

Silicate bonding of inorganic materials

Part I *Chemical reactions in sodium silicate at room temperature*

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The room-temperature setting process in compacts of various silicate and non-silicate mineral particles bonded with sodium silicate was found to be markedly accelerated by treatment with the acidic gases CO_2 , SO_2 and H_2S , but was unaffected by neutral or alkaline gases. Strength development increases with gassing time up to a maximum value which depends on the Si to Na ratio of the sodium silicate, the nature of the mineral matter and the gas used. Longer gassing times are needed to achieve ultimate strength with sodium silicates of higher pH and gases of lower solubility in water. The chemical species formed by reaction of CO_2 , SO_2 and H_2S with sodium silicate were investigated by IR spectroscopy, X-ray diffraction and ^{29}Si solid state NMR spectroscopy.

1. Introduction

The process of bonding sand and other mineral particles into a hard material by the use of sodium silicate has found a number of practical applications. One such application is as a low-temperature binder to confer green (unfired) strength on ceramic materials composed of such diverse materials as red mud [1] or fly ash [2]. Hardening of these materials is found to be extremely slow, unless the curing temperature is raised to 110°C [2], or additives such as sodium fluorosilicate are used [1]. Another variation of the sodium silicate bonding process has been used for many years for bonding foundry sands into mould cores for metal castings, which can be knocked down and removed from the casting after the metal has solidified [3]. In order to harden foundry moulds rapidly, the shaped mixture of sand and sodium silicate is exposed to CO_2 gas, which is considered to set the silicate by two possible processes [3, 4]:

- (a) physical dehydration of the sodium silicate solution by the drying action of the CO_2 gas,
- (b) neutralization of the silicate and gel formation by chemical reaction with the CO_2 . This process can be demonstrated by the use of phenolphthalein indicator, and is also evidenced by the evolution of heat [3].

The sodium silicate– CO_2 reaction has also been used for briquetting granulated ore materials [5] and for producing green strength in silicate-bonded ceramics which are subsequently fired to achieve a permanent silicate bond [6]. The interaction of atmospheric CO_2 may also be involved in the setting of silicate-bonded materials in which intentionally high CO_2 concentrations are not employed, and in which the extremely slow setting rate in the absence of elevated temperatures [2] or other hardening addi-

tives [1] is probably related to the low CO_2 concentrations normally present in the atmosphere.

In view of the practical importance of the sodium silicate– CO_2 reaction, especially in the foundry industry, considerable information is available about the effect on the bond strength of variables such as the sodium silicate composition and concentration, gas flow-rate, gassing time and temperature [3]. By contrast, less information is available about the chemistry of the process; in addition to the known formation of polymers of silicic acid, compounds such as NaHCO_3 and Na_2CO_3 have been suggested to form during CO_2 gassing [7, 8], although these species are not generally considered to contribute to the strength of the material [7].

The purpose of the present work was therefore:

- (a) to investigate the chemistry of the hardening reaction between sodium silicate and CO_2 ,
- (b) to investigate the chemistry of any related reactions with other acidic gases,
- (c) to investigate the way in which the strength of silicate-bonded mineral composites depends on other chemical factors such as the composition of the sodium silicate and the nature of the mineral particles being bonded.

The first part of this paper deals with the reactions involved in the development of unfired (green) strength. In the second part, the effects of the same chemical variables on the high-temperature reactions occurring in gassed silicate-bonded ceramic materials are reported.

