

# Silicate bonding of inorganic materials

## Part II *Reactions at high temperatures*

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The high-temperature behaviour of compacts pressed from granular minerals bonded with sodium silicate and treated with CO<sub>2</sub>, SO<sub>2</sub> or H<sub>2</sub>S to produce good green (unfired) strength was studied. Samples gassed with CO<sub>2</sub> contain bicarbonate and carbonate species which decompose on heating in at least four stages up to 1000 °C. IR spectroscopy suggests that the more thermally stable species may be silicate carbonates. The temperatures of the decomposition reactions depend on the nature of the mineral matter and the composition of the sodium silicate. On heating, the sulphite species formed during SO<sub>2</sub>-gassing are oxidized to sulphate which thermally decomposes with evolution of SO<sub>2</sub> in several stages, suggesting the presence of silicate-sulphate complexes, by analogy with the carbonated system. Heated H<sub>2</sub>S-gassed specimens form oxy-sulphur species which behave differently to those of the SO<sub>2</sub>-treated system. The fired strength of CO<sub>2</sub>, SO<sub>2</sub> and H<sub>2</sub>S-gassed specimens is generally greater than for ungasped materials. With CO<sub>2</sub> gassing, the greatest improvement in strength is obtained with sodium silicates of lower pH (higher SiO<sub>2</sub>:Na<sub>2</sub>O ratio).

### 1. Introduction

In Part 1 of this paper [1], the effect of the acidic gases CO<sub>2</sub>, SO<sub>2</sub> and H<sub>2</sub>S on the room-temperature setting reaction in sodium silicate-bonded mineral compacts was investigated, and the nature of the room-temperature reaction products reported. Although silicate bonding is normally used as a means of achieving temporary hardness in articles such as foundry moulds which are later knocked to pieces and removed from the casting, another potential use of the gassed-silicate bonding technique is to establish green (unfired) strength in ceramic materials which are subsequently permanently hardened by heating to high temperatures [2]. The effect of heating on the properties of gassed silicate-bonded mineral compacts is not well known, and neither have previous studies been reported of the way in which the chemistry of the high-temperature bonding process is modified by the presence of sulphites, carbonates or polysulphides formed during the gassing process. The present work was, therefore, carried out to investigate the thermal reactions occurring in sodium silicates gassed with CO<sub>2</sub>, SO<sub>2</sub> and H<sub>2</sub>S, and the effect of these reactions on the fired strength of a variety of mineral compacts bonded by sodium silicates hardened by exposure to these gases.

### 2. Experimental procedure

The four sodium silicates and the various types of granulated mineral materials used in this work are described in Part 1 of this paper [1]. Sodium silicate samples were hardened by bubbling either CO<sub>2</sub>, SO<sub>2</sub> or H<sub>2</sub>S through them. They were then fired to various temperatures from 110 to 910 °C for 15 min in am-

bient air in platinum-lined ceramic boats in an electric laboratory furnace. After cooling, the samples were examined by IR spectroscopy and X-ray powder diffraction, as previously described [1].

Pellets of various mineral granules containing 5 wt % sodium silicate were pressed at 20 MPa and gassed for varying times, as previously described [1]. The evolution of gaseous reaction products during heating was studied by placing a gassed pellet in a reaction boat in an electric tube furnace through which a stream of instrument-grade oxygen-free nitrogen (0.1 l min<sup>-1</sup>) was passed as a carrier gas. The outlet of the firing tube was connected to a gas cell in a Perkin-Elmer 337 spectrophotometer set to the characteristic wavelength of the gas being monitored (CO<sub>2</sub> or SO<sub>2</sub>). The sample was heated at a programmed linear rate of 10 °C min<sup>-1</sup> during which the changes in the intensity of the characteristic IR absorption band resulting from gas evolution were monitored.

In other experiments, a series of gassed pellets prepared as above were fired in a large temperature-programmable chamber kiln at a heating rate of 3 °C min<sup>-1</sup>, up to 1000 °C, held at this temperature for 60 min and cooled at 10 °C min<sup>-1</sup>. The tensile strengths of these pellets were then measured by breaking them across the diameter, as previously described [1], using an Instron model TTCM Universal testing machine at a crosshead speed of 5 mm min<sup>-1</sup>.

### 3. Results and discussion

#### 3.1. Evolved gas analysis

##### 3.1.1. Gassing with CO<sub>2</sub>

As the CO<sub>2</sub>-gassed samples are heated, the various carbonate species decompose at different temperatures, which were determined by monitoring the

temperature dependence of CO<sub>2</sub> evolution. Fig. 1 shows a series of CO<sub>2</sub> evolution curves from silica sand bonded with sodium silicate NA45 and gassed for varying times.

