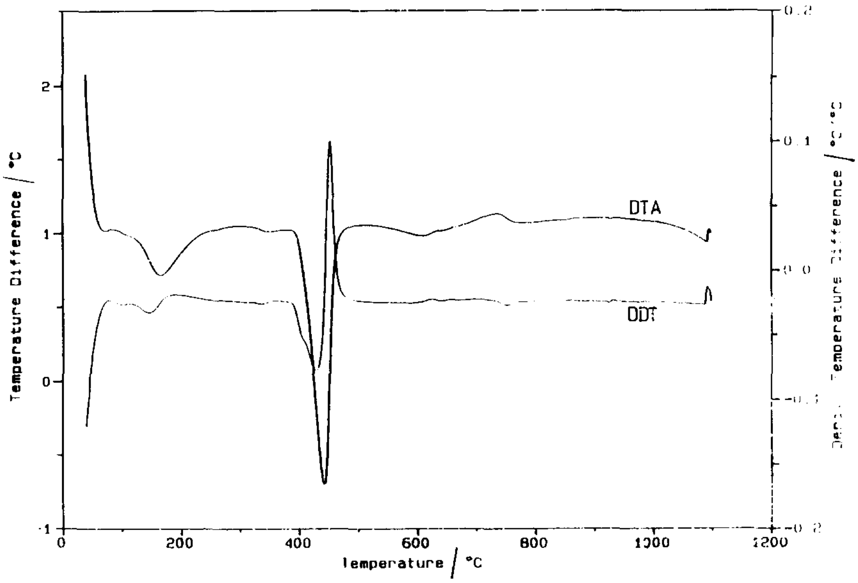

Fig. 3. Result from Figure 2 after an additional one point shift along the second y-axis of the DDT.

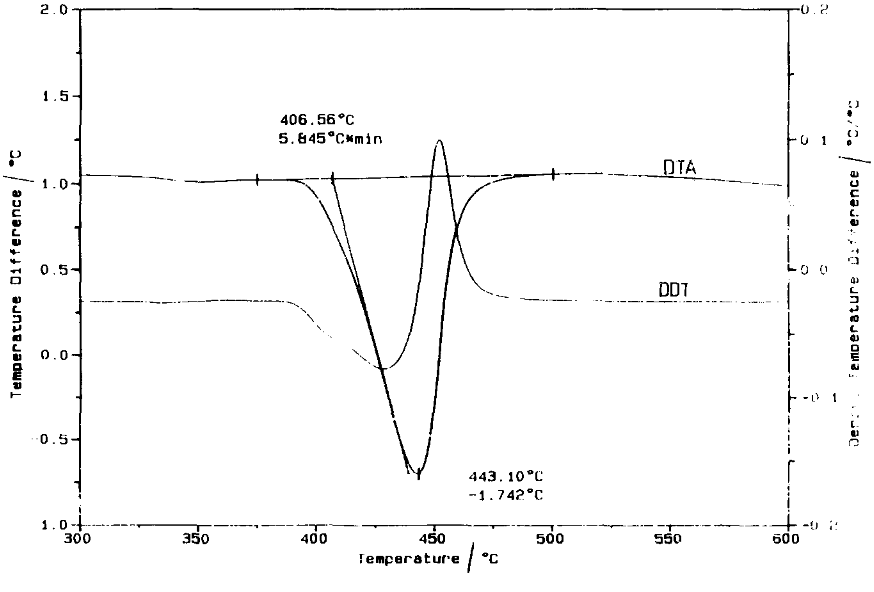

Fig. 4. Result for peak integration of the endotherm due to portlandite dehydroxylation for 24 hour precured cement paste.

The two limits required for peak integration of the DTA curve were chosen from the linear portion of the DDT curve, as this corresponds to zero temperature difference (°C/°C), and were approximately equidistant from the maximum endotherm peak temperature.

