ELSEVIER

Autoclaved Cement-Quartz Pastes with Metakaolin Additions

Danielle S. Klimesch*† and Abhi Ray*
*Department of Materials Science, University of Technology, Sydney, Australia; and
†James Hardie and Coy Pty. Ltd., Granville, Australia

Metakaolin (MK) additions to cement-quartz pastes autoclaved at 180°C affect the binding material and physical properties. At MK additions of up to 12%, the amount of tobermorite formed decreases when cement is partially replaced, whereas the opposite effect is observed in the case of partial replacement of quartz. An overall decrease in both compressive strength and drying shrinkage occurs with MK additions. In autoclaved systems, MK provides a source of silica that is more reactive than ground quartz. ADVANCED CEMENT BASED MATERIALS 1998, 7, 109–118. *© 1998 Elsevier Science Ltd.*

KEY WORDS: Autoclaving, Cement-quartz pastes, Compressive strength, Drying shrinkage, Hydrogarnet, Metakaolin, Tobermorite

Metakaolin (MK) recently has been added to the list of pozzolanic materials [1]. It is an ultrafine material produced by the dehydroxylation of a kaolin precursor upon heating at a temperature range of ~700° to 800°C [2]. MK is a silica based product that, on reaction with CH, produces C-S-H gel at ambient temperature. MK also contains alumina that, on reaction with CH, produces additional alumina containing phases, including C_4AH_{13}, C_2ASH_8, and C_3AH_6 [3–5].

Although numerous articles have reported the use of MK in ambient to low temperature cured lime [6], cement [7,8], or gypsum [4] based systems, very little information on the use of MK in autoclaved cement-quartz or lime-quartz systems is available. Interest in such systems stems from the fact that the presence of reactive aluminous materials accelerates the crystallization rate of 11 Å tobermorite ($C_5S_6H_5$), the principal binder of many autoclaved lime-quartz or cement-quartz based building materials, and raises the upper temperature limit of its stability [9]. Additionally, Al-substituted tobermorite is more resistant to carbonation than the pure CaO-SiO$_2$ variety [10], whereas additions of Al-containing materials are known to reduce the drying shrinkage in autoclaved lime-quartz bricks [11]. MK thus has the potential to be a new source of reactive Al for use in autoclaved cement and/or lime based building products.

The present article reports our findings of the effects of MK on phase formation and some of the resulting physical properties when MK is introduced as either a quartz or a cement replacement in autoclaved cement-quartz pastes. Additionally, data on the acid-insoluble residue and compressive strength, after a 24-hour precuring period, are presented.

Experimental

Raw Materials

The following materials were used:

(a) Type A ordinary Portland cement (OPC) containing: SiO_2 21.1%, CaO 64.4%, Al_2O_3 4.15%, Fe_2O_3 4.60%, SO_3 2.60%, MgO 1.14%, and TiO_2 0.22%, produced by Blue Circle Southern Portland Cement (Berrima Works, NSW, Australia). The Blaine surface area was 3550 cm^2/g.
(b) Ground quartz sand (quartz) containing: SiO_2 99.1%, Al_2O_3 0.36%, Fe_2O_3 0.10%, and TiO_2 0.07%, from Ballarat (Victoria, Australia) and supplied by Commercial Minerals (Sydney, Australia). The Blaine surface area was 3600 cm^2/g.
(c) A commercially available MK with average particle size <2.5 μm (as per supplier specification). Table 1 depicts the chemical composition of MK, as determined by X-ray fluorescence (XRF).

Sample Preparation

A control cement-quartz mixture was prepared using 61.5% OPC and 38.5% quartz with the bulk C/S molar ratio (0.83) equivalent to that of $C_5S_6H_5$. MK was introduced at 6%, 12%, 18.25%, 24%, and 30.5% as a quartz replacement (constant % cement) in one series and as a cement replacement (constant % quartz) in

---

Address correspondence to: Dr. Abhi Ray, Department of Materials Science, University of Technology, Sydney, P.O. Box 123, Broadway NSW 2007, Australia.
Received April 9, 1997; Accepted September 30, 1997

655 Avenue of the Americas, New York, NY 10010

ISSN 1065-7355/98/$19.00
PII S1065-7355(97)00073-4

TABLE 1. Chemical composition of a commercially available metakaolin (MK)

Oxide	Wt%
SiO_2	55.80
Al_2O_3	40.50
Fe_2O_3	0.64
TiO_2	2.25
MgO	—
CaO	0.05
$Na_2O + K_2O$	0.37

another series. Water (deionized) to total solids ratio was 0.46 for all mixtures. Mechanical mixing was conducted in accordance with ASTM C 305-082 with the following modifications: before mixing with cement, preweighed quantities of quartz and MK were mixed in a tumbler for 2 hours; final mixing at medium speed was extended to 2 minutes. Pastes were cast into molds and consolidated on a vibratory table, followed by a 24-hour curing period in a moist cabinet (23° ± 1.7°C, 95% relative humidity as per ASTM 511-85). Demolded samples were cut into approximately 13-mm cubes and 90-mm long prisms, and were autoclaved for 12 hours, of which 8 hours was at 180°C under saturated steam, followed by oven drying (103° to 105°C) for 24 hours. Samples, after the 24-hour precuring period, were also dried at 103° to 105°C for 24 hours.

Methods

A minimum of five precured and autoclaved cubes was tested for compressive strength after cooling oven-dried samples over silica gel and soda lime in a desiccator. After compressive strength testing, fractured surfaces of selected autoclaved cubes were carbon coated and examined with a scanning electron microscope (SEM, Jeol 6300F equipped with a Kevex Quantum EDS) at an accelerating voltage of 15 kV. Drying shrinkage on autoclaved prisms was determined as per ASTM C 426-70 with the following modifications: samples were dried at 103° to 105°C; a special jig was used to accommodate the prisms; and length measurements were made using a Mitutoyo Digimatic Indicator measuring to 0.0001 inches.

Oven-dried, 24-hour precured, and autoclaved cement-quartz and cement-quartz-MK specimens were disc milled using a Zr-disc mill head, followed by oven drying and cooling in a desiccator over silica gel and soda lime, and the following analyses were carried out.

