

## Hydration of refractory oxides in castable bond systems— II: alumina–silica and magnesia–silica mixtures

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### Abstract

Isothermal conduction calorimetry was used to investigate binary mixtures of hydratable alumina-fumed silica and reactive magnesia-fumed silica for 22 h at 20 and 30 °C. Neither alumina nor magnesia formed a crystalline hydration product with silica under these experimental conditions. Silica tended to retard the hydration of magnesia, whereas it acted as an inert diluent when added to alumina.

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### 1. Introduction

Although calcium aluminate cement (CAC) has been the main bonding agent in refractory castables for the last 20 years,<sup>1</sup> the presence of lime in the castable matrix in association with silica leads to poor high temperature properties.<sup>2</sup> Hence a range of lime-free castables, predominantly based on MgO–SiO<sub>2</sub> or MgO–Al<sub>2</sub>O<sub>3</sub> bond systems, has been developed. Setting and green strength development are achieved via the hydration of reactive magnesia or hydratable alumina resulting in suitable high-temperature properties via the formation of refractory compounds such as forsterite, Mg<sub>2</sub>SiO<sub>4</sub>, and spinel, MgAl<sub>2</sub>O<sub>4</sub>.

Previously an isothermal conduction calorimetry (ICC) study<sup>3</sup> of hydration in hydratable alumina, reactive magnesia, and their mixtures revealed that hydration of alumina–magnesia mixtures led to formation of a mixed Mg–Al hydrate (hydrotalcite-type phase). This reaction was accompanied by large amounts of heat, which were evolved later in the hydration process and were comparable in magnitude with that released from the pure MgO system.

The present paper describes a similar study of the hydration of fumed silica and its mixtures with the same

hydratable alumina and reactive magnesia since these are frequently used together in the fine fraction of modern commercial castables. Fumed silica (also termed microsilica), which is a by-product of ferro-silicon manufacture, when present in the bond system of refractory castable batches reduces the amount of mixing water required and facilitates flow and ease of placement. It has been observed to influence the hydration reactions in CAC castables possibly via development of CaO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> hydrate phases on the surface of CA particles rather than the CA hydrates (such as C<sub>2</sub>AH<sub>8</sub>) which form in the silica free systems.<sup>4</sup>

Mixing fumed silica with hydratable alumina or reactive magnesia may lead on firing to formation of compounds with high melting point, such as mullite or forsterite, in the bond phase of monolithic refractories. The high temperature stability of such mullite in an ultra low cement castable (ULCC) with an alumina–silica based bond system has been shown to be a function of the impurity concentration in the starting materials.<sup>5</sup> In such castables mullite starts to form via a liquid phase and increases the creep resistance at temperatures of ~1400 °C, but approaching 1500 °C the mullite begins to dissolve in the liquid and lowers the hot modulus of rupture (HMOR).<sup>5</sup>

Magnesia–silica bond systems have been developed in magnesia-based, cement-free castables<sup>6</sup> forming forsterite in the bond on firing. The HMOR reached a

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maximum at 1200 °C but deteriorated at higher temperatures due to the effect of raw material impurities. Improved flowability is achieved in magnesia castables if the fine MgO is protected against hydration using a nitrogen atmosphere during milling.<sup>7</sup> With a pH of about 6 when dispersed in water, fumed silica might be expected to react at low temperatures with basic compounds such as MgO.

The aim of this section of the work was to study the heat evolved during the hydration of microsilica and its binary mixtures with hydratable alumina and reactive magnesia. These results complement those already published on the same alumina and magnesia samples,<sup>3</sup> and their binary mixtures,<sup>3</sup> and also the ternary mixture.<sup>8</sup>

## 2. Experimental

Mixtures of hydratable alumina (Actibond 102) from Alcan Chemicals Ltd, magnesium oxide from Aldrich Chemical Co. (catalogue No. 30,774-2) and fumed silica 971U from Elkem Materials, Norway, were hydrated for up to 22 h at 20 °C and 30 °C in a Wexham Developments Isothermal Conduction Calorimeter, which was based on the Forrester design.<sup>9</sup> Percentages and ratios are on a weight basis unless stated otherwise. According to the suppliers' data, the loss on ignition (LOI) of the alumina was 4.5%, the Na<sub>2</sub>O content was 0.45%, while its specific surface area (SSA) was 260 m<sup>2</sup>/g, and its median particle size 6 μm. Titration purity of the magnesia was 96–100.5% and its LOI was 10% maximum. Typical purity of fumed silica was 97.5% (96% minimum), carbon content 0.5–1.3%, SSA 20 m<sup>2</sup>/g, LOI 0.6–1.5 and coarse particles, >45 μm (325 mesh) 0.2–0.6%.