3.3. Peak temperature using a sigmoidal baseline

The high-temperature exotherm displays a change in baseline slope due to a change in heat capacity of the specimen resulting from the exothermic process which has occurred [11], consequently the following analysis parameters were chosen for the subsequent evaluation:

onset + step transition:	automatic
step transition midpoint:	1/2 height
step signal change between:	onset + end
baseline type:	sigmoidal

The two points chosen for peak integration of the DTA curve, were taken from the linear portion of the DDT curve. For instance, a result depicted in Fig. 5, where the baseline "cut across" the DTA curve rather than meeting it tangentially, was rejected. A result shown in Fig. 6 was considered acceptable.

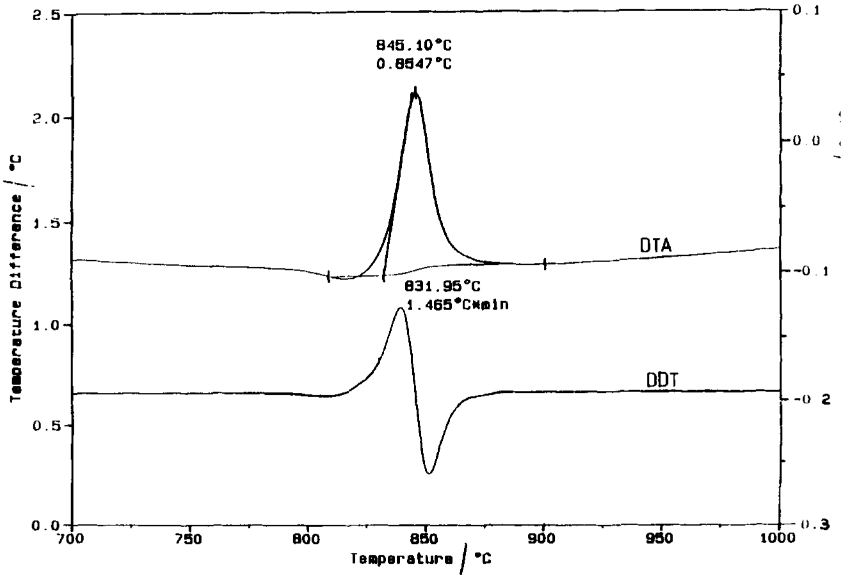

Fig. 5. Result of a peak integration for the high temperature exotherm with a sigmoidal baseline which was rejected.

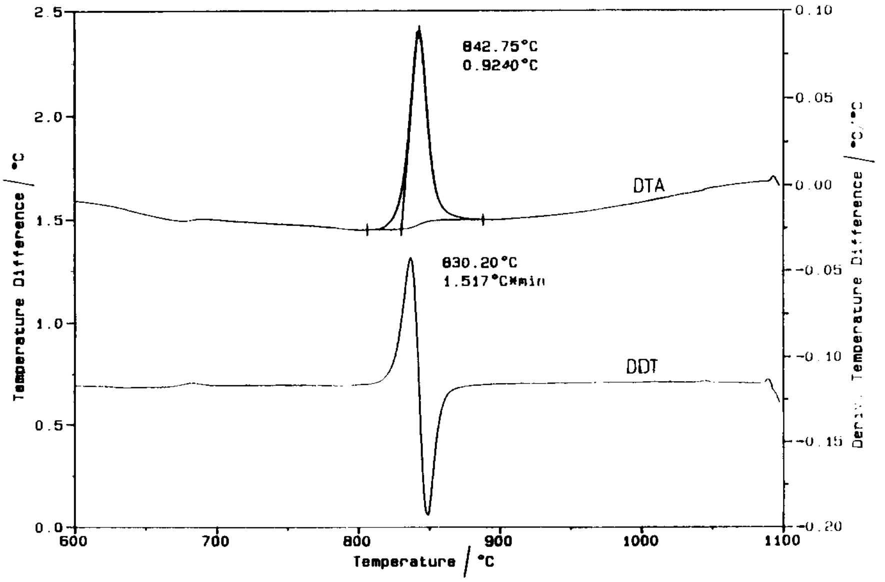

Fig. 6. Result of a peak integration for the high temperature exotherm with a sigmoidal baseline which was accepted.