The amount of acid-insoluble residue (AIR) of 24-hour precured specimens was used as a measure of total unreacted material, according to the method described by Crennan et al. [12], with modifications as described by Klimesch and Ray [13]. Analyses were conducted in triplicate. Compositional and morphological changes of the AIR for autoclaved samples have been reported elsewhere [13].

The AIR provides a measure of unreacted or uncombined material, such as quartz and MK [13]. Unreacted cement is almost completely solubilized during the AIR analysis. For instance, the AIR of OPC used in this investigation was 0.08%; consequently, any contribution to the AIR is considered negligible. MK and quartz, however, are partly solubilized by the reagents used for the AIR determination [13], rendering quantitative analysis difficult. While partial dissolution of quartz, used in this investigation, was found to be very small (AIR of 98%), dissolution of MK was more pronounced (AIR of 77.4%). In view of the previous discussion, the "corrected AIR" was calculated using the following assumptions:

1. AIR due to unreacted cement is negligible.
2. For the control sample, the difference between "actual AIR" and "actual quartz" used in the mix is due to: (a) partial dissolution of quartz during AIR determination, as a consequence of disc milling the sample and reagents used for the AIR analysis; and (b) partial solubilization and participation of quartz in reactions during the precure, as noted previously [14]. The difference between "actual AIR" and "corrected AIR" was thus set to zero for the control sample. The correction factor (CF), determined for the control sample, was applied to all other results according to eq 1:

$$\text{Corrected AIR} = \{\text{quartz added to mix}\} - \left\{\frac{\text{quartz added to mix} \times \text{CF}}{100}\right\}. \tag{1}$$

The "difference in AIR" was evaluated according to eq 2:

$$\text{Difference in AIR} = \{\text{actual AIR}\} - \{\text{corrected AIR}\}. \tag{2}$$

The bulk composition of autoclaved samples (ignited to ~1000°C) and the composition of the AIR were determined by XRF. Details of XRF analysis and AIR evaluation have been given elsewhere [13].

Differential thermal analysis (DTA) was carried out on autoclaved samples using a TA-instruments SDT 2960 simultaneous DTA/TGA analyzer at a heating rate of 10°C/min to 1150°C under flowing nitrogen (100 ml/min). Data analyses and the use of the second derivative differential thermal curve have been discussed elsewhere [15].

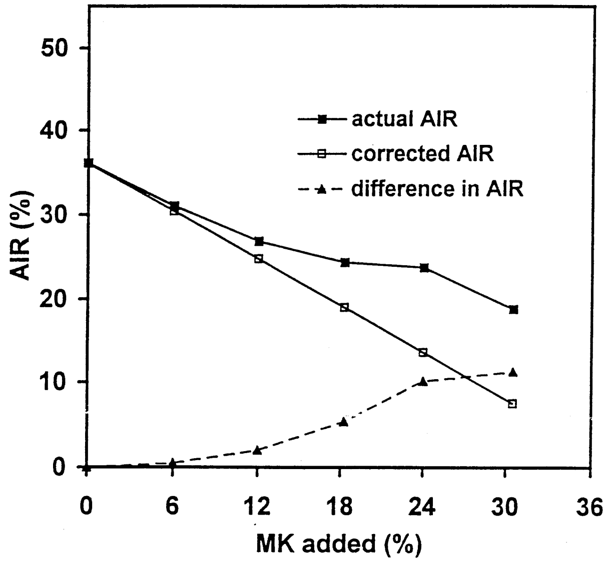

FIGURE 1. Acid-insoluble residue (AIR) data of 24-hour precured samples, when MK was used as a quartz replacement.

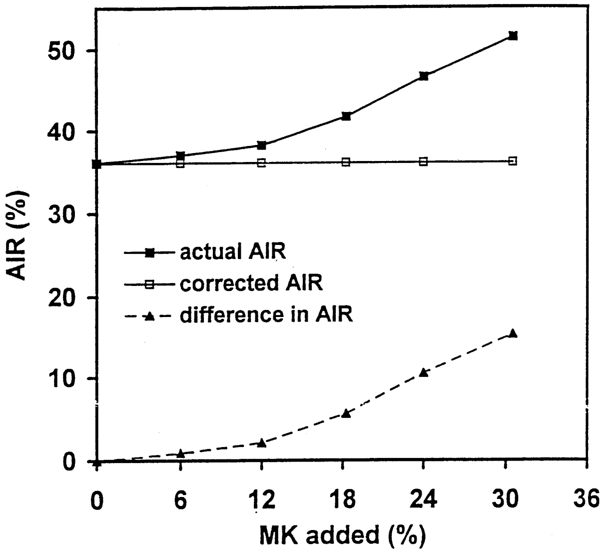

FIGURE 2. Acid-insoluble residue (AIR) data of 24-hour precured samples, when MK was used as a cement replacement.

X-ray diffraction (XRD) patterns, for all autoclaved samples, were acquired using a diffractometer with θ-θ geometry (Siemens D5000), using CuK_α radiation. DIFFRAC-AT V3.2 software was used to treat the data. The main quartz peak (3.34 Å), present in all specimens, was used for displacement correction. Additionally, an X-ray line profile fitting program was used to determine integrated peak intensities and peak positions of phases present.

Results and Discussion

24-Hour Precured Samples

Figures 1 and 2 depict results for "actual AIR," "corrected AIR," and "difference in AIR" when MK was introduced as either a quartz or a cement replacement, respectively.

It is evident from Figures 1 and 2 that the "difference in AIR" is due to unreacted MK or some modified portion of unreacted MK. The results clearly show that, at smaller additions, MK reacted almost completely during the precure, as a consequence of the pozzolanic reaction with CH produced during the hydration of OPC. As expected, the "actual AIR" was greater and increased with MK addition, when MK was used as a cement replacement. Similar observations can be made from the compressive strength values (Figure 3). The increase in strength beyond 12% MK addition, when used as a quartz replacement, is an indicator of accelerated OPC hydration and the resultant increase in hydration products. Additionally, finely divided materials such as MK have a physical effect in that they behave as fillers, which is particularly significant in the interfacial zone regions where they are likely to produce more efficient packing at the cement-aggregate particle interface leading to an increase in the strength [8].