The ungassed control sample (Fig. 1f) shows a very slight CO<sub>2</sub> evolution, arising from carbonation by atmospheric CO<sub>2</sub>. By comparison, quite different CO<sub>2</sub> evolution curves result from gassing for varying periods. At shorter gassing times, the major CO<sub>2</sub> evolutions occur at 350 to 700 °C (Fig. 1d and 1e), whereas after longer gassing times, a significant proportion of the CO<sub>2</sub> is evolved at 25 to 200 °C (Fig. 1a, 1b and 1c), possibly resulting from the decomposition of less thermally stable species such as NaHCO<sub>3</sub> [1], or from the desorption of excess chemisorbed CO<sub>2</sub>. A few experiments were made using a quadrupole mass spectrometer (Extranuclear Inc.) to analyse the evolved gas. The CO<sub>2</sub> evolution curves thus obtained

were similar to those obtained using the IR gas cell, and no other gas species were detected in the gaseous reaction products.

Another important point which emerges from Fig. 1 is the completely different CO<sub>2</sub> evolution behaviour observed when the silica sand is treated with an equivalent concentration of Na<sub>2</sub>CO<sub>3</sub> solution and dried (Fig. 1g). This sample decomposes in two stages, at about 600 and 900 °C, with a small evolution at 175 °C. The dissimilar decomposition behaviour of the gassed silicates suggests that their CO<sub>2</sub> does not simply originate from the sodium carbonate shown by IR spectroscopy to be present in the early stages [1], but indicates the presence of different carbonated species, possibly silicate carbonates.

The influence of the mineral matter on the thermal decomposition of the carbonated species formed during CO<sub>2</sub> gassing is shown in Fig. 2.

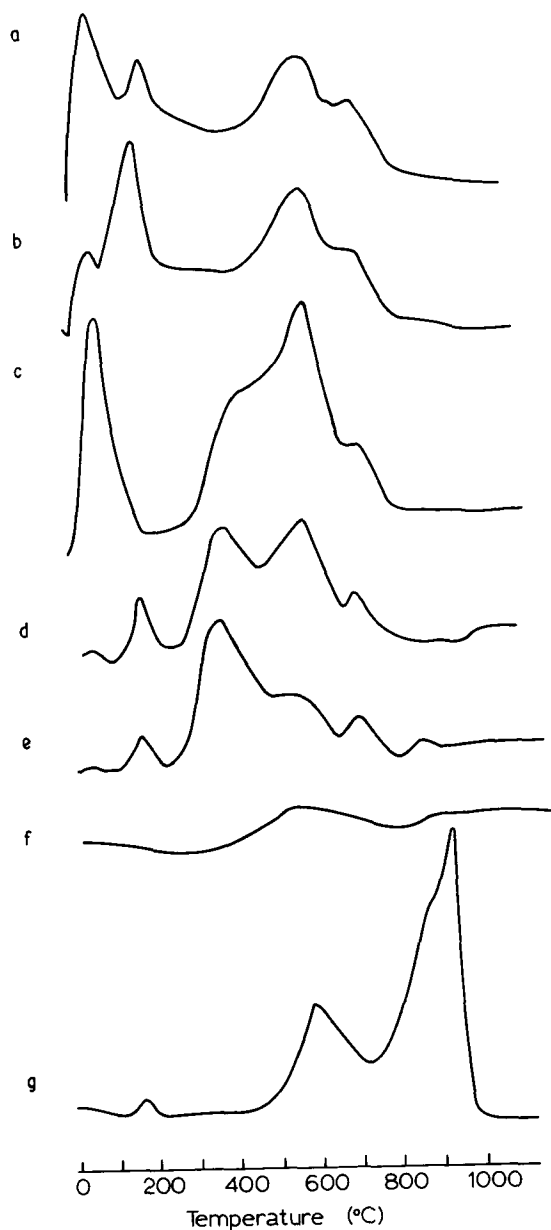


Figure 1 Effect of gas treatment time (*g*) on the thermal evolution of CO<sub>2</sub> from compacts of calcined BDH silica sand bonded with sodium silicate NA45. (a, *g* = 3 min; b, *g* = 2 min; c, *g* = 1 min; d, *g* = 0.5 min; e, *g* = 0.16 min; f, ungassed; g treated with equivalent moles of Na<sub>2</sub>CO<sub>3</sub> solution)