3.4. *Mass loss determination*

The step transition mode was selected for the mass loss determinations using the following analysis parameters:

onset + step transition:	automatic
step transition midpoint:	1/2 height
step signal change between:	start + stop
baseline type:	linear

Limits for the TG curve were selected from the linear portion of the DTG curve, approximately equidistant from the peak maximum of the DTG curve. The temperature at half-height is also given; in Fig. 7 this is 433.98°C (H).

Examination of precured and autoclaved cement:quartz pastes

3.5. *Results for 24 hours precured and autoclaved cement : ground quartz pastes*

The analysis regimes described were employed for all DTA/TGA results of 24 hour precured and subsequently autoclaved cement and cement:ground quartz pastes and are presented in Tables 2 and 3, respectively.

Figure 8 and 9 depict the DTA curves for precured and autoclaved specimens, respectively.

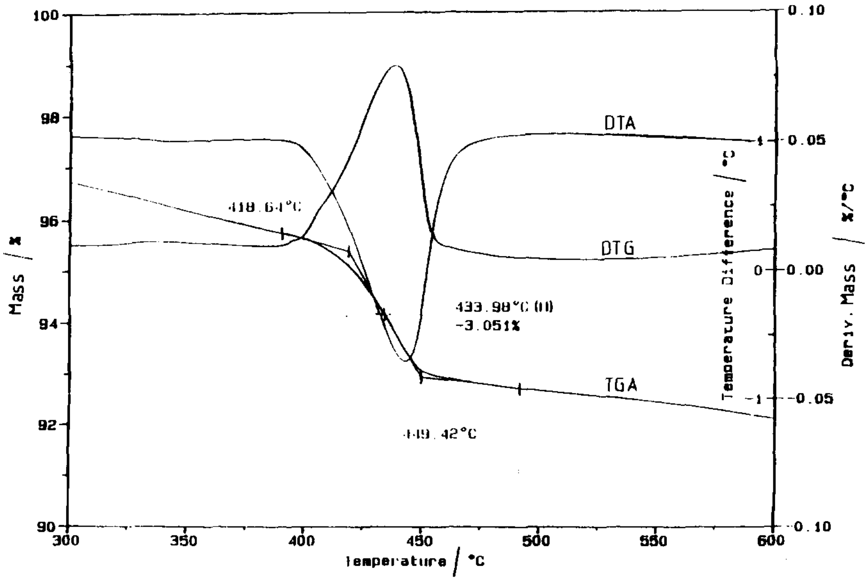

Fig. 7. Result for determining the mass loss due to the dehydroxylation of portlandite.

3.5.1. Precured samples

The total mass loss between 103°C and 1100°C is given by the % loss on ignition. The chemically bound water can be evaluated from TG mass losses as described by Bhatty et al. [12], using Eq. (1):

$$\text{chemically bound water} = L_{\mathrm{dh}} + L_{\mathrm{dx}} + 0.41(L_{\mathrm{dc}}) \tag{1}$$

Portlandite, calcium hydroxide or CH, produced during the cement hydration for the various pastes was evaluated using Eq. (2), as described by [12]. Results are included in Table 2.

$$\text{calcium hydroxide} = 4.11(L_{\mathrm{dx}}) + 1.68(L_{\mathrm{dc}}) \tag{2}$$

The results indicate that after the 24 hour precure, in the presence of ground quartz, both CH and calcium silicate hydrate were formed, indicated by an endotherm ~ 440°C and exotherm ~ 900°C, respectively. No such exotherm was apparent for 100% cement paste. The presence of calcium silicate hydrate gel in the cement paste is manifested by the broad endotherm around 150°C; referred to as phase X in earlier studies [7]. The results indicate that in the presence of ground quartz CH production and C–S–H phase formation were enhanced when compared to 100% cement paste; for cement paste 15.1% CH was produced, theoretically then 47.5% cement present in the mixtures should produce 7.2% CH. The amount of CH produced in the presence of ground quartz is depicted in Fig. 10.