MK addition, when used as a cement replacement, shows a very different trend. The compressive strength decreases marginally up to 18.25% MK addition and then appreciably. This is to be expected, as it is the OPC hydration reaction that supplies the CH that feeds the pozzolanic reaction; a reduction in OPC content results in reduced amounts of CH available for pozzolanic reactions. The results also indicate that the increase in cement hydration and concurrent pozzolanic reactions are not enough to offset the loss in strength due to the increasing dilution effect when MK is used as a cement replacement.

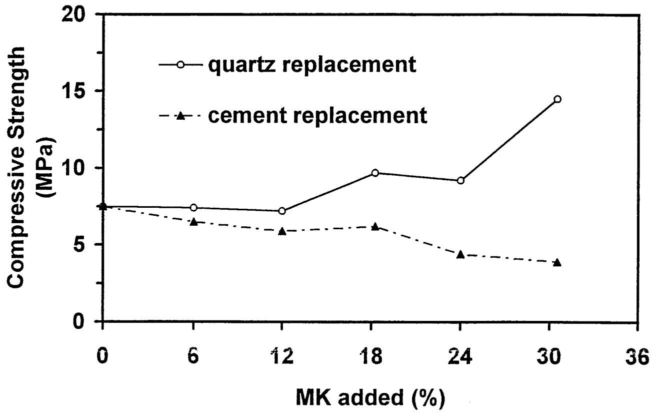

FIGURE 3. Compressive strength of 24-hour precured cement-quartz-MK cubes.

TABLE 2. Chemical composition of pastes studied, when MK was introduced as a quartz replacement

% MK Added	Cement:Quartz Ratio	Bulk Mole Ca/Si	Bulk Mole Ca/(Al + Si)	Bulk Mole Al/(Al + Si)	Bulk Mole Ca/Al
0	1.6	0.83	0.78	0.06	13.21
6	1.9	0.87	0.78	0.11	7.27
12	2.2	0.93	0.78	0.16	4.93
18.25	3.0	0.99	0.78	0.21	3.74
24	4.2	1.06	0.79	0.26	3.04
30.5	7.7	1.15	0.79	0.31	2.53

MK Introduced as Quartz Replacement in Autoclaved Samples

Table 2 contains the chemical composition of the pastes studied. Table 3 is a summary of phases identified by XRD and DTA. It also contains the detection of unreacted MK from our previous findings [13]. Figure 4 depicts the change in integrated intensities (arbitrary units) of XRD peaks due to: tobermorite, hydrogarnet (katoite), C-S-H, quartz, portlandite, and unreacted cement with increasing MK addition. The following points are noteworthy:

- 11 Å tobermorite was considered absent when the diffraction line due to the (002) tobermorite peak was no longer discernible. It is known that the 11 Å peak is affected in height by the degree of order parallel to the c-direction, and that both absolute and relative intensities of peaks in the tobermorite pattern vary with Ca/Si ratio and Al-substitution [16,17].
- Si-substituted hydrogarnet, C_3ASH_4, manifested in particular by the diffraction line at 5.05 Å (katoite, silication), was detected in all samples. C_3AH_6 was not detected in any of the samples. No attempt was made to determine the extent of silica substitution into the hydrogarnet due to the possibility of substitution of Al by Fe^{3+} as well as of 4 OH^- by SiO_4^{4-} [18]. The presence of more than one type of silica-containing hydrogarnet is nonetheless possible.
- C-S-H with main d-spacings at 3.03 to 3.04 Å and 7.3 Å, referred to as "fibrous C-S-H" by Kalousek [19], was present in all samples. Possible interference due to calcite in the ~3 Å region was considered negligible as the total $CaCO_3$ content, determined with a LECO CR 12 carbon determinator, was under 2% for all samples.
- Search results inferred the presence of gismondine, CAS_2H_4, in all samples; however, several diffraction lines were subject to overlap, rendering positive identification difficult.
- CH was present in all samples as indicated by DTA [15]. From XRD the characteristic 4.9 Å peak was only discernible at 12% MK addition and above.

In view of the previous comments, the results indicate the following:

1. Increasing levels of Al-substitution into the tobermorite crystal lattice were manifested by the increase in the (002) d-spacing from 11.38 to 11.55 Å with MK addition of up to 12%, reaching a constant value at greater MK additions.
2. With increasing MK addition and increasing cement:quartz ratio, decreasing amounts of Al-substituted tobermorite were formed while CH and α-C_2SH, where present, were found to increase. This can be explained in terms of decreasing availability of quartz with increasing cement:quartz ratio [20], resulting in the formation of more lime-rich hydration products. The presence of unreacted MK in addition to CH and α-C_2SH indicates that reactions did not go to completion

TABLE 3. Phases identified by x-ray diffraction and differential thermal analysis and detection of unreacted MK, when MK was introduced as a quartz replacement

% MK Added	Q	Al-TOB*	HYD (Katoite)	C-S-H	CH	α-C_2SH	Unreacted Cement	Unreacted MK
0	✓	✓	Trace	✓	Trace	X	✓	X
6	✓	✓	✓	✓	Trace	X	✓	X
12	✓	✓	✓	✓	✓	X	✓	X
18.25	✓	✓	✓	✓	✓	✓	✓	X
24	✓	✓	✓	✓	✓	✓	✓	✓
30.5	✓	X	✓	✓	✓	✓	✓	✓

*Al-substituted 11 Å tobermorite.