Dry powders were mixed with water externally to give water to solids ratio of 0.8, and were then located inside the calorimeter to measure the heat evolved during the experiment. Although this external mixing method usually devalues the results during the first hour of the experiment, this method was deployed for several reasons:

- (i) it allows the use of larger samples than the internal mixing method, giving more hydration product for characterisation,
- (ii) experimentally it is easier to carry out and the water can be mixed thoroughly with the powder, and
- (iii) with regard to its application, monitoring the heat evolution is more important after placement of a castable, which can take up to 40 minutes from mixing the dry mix with water.

Further details of this and other experimental procedures have been fully reported previously.<sup>3</sup>

## 3. Results and discussion

### 3.1. Hydration of silica

In part I the hydration details of the individual oxides of alumina and magnesia using both internal and external mixing methods have been reported.<sup>3</sup> The ICC curve of the alumina is shown again in Fig. 1 together with that for pure fumed-silica. Following the early stages of hydration, pure alumina showed a series of hydration peaks (Fig. 1a), whose appearance is believed to be related to the existence of complex hydration intermediates associated with its complex crystal and pore structure.<sup>3</sup> Pure alumina (curve A in Fig. 1a) showed a broad hydration peak which extended to ~15 h from mixing with water and another peak was observed after 22 h.

Fumed-silica, whose particle size was revealed by SEM to be in the range of 0.1–0.4 μm, showed no sign of heat evolution on contact with water on external mixing, in contrast to alumina and especially magnesia. After around 1 h at both 20 °C (curve E in Fig. 1a) and

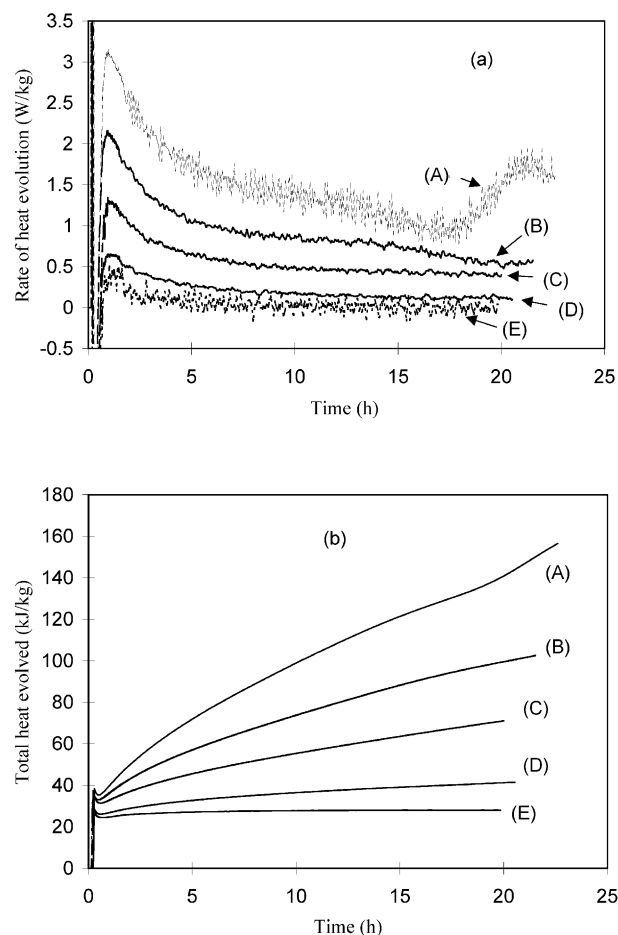


Fig. 1. ICC curves demonstrating the hydration of alumina-silica mixtures at 20 °C using external mixing, (a) rate of heat evolution and (b) total heat evolved. Al<sub>2</sub>O<sub>3</sub> : SiO<sub>2</sub> (%): (A) 100% alumina, (B) 75:25, (C) 50:50, (D) 25:75 and (E) 100% silica.