2. Experimental procedure

Four commercial sodium silicate solutions (supplied by ICI Australia Limited), of differing silica:soda

molecular ratio were used in this work

A42,	SiO ₂ :Na ₂ O = 3.30,	pH = 11.5
NA56,	SiO ₂ :Na ₂ O = 2.32,	pH = 12.2
A53,	SiO ₂ :Na ₂ O = 2.06,	pH = 12.6
A60,	SiO ₂ :Na ₂ O = 2.06,	pH = 12.7

Investigations of the chemical reactions occurring between these sodium silicates and various gases were carried out by bubbling the gas directly into the silicate solution. The gases used were CO₂, SO₂ (BDH), H₂S (Matheson), NH₃ (Matheson), N₂O and instrument-grade oxygen-free N₂. The reaction products were dried at various temperatures up to 110 °C and examined by IR spectroscopy (Perkin-Elmer model 580 spectrometer, sample suspended in KBr disc) and by X-ray powder diffraction (Philips PW1700 automatic diffractometer with Co K α radiation and graphite monochromator). High-resolution solid-state ²⁹-Si NMR measurements were made on various samples dried at 110 °C, using a Varian XL-200 spectrometer with a Doty Probe operating at 39.7 MHz, a magic-angle spinning speed of 4 kHz and 90° pulses of 7 μ sec duration with a 10 sec delay between pulses.

Experiments on bonding inorganic particles by the gassed-silicate process were carried out with a range of materials, as follows:

- silica sand (BDH), acid washed, screened to pass 44 mesh and calcined at 1000 °C,
- silica sand, as above, plus 20 wt % ground window glass, screened to pass 44 mesh,
- ironsand (titanomagnetite) from Waipipi, New Zealand, magnetically concentrated and screened to pass 44 mesh,
- ironsand, as above, plus 20 wt % 44 mesh ground window glass.

These materials were thoroughly mixed with 5 wt % sodium silicate solution, and 20 g charges were compacted in a 25 mm diameter die at 20 MPa. After pressing, the gas was introduced via a flowmeter at the bottom of the die at a flow rate of 1.3 l min⁻¹ and allowed to permeate the pellet for varying times before removal from the die. Most experiments were carried out using CO₂, but some were made with SO₂ and H₂S. The green strength of the pellet was immediately determined by crushing across its diameter using a tensile strength tester (J J Lloyd, Model T5002) at a cross-head speed of 3 mm min⁻¹. The tensile strength T is then given [9] by

$$T = 2P/\pi dt \quad (1)$$

where P is the breaking load and d and t are, respectively, the diameter and thickness of the pellet, measured by vernier callipers. Each tensile strength experiment was repeated in triplicate, with the results normally agreeing within $\pm 12.5\%$.

3. Results and discussion

3.1. The reactions between sodium silicate and various gases

Sodium silicate was found to harden and set when exposed to the acidic gases CO₂, SO₂ and H₂S, but

not with NH₄ (alkaline) or N₂O and oxygen-free N₂ (neutral), even although the latter, being dry, may have been expected to promote physical dehydration. Further investigations of the setting phenomena were therefore confined to CO₂, SO₂ and H₂S.

3.1.1. Reactions with CO₂

When CO₂ is bubbled through sodium silicate solution, a gradual thickening occurs, the final product of prolonged reaction being an extremely viscous, clear glass in which no crystalline phases are detectable by X-ray diffraction. The IR spectrum of the material immediately after gassing (Fig. 1a) indicates the presence of NaHCO₃, superimposed on the spectrum of the ungasped sodium silicate. Drying at 60 and 110 °C progressively replaces the NaHCO₃ IR spectrum with that of Na₂CO₃ (Fig. 1b), a reaction which also appears to occur slowly on standing at room temperature for several days. This observation is apparently at variance with a previous suggestion [7] that Na₂CO₃ is formed initially and is converted to NaHCO₃ on further gassing, but it should be noted that the two results may not strictly be comparable, since the present observation was made in the absence of sand, or other mineral matter. At drying temperatures up to 110 °C, the IR spectra give no indication of any modification to the silicate phase resulting from the precipitation or polymerization of the silicic acid.

The ²⁹-Si solid-state NMR spectra of gassed and ungasped NA56 sodium silicate samples are shown in Fig. 2.