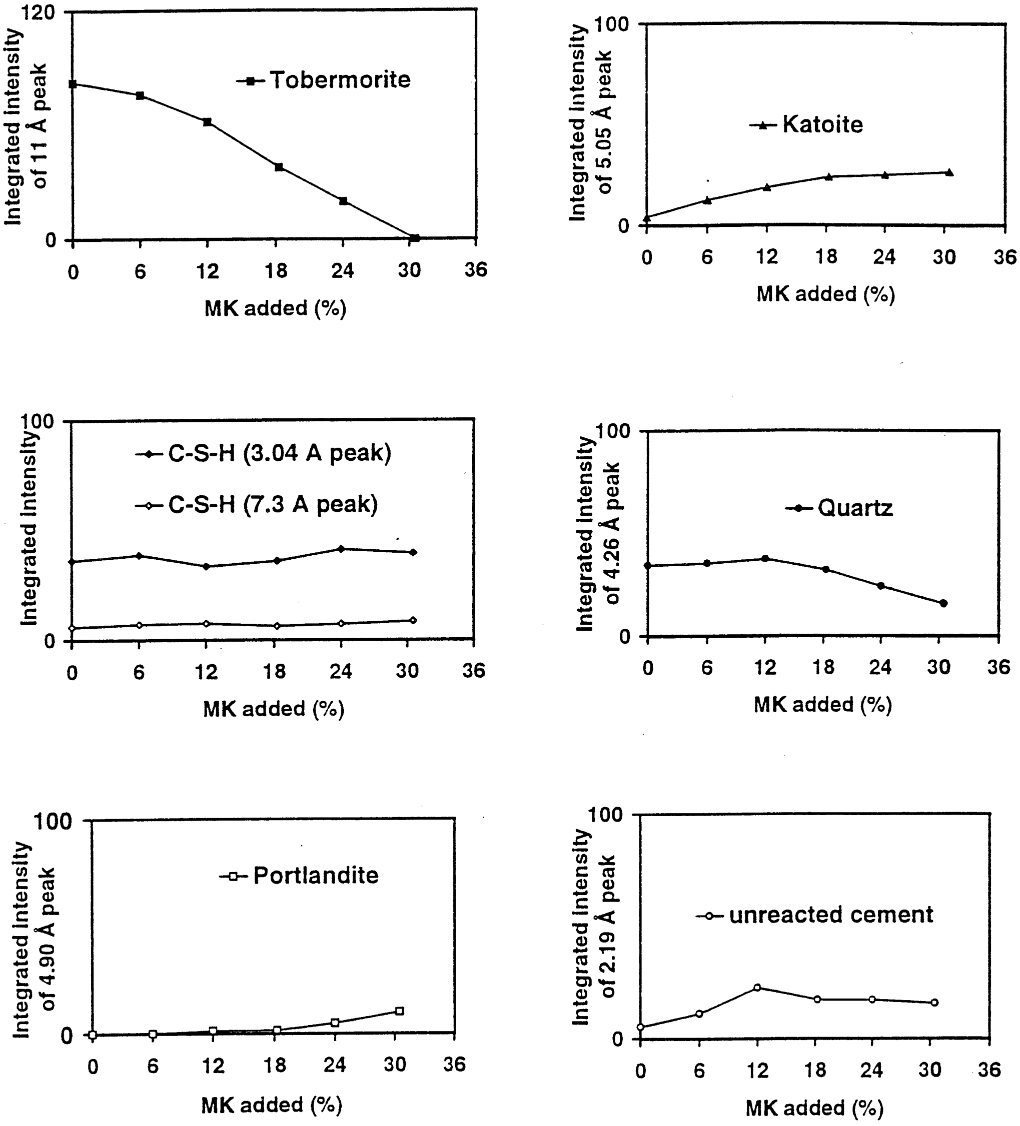

FIGURE 4. Integrated intensities of XRD peaks, when MK was used as a quartz replacement.

and/or a possible retardation of the reactions. This may be explained by the possible formation of an inhibiting layer of reaction product around the MK particles, thus terminating their reaction with CH and preventing further formation of hydration product as suggested by Khatib and Wild [1].

Figure 5 depicts crystalline platy tobermorite, containing small amounts of Al, in the autoclaved control cement-quartz specimen. In contrast, at 24% MK addition used as a quartz replacement, calcium silicate hydrates were poorly crystalline and fibrous, containing larger amounts of Al (Figure 6), whereas portlandite and unreacted cement were also evident (Figure 7).

3. Increasing amounts of Si-substituted hydrogarnet were formed up to ~18.25% MK addition, reaching a plateau at higher additions. Concurrently, the tobermorite integrated peak intensity decreased almost monotonically, presumably as a consequence of Al-substitution and decreasing crystallinity or dilution by less crystalline material. Figure 8 is an example of rounded Si-substituted hydrogarnet agglomerates present in the autoclaved cement-quartz-MK specimen, when 24% MK addition was used as a quartz replacement. Similar coexistence of Al-substituted tobermorite, Si-substituted hydrogarnet, and portlandite has been reported previously [21].
4. It is noted that the decrease in tobermorite formation did not correspond to a decrease in the overall bulk Ca/(Si + Al) ratio, which was essentially constant (Table 2). This indicates that hydrogarnet may prevail upon tobermorite by competing with

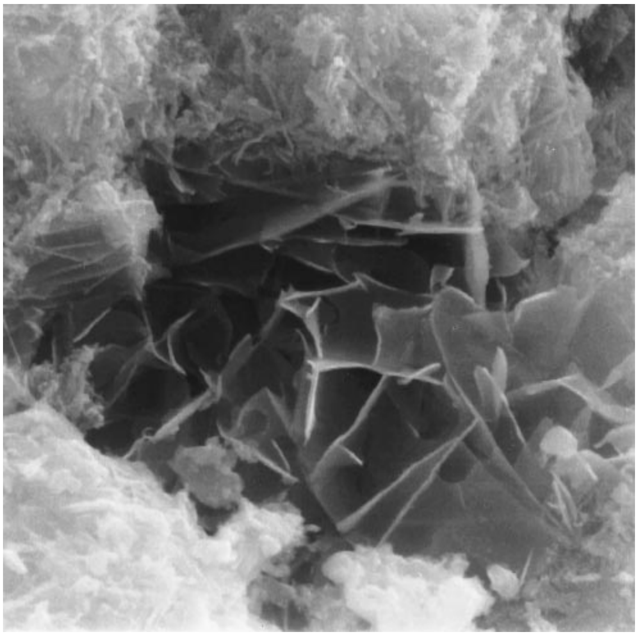

FIGURE 5. Crystalline platy tobermorite in an autoclaved cement-quartz paste specimen. Field of view (9 μm × 9 μm).

it for Al_2O_3 and possibly SiO_2. The increasing presence of hydrogarnet with increasing MK addition seems to support this notion. Alternatively, the more reactive silica species originating from MK may favor or promote formation of both a Si-containing hydrogarnet and a Si-rich type of C-S-H. The latter has been found to inhibit the formation of tobermorite [22].