30 °C (curve D in Fig. 2a) the ICC trace of pure silica is close to, and parallel with, the base line. Visual examination of the fumed silica after contact with water inside the calorimeter for 22 h showed no signs of setting or strength development, but instead the sample was like a clay slip. Environmental scanning electron microscopy (ESEM) revealed that the spherical shapes of the fumed silica remained almost unaltered. Thermogravimetry (TG) demonstrated a total weight loss of 0.74% after heating up to 550 °C and the loss was mainly associated with free moisture.

### 3.2. Hydration of alumina–silica mixtures

The ICC curves of these mixtures at 20 °C are shown as curves B, C and D in Fig. 1. An initial peak was seen with mixed samples of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> at about the same time as in the pure alumina system, although it was lower in magnitude, and became broader with increasing silica content. Hydration at 20 °C continued

throughout and after 22 h the samples were still hydraulically active. This may imply that the second peak does occur in mixed samples but at longer times. The rate and total heat evolution (Fig. 1b) decreased at higher silica contents consistent with the silica acting merely as a diluent.

At 30 °C (Fig. 2) the peaks were sharper and the major part of the heat of hydration was evolved during the first 10 h. Hydration accelerated on increasing the test temperature from 20 to 30 °C, causing the hydration peaks to move to shorter times. The rate of heat evolution at the maximum of the first peak of hydration (Fig. 2a) was almost three times higher than that at 20 °C (Fig. 1a). The height of the second peak for the alumina was similar at both temperatures. The second peak was also detected at 30 °C in the 75:25 Al<sub>2</sub>O<sub>3</sub>:SiO<sub>2</sub> mixture (curve B in Fig. 2a). After 20 h the hydraulic activity of samples with higher alumina contents hydrated at 30 °C was comparable with those hydrated at 20 °C.

The rate of heat evolution and the total heat evolved were reduced on increasing the silica content of the mixtures at 20 and 30 °C. The total heat evolved was greater at 30 °C than at 20 °C for the alumina-rich mixtures, but the quantities evolved for the 50:50 samples were similar, as indicated by the data shown in Table 1.

Data from the hydration of alumina, silica and their mixtures (Table 1) have been used to construct Fig. 3, which shows the total heat evolution after 1, 5, 10, 15 and 20 h. The total heat evolved increased systematically with increasing time and temperature and varied in proportion to the alumina content. This implies that there was no contribution to the heat of hydration from the presence of silica in the mixtures.

XRD revealed that the principal hydration products of the mixture were poorly crystalline boehmite and well crystallised bayerite, Al(OH)<sub>3</sub> (JCPDS card No. 20-11), accompanied by amorphous phases including fumed silica.