Following the nomenclature of Magi *et al.* [10], the NMR peaks labelled Q¹ correspond to species of the type Si(OSi)(OH)₃, Q² corresponds to Si(OSi)₂(OH)₂, or in general, Q^{*n*} corresponds to Si(OSi)_{*n*}(OH)_{4-*n*}. Thus, it will be seen that the degree of condensation of the polysilicate is indicated by its chemical shift, the more condensed species having more highly negative chemical shifts [10].

The spectrum of the ungasped starting material NA56 (Fig. 2a) shows a high proportion of less-condensed species Q¹ and Q². Drying this ungasped sodium silicate at 110 °C produces a slight increase in the height of the more condensed Q³ peak (Fig. 2b), but the most significant change brought about by drying is the broadening of the spectrum, suggesting the presence of a range of polymeric species. Treatment with CO₂ produces a similar spectrum, but less broadened, and with a still greater proportion of Q³, and the even more highly condensed Q⁴ species (Fig. 2c). The trend towards the more highly condensed species is even more apparent in the H₂S and SO₂-gassed samples (Fig. 2d, e and f); in the latter, the Q³ species predominates, and extreme broadening is observed. These ²⁹-Si NMR spectra of both gassed and ungasped sodium silicate are totally dissimilar to that of silica gel (our unpublished results).

3.1.2. Reactions with SO₂

Bubbling SO₂ into a sodium silicate solution rapidly produces solidification, the product being whitish and