5. The integrated peak intensity due to quartz decreased, as expected, with increasing MK addition,

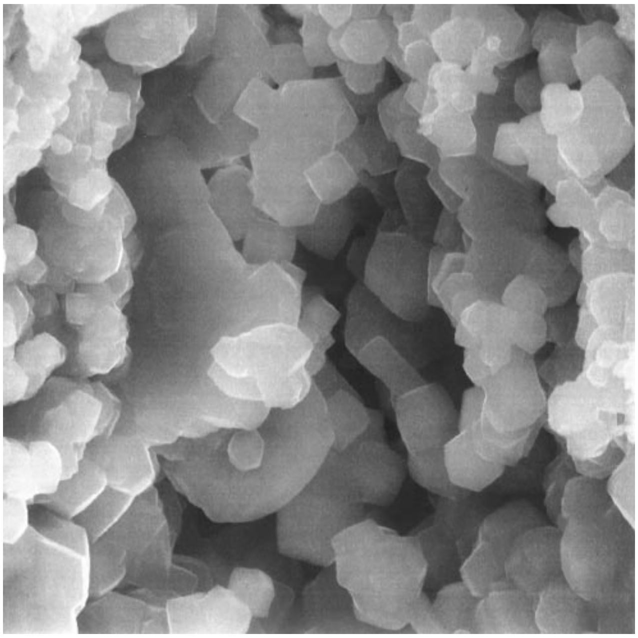

FIGURE 7. Portlandite and unreacted cement in an autoclaved cement-quartz-MK paste specimen, when 24% MK was used as a quartz replacement. Field of view (3.3 μm × 3.3 μm).

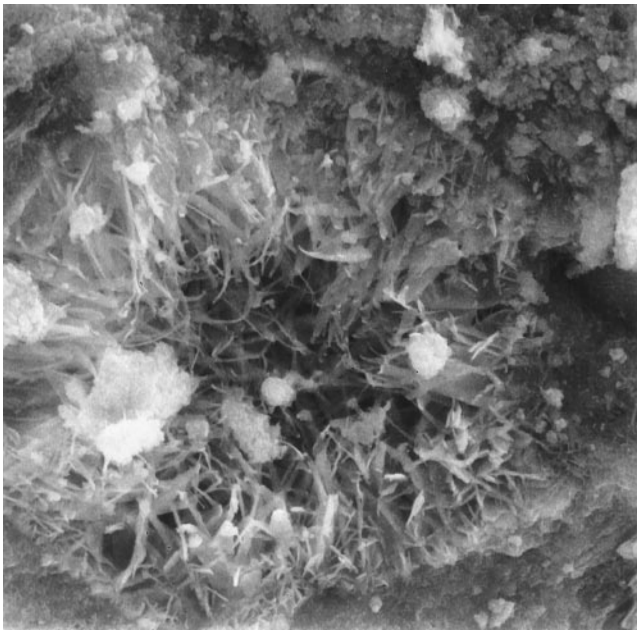

FIGURE 6. Fibrous calcium silicate hydrates in an autoclaved cement-quartz-MK paste specimen, when 24% MK was used as a quartz replacement. Field of view (18 μm × 18 μm).

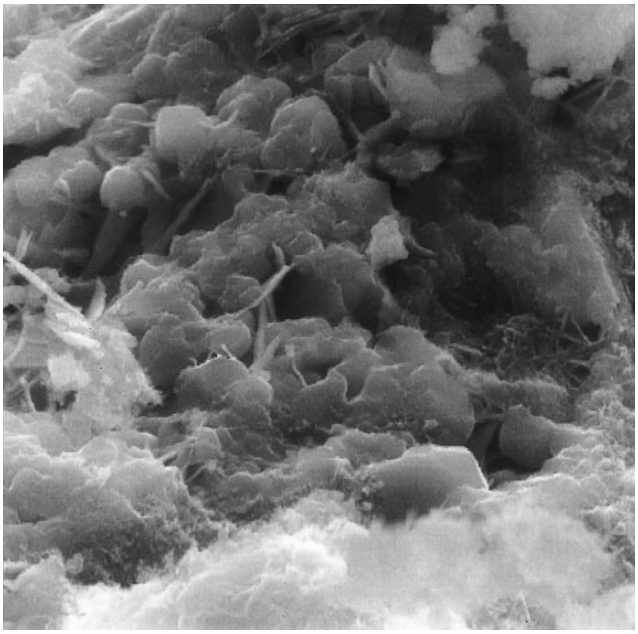

FIGURE 8. Rounded Si-substituted hydrogarnet agglomerates in an autoclaved cement-quartz-MK paste specimen, when 24% MK was used as a quartz replacement. Field of view (8.3 μm × 8.3 μm).

TABLE 4. Chemical composition of pastes studied when MK was introduced as a cement replacement

% MK Added	Cement:Quartz Ratio	Bulk Mole Ca/Si	Bulk Mole Ca/(Al + Si)	Bulk Mole Al/(Al + Si)	Bulk Mole Ca/Al
0	1.6	0.83	0.78	0.06	13.21
6	1.4	0.72	0.65	0.10	6.86
12	1.3	0.62	0.54	0.13	4.22
18.25	1.1	0.53	0.45	0.16	2.88
24	1.0	0.44	0.36	0.18	2.03
30.5	0.8	0.35	0.28	0.20	1.38

when MK was used as a quartz replacement. The presence of quartz in all samples, however, suggests a possible reaction competition between the two different silica sources, with the more reactive silica species originating from MK.