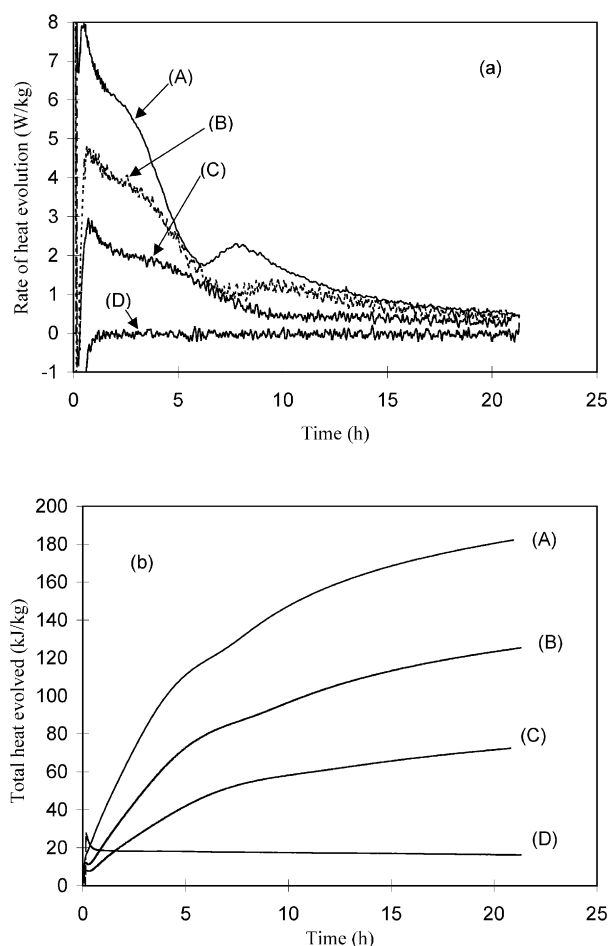


Fig. 2. ICC curves demonstrating hydration of alumina–silica mixtures at 30 °C, using external mixing, (a) rate of heat evolution and (b) total heat evolved. Al<sub>2</sub>O<sub>3</sub> : SiO<sub>2</sub> ratios: (A) 100% alumina, (B) 75:25, (C) 50:50 and (D) 100% silica.

Table 1  
Sample composition (wt.%) and total heat evolution on hydration (kJ/kg) with time at 20 and 30 °C, using external mixing

Alumina	Silica	Temp. °C	1 h	5 h	10 h	15 h	20 h
100	0	20	40	72	99	121	141
		30	37	112	147	168	180
90	10	30	32	98	129	149	160
75	25	20	36	57	74	88	100
		30	21	73	96	113	124
50	50	20	33	45	55	64	71
		30	14	43	58	66	72
25	75	20	27	33	36	39	41
0	100	20	25	27	28	28	28
		30	18.5	18	17	17	16

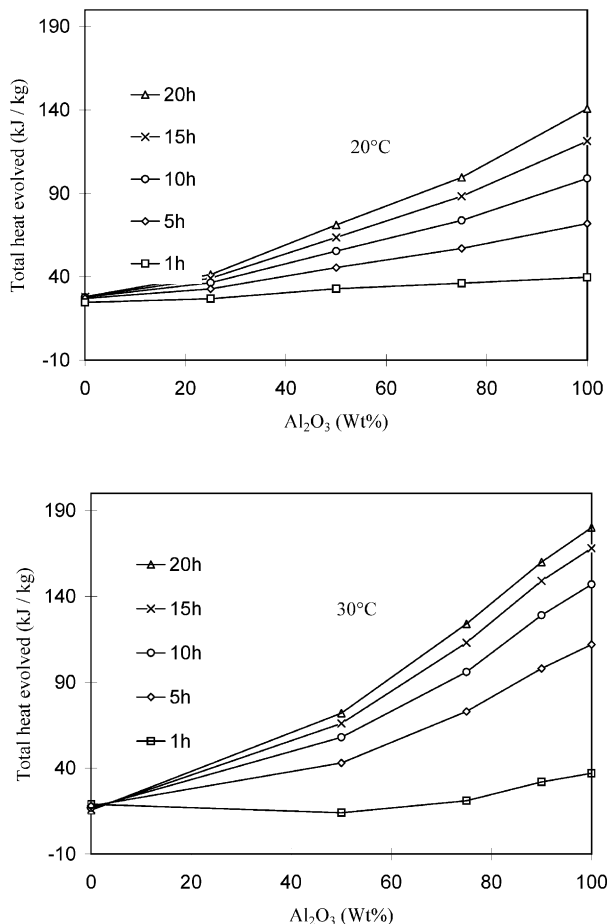


Fig. 3. Total heat evolution from mixtures with varying  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  ratios hydrated at 20 and 30 °C, using external mixing.

### 3.3. Hydration of magnesia–silica mixtures

Before describing the behaviour of these mixtures, it is necessary to discuss some unexpected observations at the start of the ICC experiments, after external mixing of the sample and water. It took 1–2 h, depending on the temperature difference between the laboratory temperature and that of the experiment, for the cell holding the sample to reach equilibrium with the water bath, once the test had started. The calorimeter did not immediately respond and the delay was sometimes as long as 60 min, then a huge off-scale exothermic departure from the base line was initiated followed by an endothermic deviation if there was no heat evolved from the sample. These features are shown in Fig. 4 for the ICC at 30 °C for mixtures of magnesia–silica using a log scale on the x-axis to expand the curves at the early stages of the experiment for further clarification. It demonstrates that with pure silica (curve E), which did not hydrate, the maximum endothermic deviation occurred, while on increasing the magnesia content of the samples this endothermic effect gradually decreased until it disappeared. A similar endothermic effect was