The effect of ground quartz on enhanced CH production and C–S–H phase formation is therefore apparent. The results may be explained by considering the

Table 2
Results for 24 hours precured cement and cement:quartz pastes using TA instruments DTA-TGA data analysis software

Sample	% Mass loss for various step transitions			Actual water loss ($L_{dh} + L_{dx}$)	Chemically bound water (mass %)	Portlandite formed (mass %)	Portlandite peak maximum (°C)	High temperature exotherm peak maximum (°C)
	Dehydration ~ 103–400°C (L_{dh})	Dehydroxylation ~400–500°C (L_{dx})	Decarbonation ~500–1000°C (L_{dc})					
100% cement	3.57	3.05	1.54	6.62	7.25	15.12	443	not present
@ 60G	1.80	1.43	1.37	3.23	3.79	8.18	443	902
@ 100G	1.97	1.65	1.08	3.62	4.06	8.60	434	901
@ 200G	2.18	1.91	1.04	4.09	4.52	9.60	441	903
@ 300G	1.90	1.49	1.48	3.39	4.00	8.61	444	905
@ 400G	2.16	1.76	1.01	3.92	4.33	8.93	437	901

Table 3
Results for autoclaved cement and cement:quartz pastes using TA instruments DTA-TGA data analysis software

Sample	High temperature exotherm peak maximum (°C)	High temperature exotherm peak height (°C)	High temperature exotherm peak area (°C* min/mg)
@ 60G	846	0.69	1.26
@ 100G	845	0.85	1.47
@ 200G	843	0.95	1.47
@ 300G	844	0.99	1.46
@ 400G	843	0.92	1.52

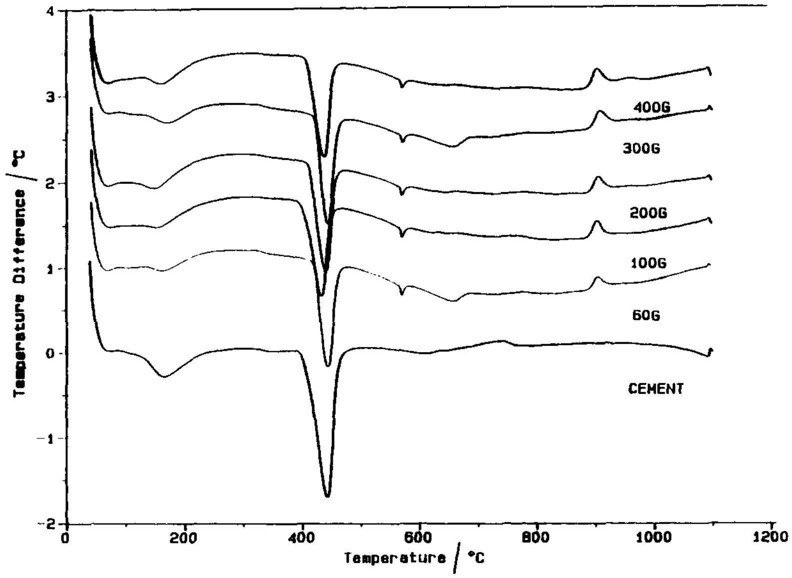

Fig. 8. DTA curves for 24 hour precured cement and cement : quartz pastes.

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 [13], here calcium silicate hydrates and CH. Quartz surfaces may become a substrate on which nucleating points may form, as discussed by Moorehead et al. [14]. The number of nucleating points would then be proportional to the surface areas of the quartz.

The apparent drop in CH production when the finer quartz materials were used, for 300G and for 400G being slightly lower than for the 200G, as depicted in Fig. 10, may have been due to agglomeration in the raw materials, which 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 agglomerations in the finer material