6. Integrated peak intensities for both C-S-H and unreacted cement followed a more irregular pattern with increasing MK addition. C-S-H appeared to increase slightly, whereas the unreacted cement increased up to 12% MK addition and then remained constant at greater MK additions.

MK Introduced as Cement Replacement in Autoclaved Samples

Table 4 contains the chemical composition of the pastes studied, whereas Table 5 is a summary of phases identified by XRD and DTA. Once again, it includes the detection of unreacted MK [13]. Figure 9 depicts the change in integrated intensities (arbitrary units) of XRD peaks as described previously. The results indicate the following:

1. Increasing levels of Al-substitution into the tobermorite crystal lattice were manifested by the increase in the (002) d-spacing, as noted previously, reaching a constant value of 11.51 Å at 12% MK addition and above.
2. Tobermorite formation was enhanced compared to the control sample up to 12% MK addition followed by a sharp decrease at greater additions. At 24% and 30.5% MK additions, tobermorite was no longer discernible, whereas calcium silicate hydrates exhibiting a honeycomb structure predominated the matrix (Figure 10). This can be explained, at least in part, in terms of the decreasing bulk Ca/Si and Ca/(Si + Al) molar ratios as shown in Table 4. Concurrently, Si-substituted hydrogarnet increased up to 18.25% addition of MK and then decreased, whereas unreacted quartz increased with increasing MK addition, once again indicating that the silica species originating from MK was more reactive.
3. From our previous findings [13], unreacted MK was detected at 18.25% addition, when MK was introduced as a cement replacement, which corresponds to a bulk Ca/Al molar ratio of ~2.9. When MK was used as a quartz replacement, it corresponded to a bulk Ca/Al molar ratio of ~3.0, indicating that unreacted MK will remain at Ca/Al molar ratios less than ~3.0. Alternatively, this corresponds to bulk cement:MK ratios of 2.4 and 2.6, respectively, indicating that unreacted MK will remain, approximately, at and below these ratios.
4. The decrease in both tobermorite and katoite with increasing MK addition coincided with the detection of unreacted MK, whereas unreacted cement increased, indicating a possible retardation of the reactions, as explained previously.

The possible formation or presence of gismondine in all samples, as inferred by the search results, is of considerable interest as far as zeolite formation is

TABLE 5. Phases identified by x-ray diffraction and differential thermal analysis and detection of unreacted MK, when MK was introduced as a cement replacement

% MK Added	Q	Al-TOB*	HYD (Katoite)	C-S-H	CH	α-C_2SH	Unreacted Cement	Unreacted MK
0	✓	✓	Trace	✓	Trace	X	✓	X
6	✓	✓	✓	✓	Trace	X	✓	X
12	✓	✓	✓	✓	Trace	X	✓	X
18.25	✓	✓	✓	✓	✓	✓	✓	✓
24	✓	X	✓	✓	✓	✓	✓	✓
30.5	✓	X	Trace	✓	✓	X	✓	✓

*Al-substituted 11 Å tobermorite.

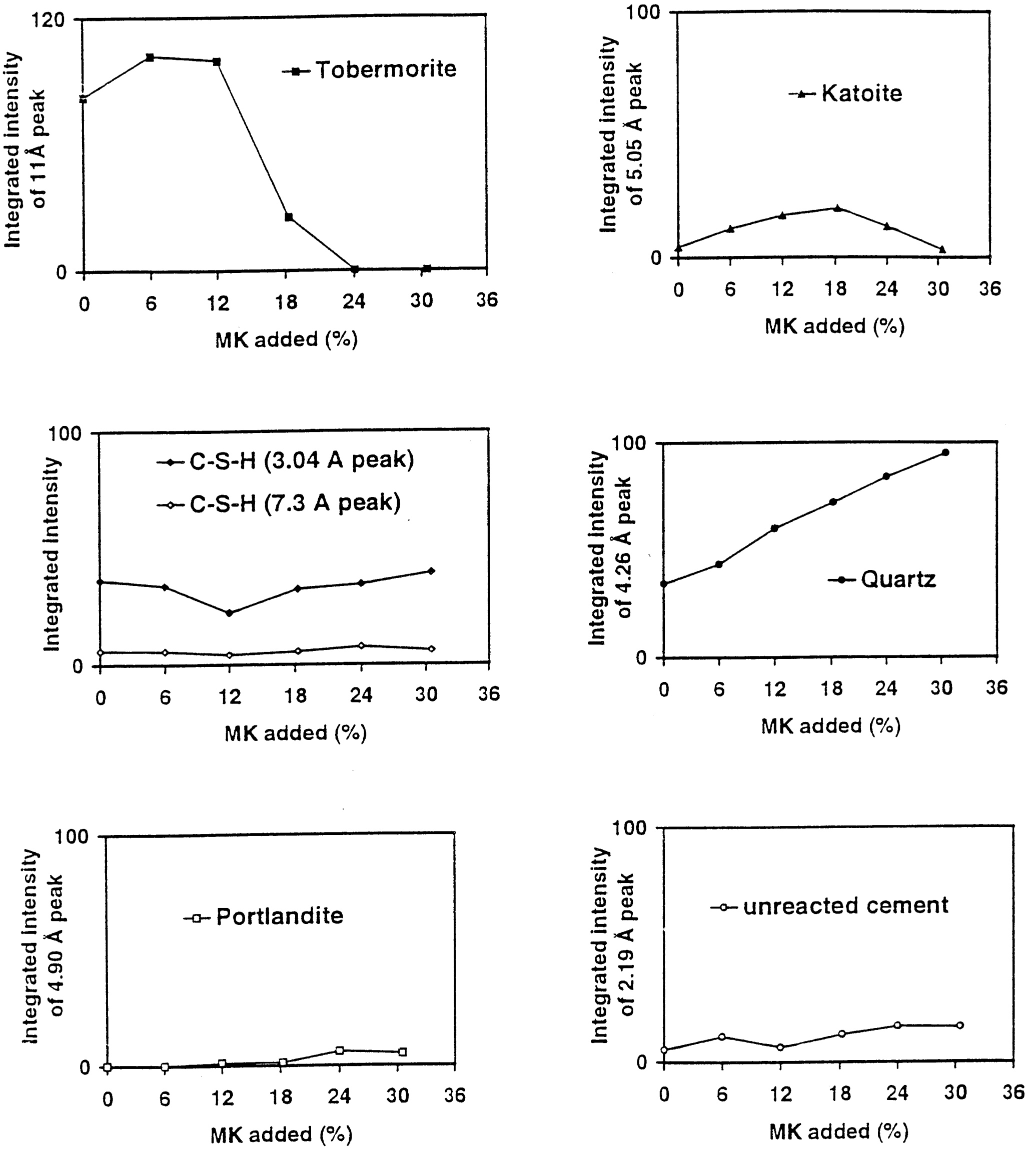

FIGURE 9. Integrated intensities of XRD peaks, when MK was introduced as a cement replacement.