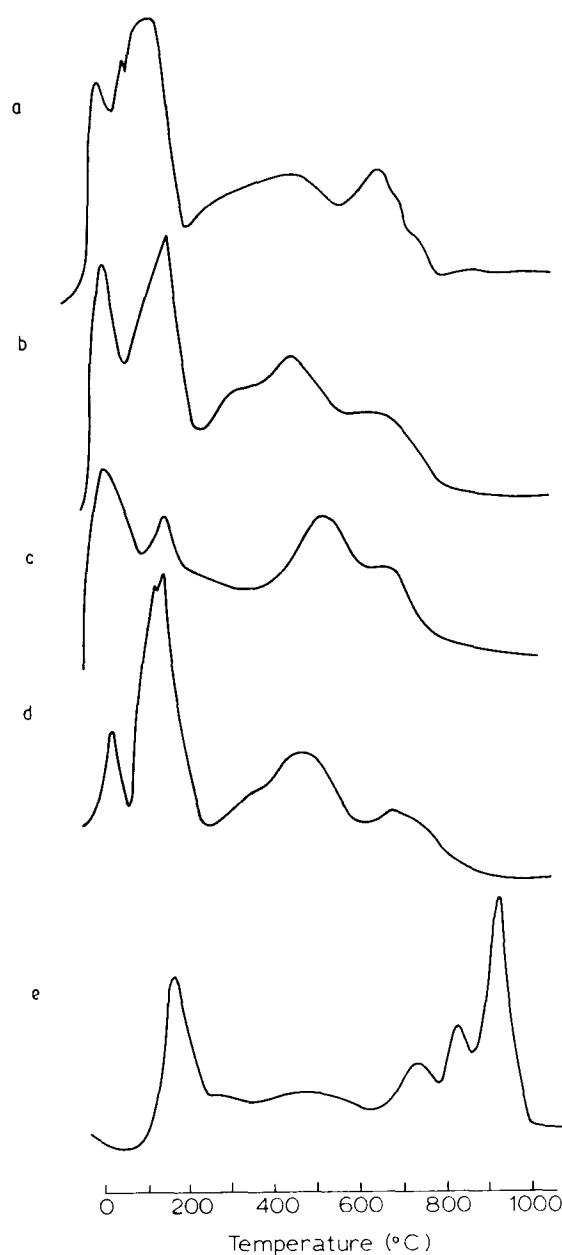


Figure 2 Thermal evolution of CO<sub>2</sub> from various mineral compacts bonded with sodium silicate N42, CO<sub>2</sub> gassing time 5 min (a, ironsand; b, ironsand and glass; c, silica sand; d, silica sand and glass; e, sodium silicate alone)

A common feature of all these mineral samples is the presence of four major carbonate decomposition peaks in each, but the relative magnitude of these thermal events varies with the nature of the mineral matter being bonded. This effect is particularly evident in the two lowest-temperature reactions, and is clearly seen to be a function of the presence of the mineral matter, since with the same sodium silicate, gassed under identical conditions in the absence of mineral matter, an entirely different CO<sub>2</sub> evolution curve is obtained (Fig. 2e). The presence of the mineral matter lowers the temperature at which all the CO<sub>2</sub> is evolved from 925 °C (Fig. 2e) to about 700 °C (Fig. 2a to 2d).

The effect of gassing sodium silicates of different pH is shown in Fig. 3.

Again, the thermal decomposition behaviour of the lowest-temperature reactions shows the greatest variation with pH of the sodium silicate; at the lowest pH, under identical gassing conditions, neutralization will

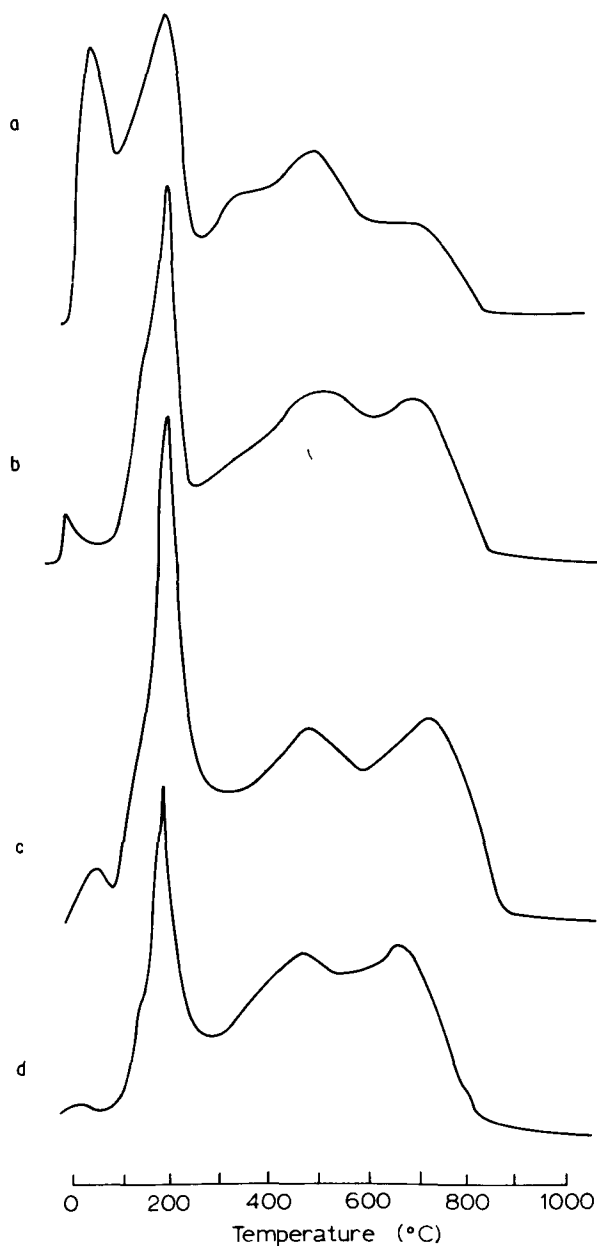


Figure 3 Thermal evolution of CO<sub>2</sub> from ironsand-glass compacts bonded with sodium silicates of various pH, CO<sub>2</sub> gassing time 5 min. (a, pH = 11.5; b, pH = 12.2; c, pH = 12.6; d, pH = 12.7)

occur more rapidly than in sodium silicates of higher pH. Thus, the reaction in the lowest pH sodium silicate is characterized by a marked increase in the evolution of CO<sub>2</sub> at lower temperatures, suggested previously to be due to the decomposition of NaHCO<sub>3</sub> [1], or to the desorption of excess chemisorbed CO<sub>2</sub>.