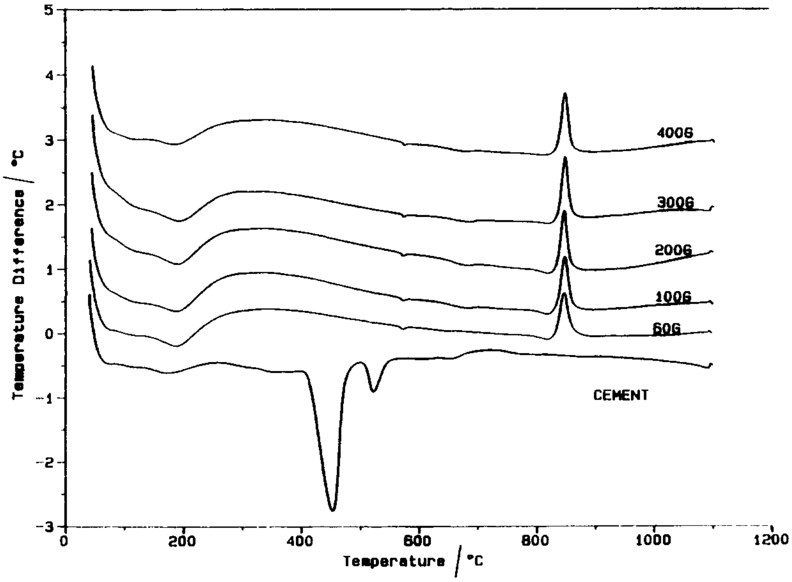

Fig. 9. DTA curves for autoclaved cement and cement : quartz pastes.

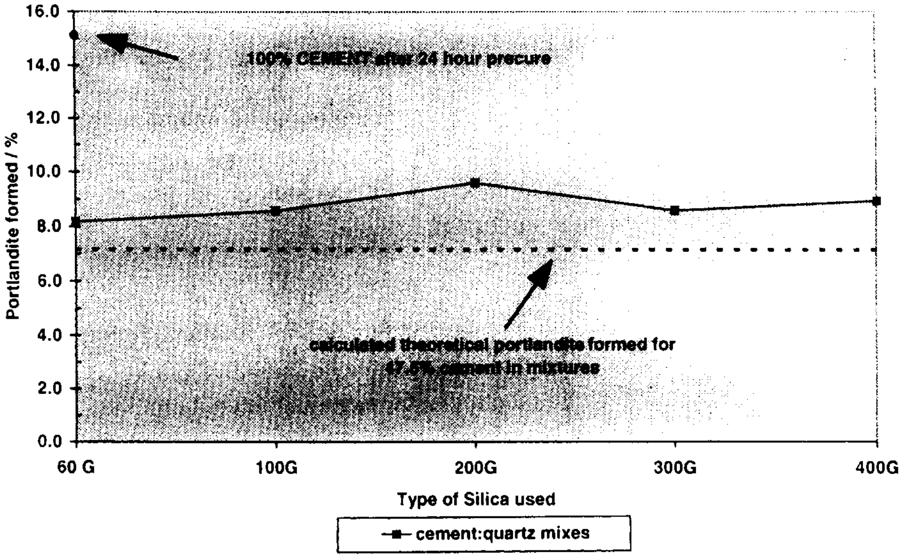

Fig. 10. Amount of portlandite formed in 24 hour precured cement : quartz pastes when using quartz of different surface areas.

may have been present. Alternatively, the results may indicate that the 200G grade quartz was of optimum surface area, viz had the optimum particle size distribution, for enhancing CH production and C–S–H phase formation.

The positive influence of ground quartz on the degree of tricalcium silicate hydration during precuring and subsequent autoclave treatment has been demonstrated by Berardi et al. [15].

Wczelik [16] showed that active SiO_2, Aerosil, introduced into hydrating tricalcium silicate suspensions accelerated the decomposition of the latter. The SiO_2 was found to "stimulate" the portlandite nucleation and growth. In cases of high SiO_2 contents, the process of calcium silicate hydrate phase formation was said to prevail over the portlandite crystallisation.

3.5.2. Autoclaved samples

Results presented in Table 3 and Fig. 9 suggest the following:

- The main phases in autoclaved cement were found to be CH, endotherm ~ 453°C and α-dicalcium silicate hydrate, α-C_2S hydrate, endotherm ~ 523°C. The increase in peak temperature for CH in the autoclaved sample compared to the 24 hours precured one, 443°C, indicates a more ordered CH phase [16].
- All cement: quartz specimens contained unreacted quartz, endotherm 571°C.
- The broad endotherm between ~ 100–300°C is due to dehydration of the calcium silicate hydrates.
- The exotherm exhibited by all autoclaved cement: quartz samples in the range 843–846°C, marking the crystallisation to β-wollastonite, β-CS, is due to aluminous tobermorite or C–S–H(I) of C/S ratio 0.8–1.0 [13], or both.
- Peak areas indicate slight variations in the amount of binder present, indicating a smaller amount for the coarser quartz used when compared to the finer material used. The peak heights indicate a similar trend.
- In this instance the peak areas are probably a better indicator than the peak heights due to peak asymmetry and differences in the peak height: peak width ratios [17].