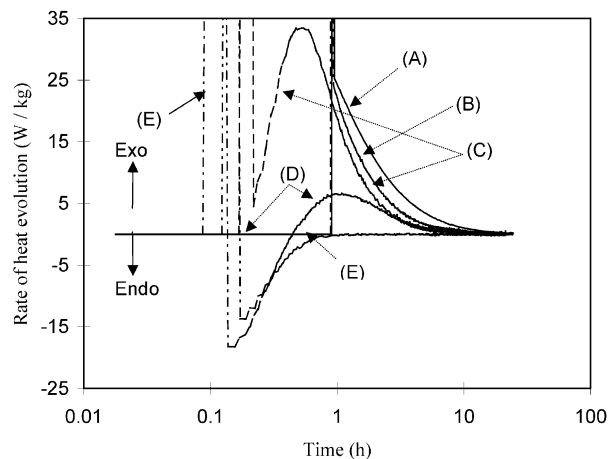


Fig. 4. Rate of heat evolution curves demonstrating hydration of magnesia–silica mixtures at 30 °C, using external mixing, with log-scale on the x-axis to show details of hydration at early stages of experiments.  $\text{MgO}$ :  $\text{SiO}_2$  ratios: (A) 100% magnesia, (B) 50:50, (C) 30:70, (D) 10:90, (E) 100% silica.

observed when 10%  $\text{MgO}$  was incorporated (curve D) and subsequently an exothermic peak was observed after about 1 h. Otherwise (curves A, B and C) no endothermic deviation was seen because it was overwhelmed by the exothermic heat evolution from the hydration of  $\text{MgO}$ .

ICC curves of magnesia and the magnesia–silica mixtures at 20 °C are shown in Fig. 5. Note the change of scale from Fig. 1. Hydration of pure magnesia started almost immediately after wetting, showed no dormant period and gave rise to a huge asymmetric hydration peak (curve A in Fig. 5a). This is in spite of much of the heat from the early stages of hydration being not recorded because of the use of external mixing. Further details of magnesia hydration were reported previously<sup>3</sup> and it was suggested that the heat of hydration of  $\text{MgO}$  is at least 600 kJ/kg. Only one hydration peak was observed in the magnesia–silica mixtures. In mixtures with higher magnesia content (e.g. pure  $\text{MgO}$  and 50:50) the early stages of hydration had taken place before the sample was placed in the calorimeter. With increasing silica content (magnesia–silica ratios of 30:70 and 10:90 shown as curves C and D in Fig. 5a) the hydration peak was delayed. Moving from curve A to curve E (pure magnesia to pure silica), the magnitude of the main hydration peak decreased and its maximum moved towards longer times. It is believed that the main peaks of the curves A and B are distorted by the artefact discussed above, and this was previously established by the use of internal mixing<sup>3</sup> (see Fig. 3 in part I).

ICC curves of the magnesia–silica mixtures at 30 °C are shown in Fig. 6. Rate of heat evolution curves (Figs. 5a and 6a) revealed that increasing the temperature from 20 to 30 °C accelerated the hydration reaction since the hydration peak in curve C moved to shorter times and became sharper and of greater magnitude.