Attempts were made to identify the phases formed at various stages of the thermal decarboxylation sequence, using X-ray diffraction and IR spectroscopy. To avoid masking the small concentrations of reaction products, the samples for this work did not contain mineral matter, and are thus more comparable with the sample shown in Fig. 2e. This drawback was, unfortunately, unavoidable.

X-ray powder diffraction indicates that the as-prepared samples are non-crystalline, and remain so up to about 500 °C, when they assume a crystalline structure strongly resembling Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> (JCPDS card no. 22-1396). This phase persists up to > 700 °C, but by 900 °C, the sample has re-melted and again become X-ray amorphous. Since CO<sub>2</sub> is evolved in at least three stages between 700 to 900 °C (Fig. 2e), the crystalline silicate phase must contain carbonate in at least three types of environment. The alternative possibility, that the carbonate is associated with a residual non-crystalline phase, is not consistent with the X-ray patterns of samples heated at 500 and 700 °C, which show no evidence of amorphous material. Note, however, that X-ray diffraction is not very sensitive to small amounts of amorphous material such as the silica which is predicted from stoichiometric considerations to accompany the formation of crystalline Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>. The IR spectra of these samples (Fig. 4) indicate the presence of some Na<sub>2</sub>CO<sub>3</sub> in the sample heated to 310 °C (Fig. 4a), in common with samples dried at 110 °C [1]. Heating to 510 °C removes the characteristic sodium carbonate band at 860 cm<sup>-1</sup> (Fig. 4b), but the CO<sub>2</sub>-gassed spectrum is dissimilar from that of the un-gassed silicate heated at 510 °C (Fig. 4c); the latter contains less fine structure in the Si-O stretching region (970 to 1120 cm<sup>-1</sup>) and the Si-O bending region (460 to 510 cm<sup>-1</sup>). A strong band at 545 cm<sup>-1</sup> in the gassed material may correspond to a lower-intensity band at 590 cm<sup>-1</sup> in the un-gassed sample. These changes, which are consistent with an increase in the crystallinity of the gassed sample fired at 510 °C by comparison with the un-gassed, are still evident in samples fired at 710 °C, by which temperature the gassed and un-gassed spectra have become more similar. By 910 °C, the spectra are much broadened (Fig. 4d), consistent with re-melting, and there are no significant spectral differences between the gassed and un-gassed materials.

These results suggest that the formation of carbonate compounds other than sodium carbonate may occur at 300 to 500 °C; although the X-ray pattern of the crystalline sodium silicate which is the most likely host of these carbonate groups is not significantly altered in the gassed specimens, the IR spectra are considerably different. The incorporated carbonate groups are progressively eliminated on further heating above 710 °C.

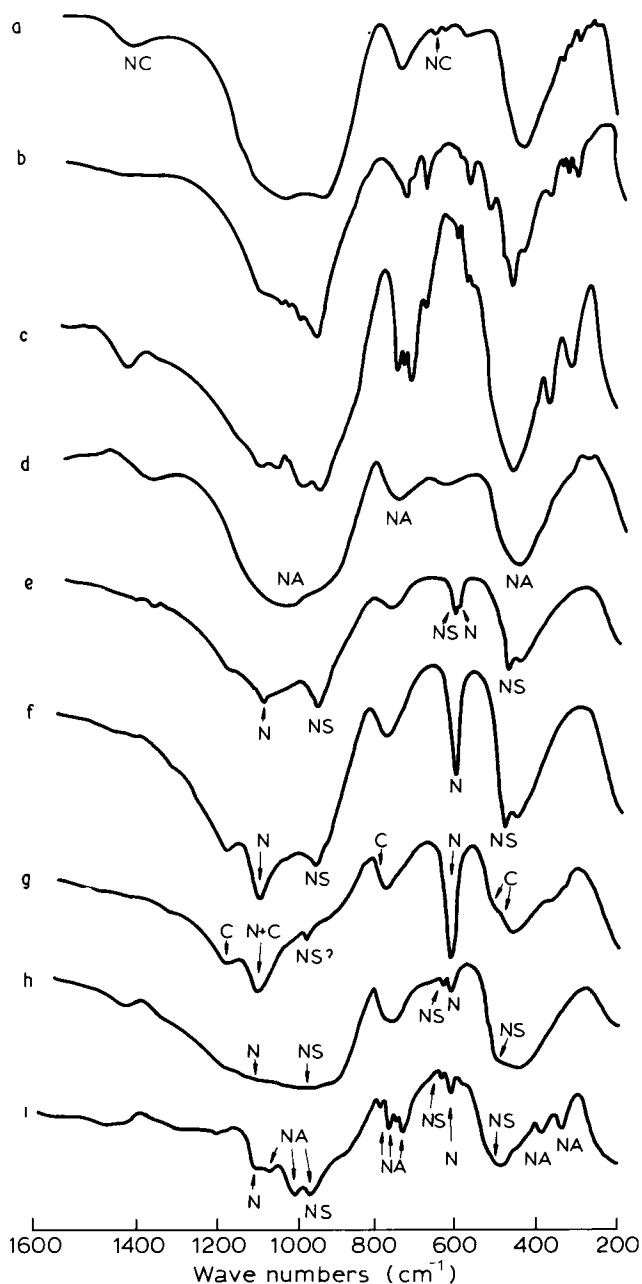
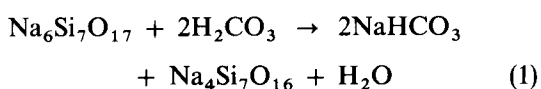
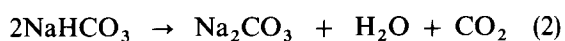