Table 3
Results for autoclaved cement and cement:quartz pastes using TA instruments DTA-TGA data analysis software

Sample	High temperature exotherm peak maximum (°C)	High temperature exotherm peak height (°C)	High temperature exotherm peak area (°C* min/mg)
@ 60G	846	0.69	1.26
@ 100G	845	0.85	1.47
@ 200G	843	0.95	1.47
@ 300G	844	0.99	1.46
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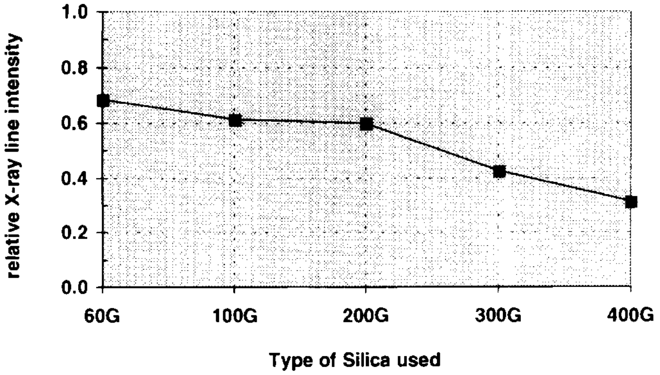

Fig. 11. Ratio of relative 2.97/3.07 Å X-ray line intensities of the binder in autoclaved cement : quartz pastes when using ground quartz of different surface areas.,

Even though small differences in both peak temperature and peak areas are apparent overall the results indicate the binder to be a mixture of C–S–H(I) of C/S ratio 0.8–1.0 and aluminous tobermorite with no attempt being made to quantify either phase present.

XRD results indicated the presence of 11 Å tobermorite and C–S–H(I) and unreacted quartz. The 002 peak, d-spacing 11.3 Å, was of weakest intensity for the sample prepared with the finest ground quartz suggesting that the tobermorite was poorly crystalline.

The ratios of the relative intensities of the 2.97/3.07 Å lines indicated a progressive decrease the finer the ground quartz used. According to Kalousek [13], this ratio of intensities can be used to differentiate between Taylor's C–S–H(I), (intensity ratio = 0), and tobermorite (ratio = 0.7 – 0.8). The tentative conclusion is made that the binder became more "C–S–H(I) in character" and less crystalline the finer the ground quartz used, viz the greater the surface area used. The ratio of relative intensities is depicted in Fig. 11.

These results thus suggest, that the crystallinity of the binder formed in autoclaved cement:quartz pastes, all other variables kept constant, is dependent on the ground quartz surface area. Ground quartz of a large surface area was found to produce a less crystalline binder in comparison to ground quartz with a small surface area.

The results show good agreement with findings by Isu et al. [18] in their studies of autoclaved aerated concrete using quartz of different particle sizes, where coarser quartz was found to produce more crystalline tobermorite than finer quartz.

4. Conclusions

This study has led to the following conclusions:

1. When conducting thermal analysis, in particular for comparative studies, consistent sample preparation and thermal running parameters are essential.

2. The method of subsequent data analysis should also be consistent as variations may cause differences in the results not due to the actual samples studied.
3. The presence of ground quartz in cement paste enhanced the production of portlandite and calcium silicate hydrate formation possibly by acting as a nucleating agent.
4. DTA results indicated that similar products had formed after autoclaving when using ground quartz of different surface areas. XRD results indicated the presence of both C–S–H(I) and aluminous tobermorite, the binder being less crystalline when the finer quartz was used. XRD was found to be more sensitive in identifying differences in the phases formed.

Studies are currently being conducted using ground quartz of narrow size ranges to eliminate the possible opposing factors of particle size distribution and surface area.

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