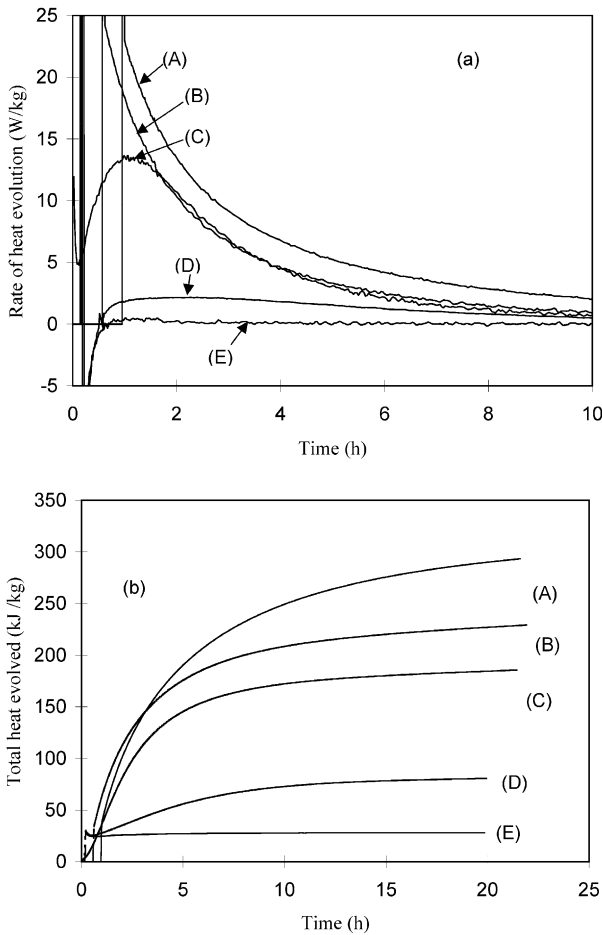


Fig. 5. ICC curves demonstrating hydration of magnesia-silica mixtures at 20 °C, using external mixing, (a) rate of heat evolution and (b) total heat evolved. MgO: SiO<sub>2</sub> ratios: (A) 100% magnesia, (B) 50:50, (C) 30:70, (D) 10:90 and (E) 100% silica.

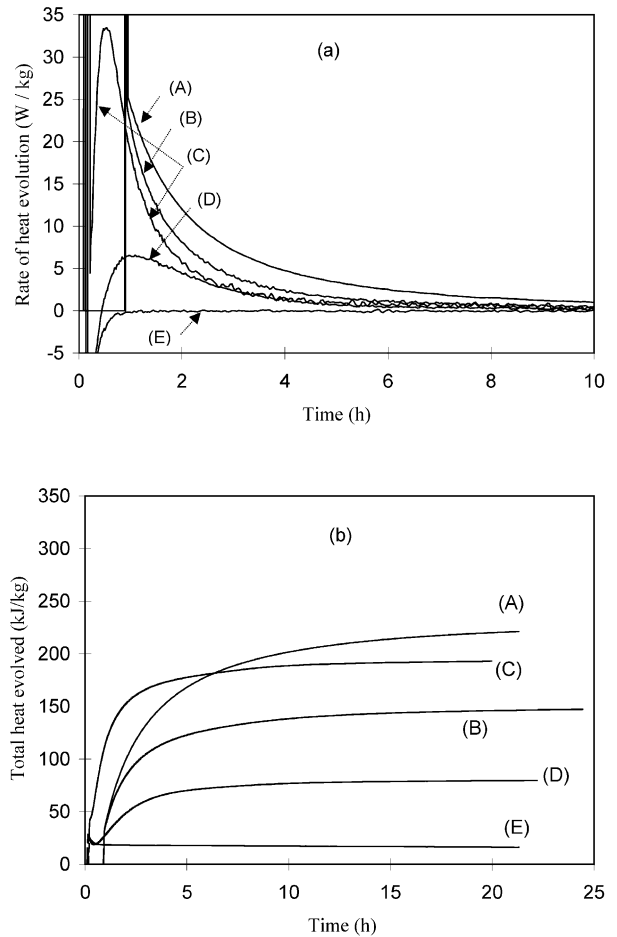


Fig. 6. ICC curves demonstrating hydration of magnesia-silica mixtures at 30 °C, using external mixing, (a) rate of heat evolution and (b) total heat evolved. MgO: SiO<sub>2</sub> ratios: (A) 100% magnesia, (B) 50:50, (C) 30:70, (D) 10:90, (E) 100% silica.

The accelerating effect of the temperature rise is not revealed by the total heat evolution curves (Figs. 5b and 6b) for mixtures with the higher MgO content, as a large portion of the hydration heat of these samples was not detected when using external mixing.

Hydration progressed rapidly at both temperatures and the rate of heat evolution after 20 h approached zero (Figs. 5a and 6a), which indicates reaction termination. This is also shown in the total heat evolution curves (Figs. 5b and 6b). The total heat evolution at 20 °C was usually greater than at 30 °C (Table 2) implying that the portion of undetected heat during initial mixing and placement in the calorimeter, which was more than 50% of the total heat, was greater at 30 °C than at 20 °C.