Figure 4 IR spectra of gas-treated sodium silicate NA56 heated to various temperatures. (NA sodium silicate, NC sodium carbonate, NS sodium sulphite, N sodium sulphate, C cristobalite). (a, CO<sub>2</sub>, 310 °C; b, CO<sub>2</sub>, 510 °C; c, ungasged, 510 °C; d, CO<sub>2</sub>, 910 °C; e, SO<sub>2</sub>, 310 °C; f, SO<sub>2</sub>, 510 °C; g, SO<sub>2</sub>, 710 °C; h, H<sub>2</sub>S, 510 °C; i, H<sub>2</sub>S, 710 °C)

Since the initial composition of sodium silicate NA56 approximates to Na<sub>6</sub>Si<sub>7</sub>O<sub>17</sub> [1], the reaction sequence with CO<sub>2</sub> may be written as follows

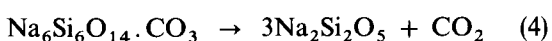
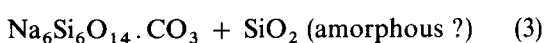


On heating, the bicarbonate decomposes



On further heating,

Na<sub>4</sub>Si<sub>7</sub>O<sub>16</sub> + Na<sub>2</sub>CO<sub>3</sub> → Carbonato species such as



### 3.1.2. Gassing with SO<sub>2</sub>

The evolution of SO<sub>2</sub> from SO<sub>2</sub>-gassed samples is shown as a function of heating temperature in Fig. 5.

The SO<sub>2</sub> is evolved in at least four separate steps, the temperatures of which depend on the mineral matter being bonded. X-ray powder diffraction of sodium silicate treated with SO<sub>2</sub> in the absence of mineral matter indicates the initial formation of Na<sub>2</sub>SO<sub>3</sub> · 7H<sub>2</sub>O and possibly Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>, which transforms to crystalline Na<sub>2</sub>SO<sub>3</sub> below 100 °C. The Na<sub>2</sub>SO<sub>3</sub> persists up to 500 °C, by which temperature some oxidation to Na<sub>2</sub>SO<sub>4</sub> has occurred. This result is confirmed by the IR spectra, in which at 510 °C the bands of both Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> appear (Fig. 4f). By 710 °C, oxidation to Na<sub>2</sub>SO<sub>4</sub> is complete and SiO<sub>2</sub> (cristobalite) is also present (Fig. 4g), resulting from the breakdown of the sodium silicate. Based on the

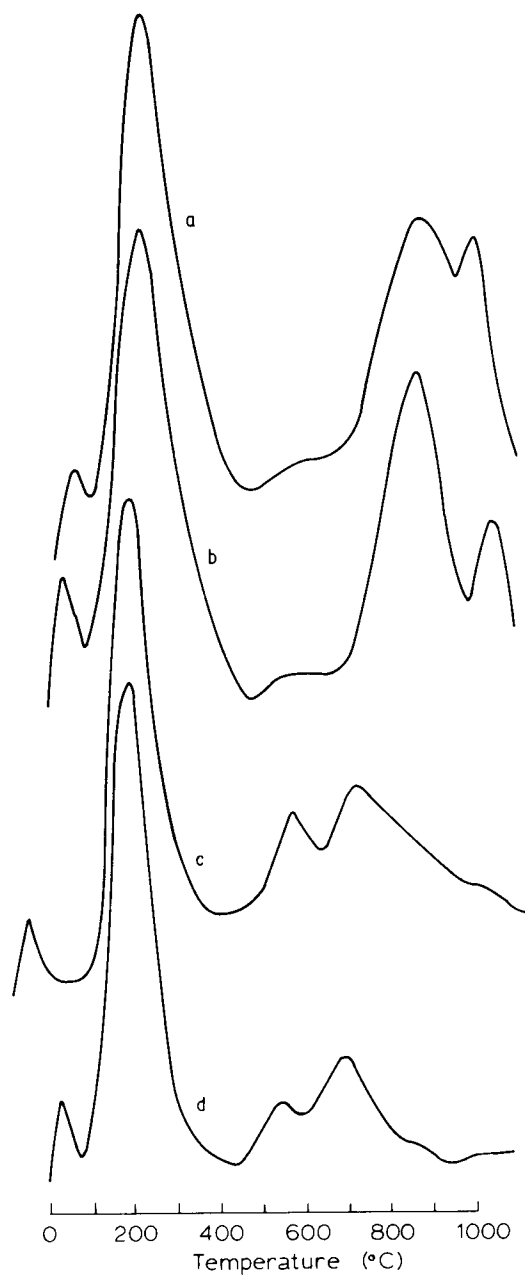
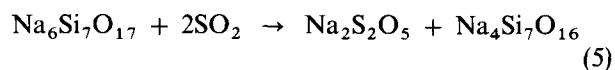
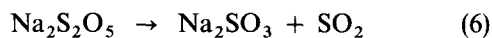