concerned and remains to be verified. We are currently investigating the effect of MK addition on the rate and mechanism of phase formations in autoclaved systems and will report the results in future publications.

Compressive Strength and Drying Shrinkage

Figures 11 and 12 show the changes in compressive strength and drying shrinkage, respectively, with increasing MK addition, when introduced as either a quartz or a cement replacement. The general trend is a decrease in both drying shrinkage and compressive strength, particularly for additions exceeding 12% MK. For instance, when MK was introduced as a cement replacement, a sharp decrease in strength is apparent at 18.25% addition followed by a further slight decrease coinciding with the detection of unreacted MK [13].

The general decrease in compressive strength and drying shrinkage can be explained in terms of increasing amounts of hydrogarnet (katoite) and α-C_2SH, both of which are known to reduce the strength and the drying shrinkage [23,24], and a general decrease in the C-S-H type binding phases. The decrease in compressive strength may also be due, at least in part, to the differing degrees of compaction, as indicated by the average bulk densities determined prior to the compressive strength tests. For instance, when MK was introduced as a cement replacement, the average bulk density decreased from ~1410 to ~1250 (kg/m^3). Bulk

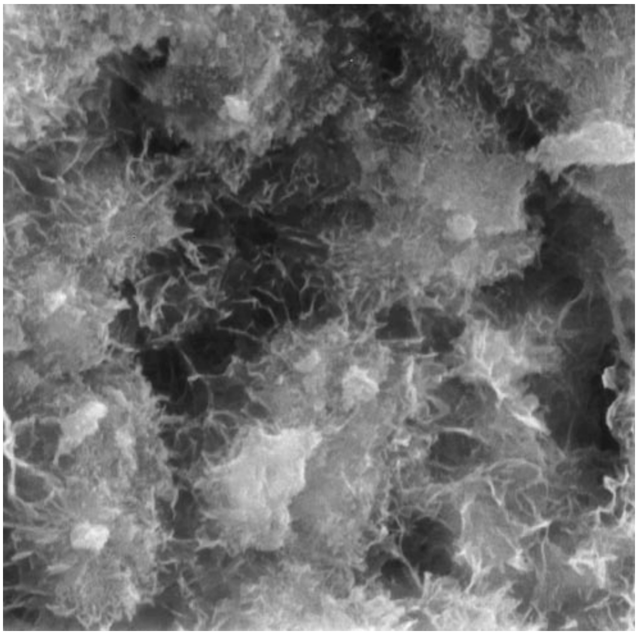

FIGURE 10. Calcium silicate hydrates exhibiting a honeycomb structure in an autoclaved cement-quartz-MK paste specimen, when 24% MK was used as a cement replacement. Field of view (10 μm × 10 μm).

densities followed a slightly irregular pattern, when MK was introduced as a quartz replacement, decreasing up to 18.25% MK addition (~1380 kg/m^3) followed by a slight increase at 24% addition and a decrease at 30.5% addition. It is also possible that a transformation from a less to a more dense hydrogarnet occurred and that this transformation may have been associated with a decrease in solid volume and hence increase/decrease in porosity and compressive strength, respectively, as suggested by Khatib and Wild [1].

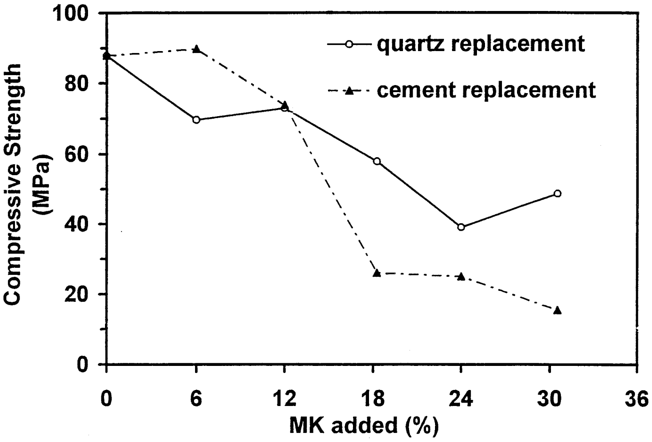

FIGURE 11. Compressive strength of autoclaved cement-quartz-MK cubes.

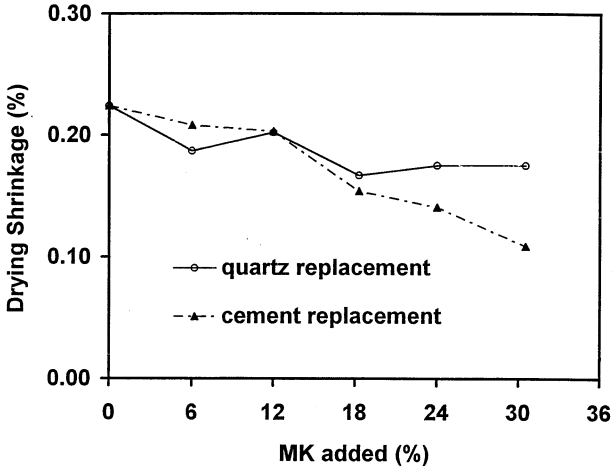

FIGURE 12. Drying shrinkage of autoclaved cement-quartz-MK prisms.