Data from the hydration of magnesia, silica and their mixtures (Table 2) have been used to construct Fig. 7, which shows the total heat evolution after 1, 5, 10, 15 and 20 h. Total heat evolution was proportional to magnesia content up to 30% MgO at 20 and 30 °C. Above this level of MgO the slopes of the curves change due to loss of much of the heat from the early stages of

Table 2

Sample composition (wt.%) and total heat evolution on hydration (kJ/kg) with time at 20 and 30 °C, using external mixing

Magnesia	Silica	Temp. °C	1 h	5 h	10 h	15 h	20 h
100	0	20	38	190	249	276	290
		30	38	168	202	214	220
90	10	20	54	174	224	245	255
		30	42	157	184	193	198
80	20	20	59	184	232	252	262
		30	35	142	162	168	171
50	50	20	63	176	208	220	227
		30	37	123	138	144	146
40	60	30	89	163	176	180	182
		30	70	145	172	180	184
25.8	74.2	30	115	178	190	192	193
		30	91	153	168	173	175
25	75	30	82	149	160	163	165
		30	82	149	160	163	165
10	90	20	28	56	73	78	81
		30	28	70	77	79	80
0	100	20	25	27	28	28	28
		30	18.5	18	17.4	17	16.3

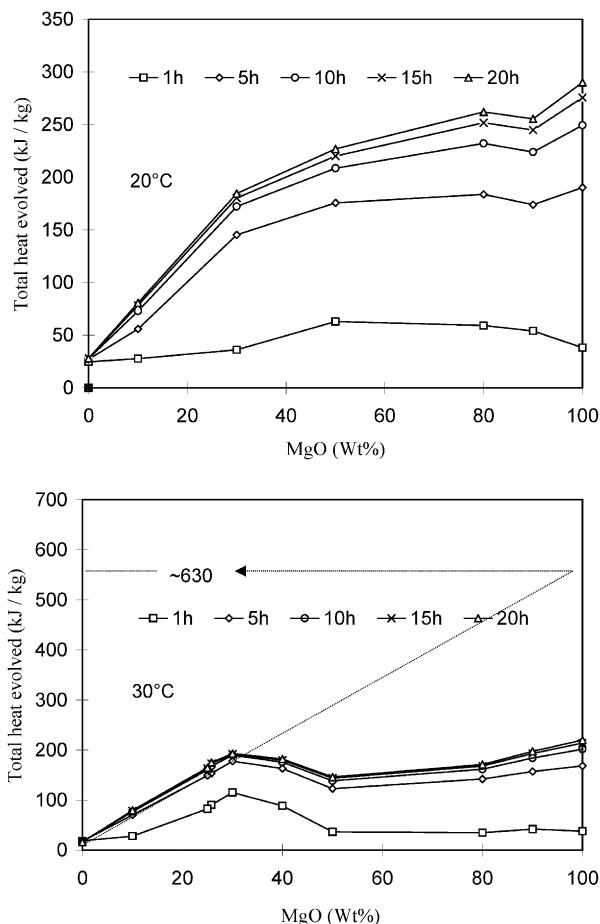


Fig. 7. Total heat evolution from mixtures with varying MgO : SiO<sub>2</sub> ratios hydrated at 20 and 30 °C, using external mixing.

hydration. It seems that at higher silica concentration the magnesia hydration was delayed and the heat evolved during its hydration was fully measurable. Extrapolation gives a linear relationship between total heat evolved and magnesia content at 30 °C as shown in Fig. 7b and gives an estimated heat of hydration for pure magnesia of about 630 kJ/kg.

XRD curves, shown in Fig. 8, showed that brucite was the major crystalline hydration product of the mixtures, and fumed silica remained amorphous during the hydration process. A few small peaks ( $d=3.03$ , 2.40 and 1.54 Å) were observed, which might be related to the presence of calcite impurity and/or to the emergence of a new magnesia–silica hydrated compound.

The strong brucite peaks were more intense in samples hydrated at the lower temperature, which might be related to the higher level of brucite formed. Attempts to measure the crystallite sizes of brucite in samples, with MgO : SiO<sub>2</sub> ratio of 30:70 revealed that the average crystallite size of the sample hydrated at 20 °C was higher (302 nm based on the (100) peak; 268 nm based on (101) peak) than that at 30 °C (252 nm based on the (100) peak; 231 nm based on the (101) peak).