Figure 5 Thermal evolution of SO<sub>2</sub> from various mineral compacts bonded with sodium silicate NA56, SO<sub>2</sub> gassing time 2 min (a, ironsand, b, ironsand and glass; c, silica sand, d, silica sand and glass).

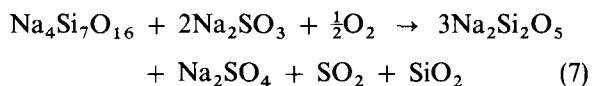
initial composition of sodium silicate NA56, the initial reaction with  $\text{SO}_2$  may be written



followed almost immediately by



This provides an explanation for the low-temperature elimination of  $\text{SO}_2$ . On heating in air, one of the principal reactions can be written



By contrast with the reaction in the  $\text{CO}_2$ -gassed and un-gassed samples, crystalline  $\text{Na}_2\text{Si}_2\text{O}_5$  does not appear during thermal decomposition of the  $\text{SO}_2$ -gassed sodium silicate. The only crystalline phases to be detected ( $\text{Na}_2\text{SO}_4$  and cristobalite) survive heating at  $910^\circ\text{C}$ . Further, the evolution of  $\text{SO}_2$  in several discrete steps suggests that Reaction 7 is not the only mechanism for higher temperature  $\text{SO}_2$  elimination. Other reaction paths may involve the decomposition of silicate sulphate complexes, analogous to the reactions with  $\text{CO}_2$ . Surface reactions with the mineral matter, when present, may also be important, but the present data give no information on the possible nature of such interactions.

### 3.1.3. Gassing with $\text{H}_2\text{S}$

Evolved gas analysis experiments with  $\text{H}_2\text{S}$ -gassed samples were unsuccessful; neither  $\text{H}_2\text{S}$  nor oxidised species such as  $\text{SO}_2$  could be detected. This result is consistent with the known stability of sulphur-containing species in glasses, which forms the basis for the production of amber and blue colours in glass [3]. Other factors possibly contributing to the absence of an observed evolved gas signal are the lack of sensitivity in the IR detection of  $\text{H}_2\text{S}$  and the presence of only low concentrations of  $\text{SO}_2$ . X-ray diffraction of heated sodium silicate NA56 gassed with  $\text{H}_2\text{S}$  showed the material to be amorphous below  $310^\circ\text{C}$ , at which temperature a small amount of crystalline  $\text{SiO}_2$  (quartz) appears. Between  $510$  and  $710^\circ\text{C}$ , a small amount of crystalline  $\text{Na}_2\text{Si}_2\text{O}_5$  appears, in addition to the amorphous material and quartz. The  $\text{Na}_2\text{Si}_2\text{O}_5$  disappears on remelting at  $910^\circ\text{C}$ , leaving a small amount of quartz as the only crystalline phase at this temperature. IR spectroscopy suggests the possible presence of small traces of  $\text{Na}_2\text{SO}_3$  and  $\text{Na}_2\text{SO}_4$  at  $310^\circ\text{C}$ . These phases become increasingly evident as heating progresses up to  $710^\circ\text{C}$  (Fig. 4h and 4i). Remelting at  $910^\circ\text{C}$  produces a broad spectrum very similar to un-gassed sodium silicate heated to this temperature, but with some differences in the Si-O bending region, in which peaks occur at  $440$  and  $490\text{ cm}^{-1}$  (cf. a single peak at  $455\text{ cm}^{-1}$  in the un-gassed sample). Further, although some of the species formed during heating of  $\text{H}_2\text{S}$ -gassed sodium silicate are similar to those found in  $\text{SO}_2$ -gassed samples, the final outcomes of the two reaction sequences are not identical; cristobalite and  $\text{Na}_2\text{SO}_4$  are present at

$910^\circ\text{C}$  in  $\text{SO}_2$ -gassed materials, by contrast with quartz and an X-ray amorphous phase in  $\text{H}_2\text{S}$ -gassed samples at that temperature. The  $\text{H}_2\text{S}$ -treated system offers considerable scope for the formation of sulphur-bearing phases, especially in the presence of mineral matter, which could act as a source of other cations present in such sulphide-bearing silicates as ultramarine ( $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_2$ ) or the helvine family ( $[\text{Fe}, \text{Mn}, \text{Zn}]_4 [\text{Be}_3\text{Si}_3\text{O}_{12}]_4\text{S}$ ).