Additionally, when MK was used as a cement replacement, the strength increased marginally at first and then decreased. This may be explained in terms of enhanced tobermorite formation initially (Figure 5) and the presence of C-S-H, whereas at 12% MK addition the slight reduction in strength coincided with the decrease in C-S-H. It has been reported [20] that the best correlation exists between the total sum of tobermorite and C-S-H present and the compressive strength. It has also been noted that if much unreacted quartz remains, strength is controlled by its particle size distribution and the porosity, whereas if the material is largely C-S-H type, the distribution of particle types within the C-S-H has a major effect [12].

As noted previously, the general trend in drying shrinkage was a decrease with increasing MK addition. This trend follows previous observations that some factors affect the strength and drying shrinkage in a similar way [25]. Additionally, an increase in unreacted quartz, when MK was introduced as a cement replacement, provides additional restraint for the drying shrinkage, explaining the lower values.

Conclusion

MK provides a source of silica that is more reactive than ground quartz in autoclaved cement based systems. MK in these systems has differing effects on phase formation and the resulting physical properties, depending on whether it is added as a replacement for quartz or cement. For instance, when added as a quartz replacement, the amount of tobermorite decreased while hydrogarnet (katoite) increased concurrently with increasing amount of MK, indicating that hydrogarnet may prevail upon tobermorite by competing with it for Al_2O_3 and possibly SiO_2. In contrast, when MK is added as a cement replacement, an increase in the tobermorite content is noted up to 12% addition followed by a sharp decrease at greater additions. Results of MK addition, as either a quartz or a cement replacement, also indicate that unreacted MK will be present if the bulk Ca/Al molar ratio is less than 3.

Both compressive strength and drying shrinkage decreased with increasing MK addition, particularly for additions exceeding 12%. The general trend followed previous observations that some factors affect the strength and drying shrinkage in a similar way. The decrease in these physical properties can be attributed mainly to increasing amounts of both hydrogarnet and α-C_2SH, and a general decrease in the C-S-H type binding phases. Additionally, when MK was used as a cement replacement, increasing amounts of unreacted quartz provide a further restraint for the drying shrinkage.

Data on the AIR and compressive strength, after a 24-hour precuring period, indicated an accelerating effect on OPC hydration in the presence of MK, the overall effect being more pronounced when MK was introduced as a quartz replacement.

Acknowledgments

We gratefully acknowledge support given for this project by James Hardie & Coy Pty. Limited of Australia. Special thanks to Dr. L. Aldridge from the Australian Nuclear Science & Technology Organisation for useful discussions regarding the XRD work. Special thanks to Richard Wührer from the Microstructural Analysis Unit at the University of Technology for his assistance regarding the SEM work.

References

1. Khatib, J.M.; Wild, S. *Cem. Concr. Res.* **1996,** *26*, 1545–1553.
2. Ambroise, J.; Maximilien, S.; Pera, J. *Adv. Cem. Based Mater.* **1994,** *1*, 161–168.
3. Bredy, P.; Chabannet, M.; Pera, J. *Mater. Res. Soc. Symp. Proc.* **1989,** *137*, 431–436.
4. De Silva, P.S.; Glasser, F.P. *Proc. 9th Int. Congr. Chem. Cem., New Delhi,* **1992,** *4*, 671–677.
5. He, C.; Osbaeck, B.; Makavicky, E.; *Cem. Concr. Res.* **1995,** *25*, 1691–1702.
6. Murat, M. *Cem. Concr. Res.* **1983,** *13*, 259–266.
7. Zhang, M.H.; Malhotra, V.M. *Cem. Concr. Res.* **1995,** *25*, 1713–1725.
8. Wild, S.; Khatib, J.M.; Jones, A. *Cem. Concr. Res.* **1996,** *26*, 1537–1544.
9. Roy, D.M.; Johnson, A.M. In *Autoclaved Calcium Silicate Building Products*; Society of Chemical Industry: London, 1967; pp 114–121.
10. Sauman, Z.; Lach, V. *3rd Int. Symp. Autoclaved Calcium Silicate Building Materials*, Utrecht, **1973,** paper 3.4.
11. Noorlander, A. In *Autoclaved Calcium Silicate Building Products*; Society of Chemical Industry: London, 1967; pp 152–154.
12. Crennan, J.M.; El-Hemaly, S.A.S.; Taylor, H.F.W. *Cem. Concr. Res.* **1977,** *7*, 493–502.
13. Klimesch, D.S.; Ray, A. *Adv. Cem. Res.* **1996,** *9*, 157–165.
14. Klimesch, D.S.; Ray, A.; Sloane, B. *Cem. Concr. Res.* **1996,** *26*, 1399–1408.
15. Klimesch, D.S.; Ray, A. *Thermochim. Acta.* **1997** (in press).
16. Dyczek, J.R.L.; Taylor, H.F.W. *Cem. Concr. Res.* **1971,** *1*, 589–605.
17. Kalousek, G.L. *J. Am. Ceram. Soc.* **1957,** *40*, 74–80.
18. Flint, E.P.; McMurdie, H.F.; Wells, L.S. *J. Res. Natn. Bur. Stand.* **1941,** *26*, 13–33.
19. Kalousek, G.L. *ACI J.* **1955,** *51*, 989–1011.
20. Crennan, J.M.; Dyczek, J.R.L.; Taylor, H.F.W. *Cem. Concr. Res.* **1972,** *2*, 277–289.
21. Barnes, M.W.; Scheetz, B.E. *Mater. Res. Soc. Symp. Proc.* **1995,** *179*, 243–272.
22. Sato, H.; Grutzeck, M. *Mater. Res. Soc. Symp. Proc.* **1992,** *245*, 235–240.
23. Taylor, H.F.W. In *Autoclaved Calcium Silicate Building Products*; Society of Chemical Industry: London, 1967; pp 195–205.
24. Bessey, G.E. In *The Chemistry of Cement, II*; Taylor, H.F.W., Ed.; Academic Press: London, 1964; pp 101–134.
25. Kalousek, G.L. *5th Int. Symp. Chem. Cement, Tokyo* **1968,** *3*, 523–540.