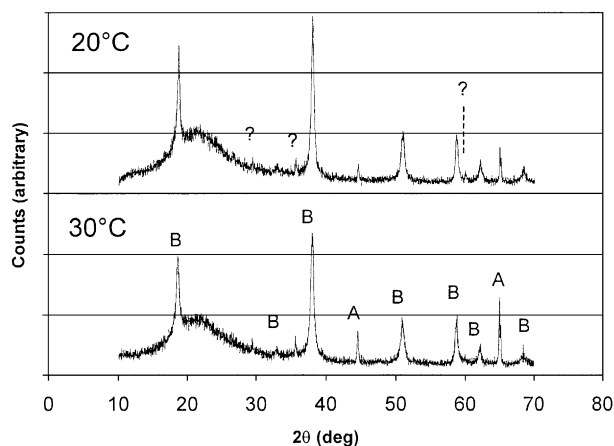


Fig. 8. XRD of magnesia–silica mixture [MgO:SiO<sub>2</sub> (30:70)] hydrated for 22 h at 30 °C, (a) 20 °C and (b) 30 °C. B = brucite, A = aluminium (sample holder).

Thermal decomposition studies of the hydration products of a mixed sample by TG (Fig. 9) showed a similar weight loss pattern to that of pure brucite,<sup>3</sup> where the magnitude of the weight loss is proportional to the amount of magnesia in the original sample. Decomposition of the sample hydrated at the higher temperature seemed to be slightly delayed and showed a lower total weight loss.

#### 4. Further discussion

Hydration of alumina–silica mixtures at 20 and 30 °C showed no sign of hydrate phase formation, in contrast to the alumina–magnesia mixtures when hydrotalcite was clearly formed.<sup>3</sup> To form mullite in such bond systems requires a higher temperature, which is dependent on the intimacy of the mixing of the alumina and silica. Addition of other sources of combined silica and alumina

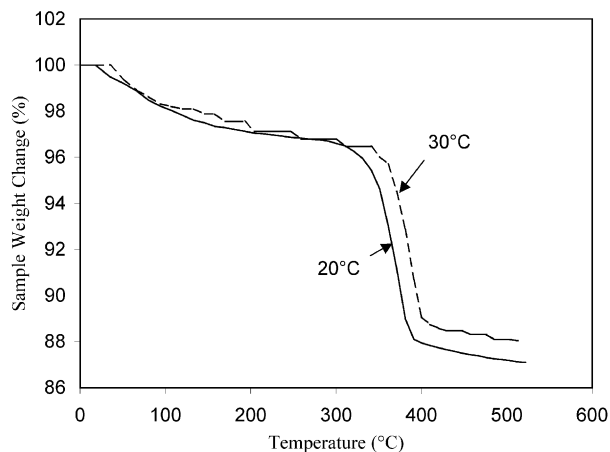


Fig. 9. TG demonstrating dehydration sequences of magnesia–silica mixture [MgO : SiO<sub>2</sub> (30:70)] hydrated for 22 h at 20 and 30 °C.

such as fine pure kaolinite, metakaolin, kyanite, sillimanite and andalusite might assist mullite formation.

With regard to the hydration of magnesia–silica mixtures, silica had a retarding effect on the hydration of magnesia. Therefore with lower concentration of magnesia (up to 30%) almost all of the hydration heat is measurable on using external mixing. Samples with higher magnesia concentration hydrated rapidly and a large portion of the heat escaped without detection.

Crystallite sizes of the magnesia are an important parameter on hydration of magnesia and its mixtures. Highly reactive magnesia when used in castable formulations requires more water and fully hydrates before setting the cast body. The presence of this type of magnesia creates difficulties in the flow and placement of the castables. Using fine magnesia with larger crystallite size lessens placement problems but increases the potential for swelling and cracking of the cast body due to in service hydration.

## 5. Conclusions

1. The rate and total heat evolved during hydration of binary mixtures of alumina (Actibond 102) and reactive magnesia with fumed silica have been determined.
2. Pure fumed silica showed no sign of hydration.
3. Alumina did not form a hydrated compound with silica under the experimental conditions. The first exotherm (at ca. 1 h at 20 °C and slightly less at 30 °C) changed little in time, but decreased in magnitude, with increase in silica content, which simply acted as an inert diluent. The second exotherm (ca. 22 h at 20 °C and ca. 9 h at 30 °C) was delayed by the incorporation of silica.
4. Magnesia hydration was retarded at high silica concentrations and there was little evidence for any interaction between the two oxides.

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