## 3.2. The effect of gas treatment on the fired strength of mineral compacts

### 3.2.1. $\text{CO}_2$ -gassed samples

The statistical nature of tensile strength measurements means that these are subject to considerable scatter. To take account of this, the strengths of the mineral compacts fired at  $1000^\circ\text{C}$  for 60 min were deduced from the mean of a number of measurements (between 4 and 15 samples). Experiments made at different gassing times from 30 to 150 sec showed no statistically significant dependence of fired strength on gassing time for any of the sodium silicates or mineral compositions investigated. There was, however, an increase in the mean fired strength of the gassed samples over the un-gassed controls, as shown in Fig. 6. The mean fired strengths of the un-gassed samples are shown in Table I.

Fig. 6 shows that with  $\text{CO}_2$  gassing, the greatest increases in fired strength in all the mineral compacts investigated was produced with the sodium silicates of

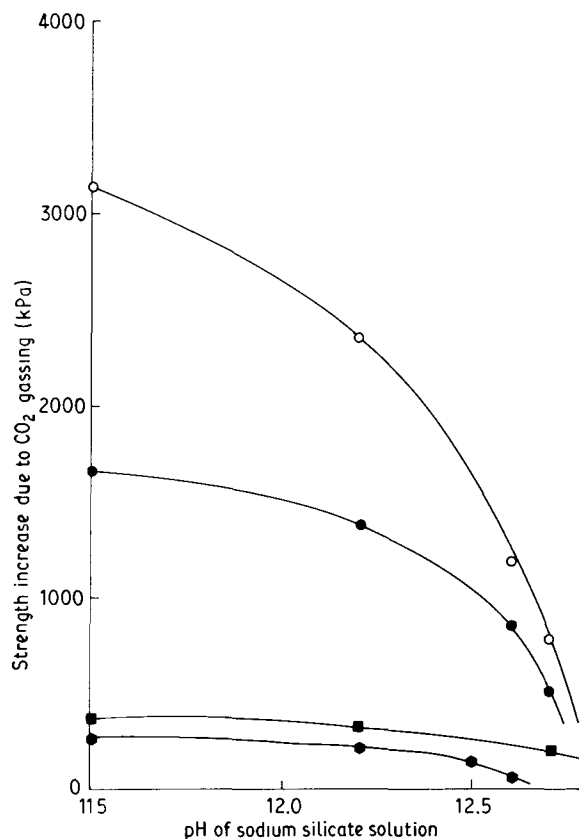


Figure 6 Increase in fired strength of various mineral compacts bonded with sodium silicates of various pH,  $\text{CO}_2$  gassed and fired to  $1000^\circ\text{C}$ . (○ ironsand and glass, ● ironsand, ■ silica sand and glass, ● silica sand).

TABLE I Mean fired strengths of ungasged mineral compacts bonded with various sodium silicates. Standard deviations range from 30 to 691 kPa

Mineral compact	Ungasged fired strength (kPa)			
	NA42	NA56	A60	A53
Ironsand	2753	2853	5572	5025
Ironsand-glass	6966	13190	14025	14570
Silica sand	208	548	535	735
Silica sand-glass	2299	2442	2491	—

lowest pH (highest SiO<sub>2</sub>:Na<sub>2</sub>O ratio), the effect decreasing as the pH increases. The greatest strength gains on gassing were achieved in the ironsand-containing samples, especially those containing glass (Fig. 6); silica sand showed only small gains in fired strength as a result of gassing, although the inclusion of glass improved the strength gain slightly.

In the first part of this paper [1] it was shown that the ultimate green strength of CO<sub>2</sub>-gassed mineral compacts *increases* with increasing pH of the sodium silicate used, although the sodium silicates of highest pH require longer gassing times to achieve ultimate strength, and give compacts which have been reported to deteriorate on ageing. By contrast, the greatest increases in fired strengths are achieved with sodium silicates of lower pH. In optimizing the gassed silicate bonding method for the production of fired ceramic materials, the selection of the sodium silicate would, therefore, represent a compromise between the conflicting requirements of green strength and fired

strength. On this basis, a silicate of intermediate pH such as NA56 should provide the best combination of green and fired strengths in minerals of the type studied here.

### 3.2.2. SO<sub>2</sub> and H<sub>2</sub>S-gassed samples

The only experiments carried out using these gases were made with sodium silicate NA56 (pH = 12.2). As with CO<sub>2</sub>, no dependence of fired strength on gassing time was observed with SO<sub>2</sub> or H<sub>2</sub>S, but the gassed samples generally showed an increase in strength over the ungasged. As with CO<sub>2</sub>, the greatest increase in strength occurred with ironsand-containing compositions, but unlike the CO<sub>2</sub>-gassed samples, the addition of glass to the ironsand produced weaker rather than stronger compacts. These results are summarized semi-schematically in Fig. 7.

Fig. 7 illustrates the comparatively strong effect exerted by SO<sub>2</sub> and H<sub>2</sub>S-gassing on both ironsand- and silica sand-glass compositions. These results suggest the operation of quite complex high-temperature interactions between the mineral grains being bonded and the glass, the composition of which is modified by the presence of the gassing products as identified in the previous section. The point of practical significance which emerges from Figs 6 and 7 is that gassing treatments which can be used to provide good green strength in the silicate-bonded mineral compacts studied here do not compromise the fired strength of any of the specimens and, with some combinations of mineral matter and sodium silicates, produce a very significant increase in the fired strength.

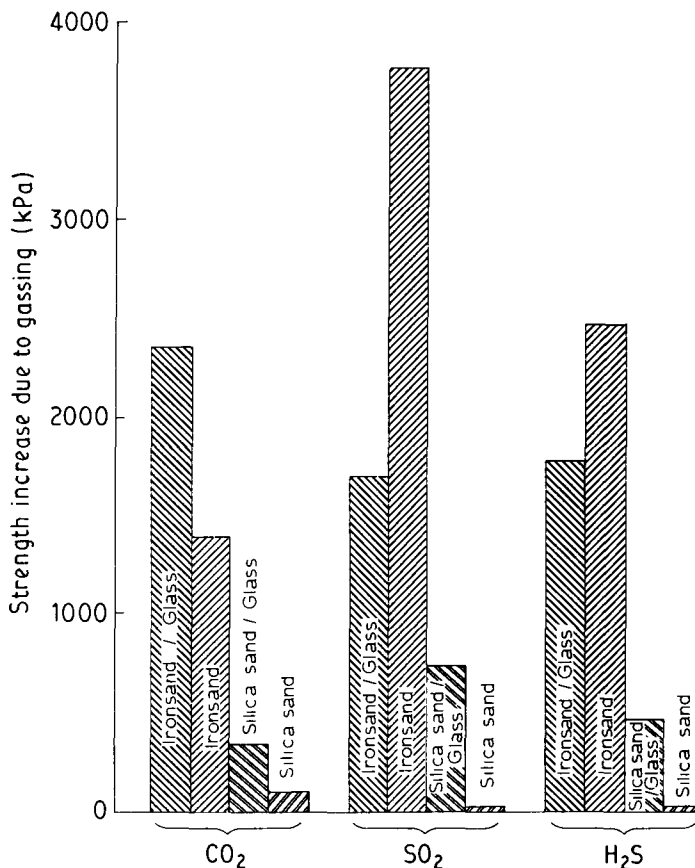


Figure 7 Semi-schematic representation of the increase in fired strength of various mineral compacts bonded with sodium silicate, NA56, gassed with CO<sub>2</sub>, SO<sub>2</sub>, or H<sub>2</sub>S and fired to 1000 °C.

#### 4. Conclusions

The conclusions are as follows.

(1) The carbonate species formed by reaction of CO<sub>2</sub> with sodium silicate in the presence of mineral matter decompose in at least four steps when heated to 1000 °C. The lowest-temperature reaction corresponds to the decomposition of bicarbonate to form carbonate, but IR spectroscopy suggests that the more thermally stable species may be silicate carbonates. Furthermore, the evolution of CO<sub>2</sub> from the gassed silicate specimens follows a quite different pattern to the thermal decomposition of samples containing an equivalent concentration of Na<sub>2</sub>CO<sub>3</sub>, suggesting the formation of complex carbonate species in the heated carbonated samples. The gas evolution patterns from these materials vary with the mineral matter being bonded and, to a lesser extent, with the composition of the sodium silicate.

(2) The reaction between sodium silicate and SO<sub>2</sub> forms crystalline Na<sub>2</sub>SO<sub>3</sub> which on heating at 500 to 700 °C oxidizes to Na<sub>2</sub>SO<sub>4</sub>. Thermal evolution of SO<sub>2</sub> occurs in several stages, suggesting the presence of silicate sulphate species analogous to those formed in the carbonated system, although no direct evidence of such complex species was found by IR spectroscopy or X-ray diffraction.

(3) Although the detection of thermally evolved gas from H<sub>2</sub>S-treated samples proved impossible, probably due to the thermal stability of sulphide species in glass, small amounts of Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> were detected by IR spectroscopy in samples heated at 300

to 700 °C. On further heating, these phases behave differently to those of the SO<sub>2</sub>-treated system, possibly due to the greater scope for forming sulphide-silicate phases, particularly in the presence of mineral matter which acts as a source of other cations.

(4) The treatment of sodium silicate-bonded mineral compacts with CO<sub>2</sub>, SO<sub>2</sub> or H<sub>2</sub>S to secure green (unfired) strength generally also increases the fired strength of the pellets. The magnitude of the improvement depends on the nature of the minerals being bonded and on the composition of the sodium silicate, the greater fired strengths in CO<sub>2</sub>-gassed samples being obtained with sodium silicates of lower pH (higher SiO<sub>2</sub> to Na<sub>2</sub>O ratio).

#### Acknowledgements

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