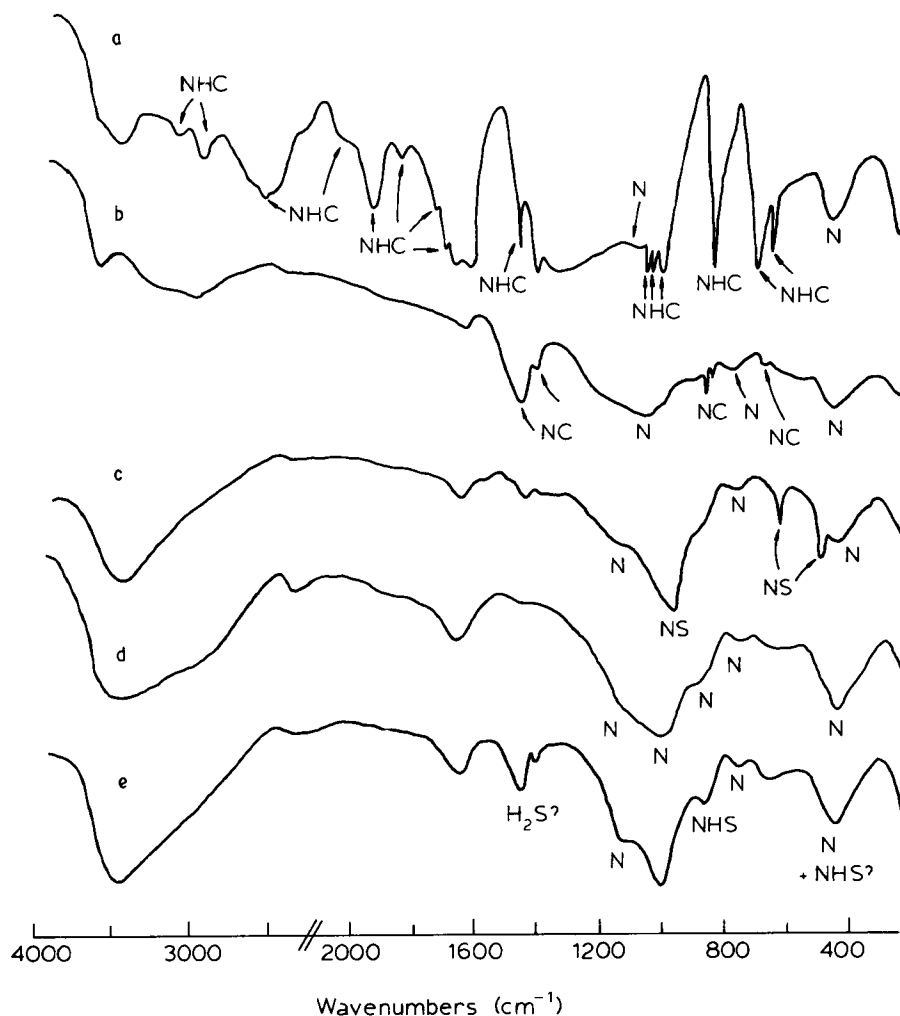


Figure 1 Typical IR spectra of gas-treated sodium silicate NA56. (a) Gassed with CO_2 , dried at room temperature. (b) Gassed with CO_2 , dried at 110°C . (c) Gassed with SO_2 , dried at 110°C . (d) Ungassed, dried at 110°C . (e) Gassed with H_2S , dried at 110°C . (NHC sodium bicarbonate, NC sodium carbonate, NS sodium sulphite, N sodium silicate, NHS sodium polysulphide.)

slightly gritty in texture. X-ray diffraction indicates the presence of crystalline $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ (JCPDS card No. 1-954) and a smaller amount of $\text{Na}_2\text{S}_2\text{O}_5$ (JCPDS card No. 1-1090) superimposed on an amorphous component. Drying at 60°C converts the crystalline phases to anhydrous Na_2SO_3 (JCPDS card No. 5-653), which is still present at 110°C . The IR spectra of samples dried at room-temperature and 60°C contain the characteristic bands of Na_2SO_3 , together with the spectrum of ungasped sodium silicate (Fig. 1c). Drying at 110°C , however, produces significant shifts in all the silicate spectral bands, by comparison with those of ungasped sodium silicate dried at 110°C (Fig. 1d), e.g.

(i) the symmetrical Si–O–Si stretching vibration [11] at 1010 cm^{-1} shifts to 1075 cm^{-1} in SO_2 -gassed samples (but the apparent position of this band may be influenced by the presence of the strong Na_2SO_3 band at 970 cm^{-1}),

(ii) the Si–OH stretching vibration [11] at 885 cm^{-1} has virtually disappeared in SO_2 -gassed samples, an indication that condensation has occurred [11],

(iii) the Si–O–Si stretching vibration at 760 cm^{-1} shifts to 790 cm^{-1} in SO_2 -gassed samples,

(iv) the O–Si–O bending vibration at 445 cm^{-1} shifts to 460 cm^{-1} in SO_2 -gassed samples.

Although these changes could simply be a consequence of polymerization and condensation of the

silicate, they may also be related to the formation of sulphate–silicate complexes, the presence of which are suggested by the thermal decomposition studies reported in Part 2 of this paper. Evidence for the presence of such complexes was sought in the 29-Si NMR spectra of the SO_2 -gassed samples (Fig. 2f); the extreme broadness of the spectral envelope, although indicating predominantly Q^3 species, could also conceal a range of other structures.

3.1.3. Reactions with H_2S

Like the reaction with SO_2 , the reaction between H_2S and sodium silicate is rapid, but results in a solid product of rubbery texture. An initial pale brown colouration changes to deep blue as the reaction proceeds; on prolonged standing at room temperature or ageing at 60 to 110°C , the colour changes to yellowish-green. All these samples were X-ray amorphous, but their IR spectra (Fig. 1e) contain bands additional to those of ungasped sodium silicate. Of these, the broad feature at 1450 cm^{-1} and its associated sharper band at 1405 cm^{-1} may indicate the presence of free H_2S , which absorbs in a broad envelope of bands at 1200 to 1400 cm^{-1} [12]. The new, sharp band at 860 cm^{-1} may be related to the presence of polysulphide, S_2^- (solid H_2S_2 exhibits weak S–H bending vibrations at 857 and 881 cm^{-1} [13].) In both solids and solutions, the presence of S_2^- is characterized by a deep blue colour [14]. Attempts

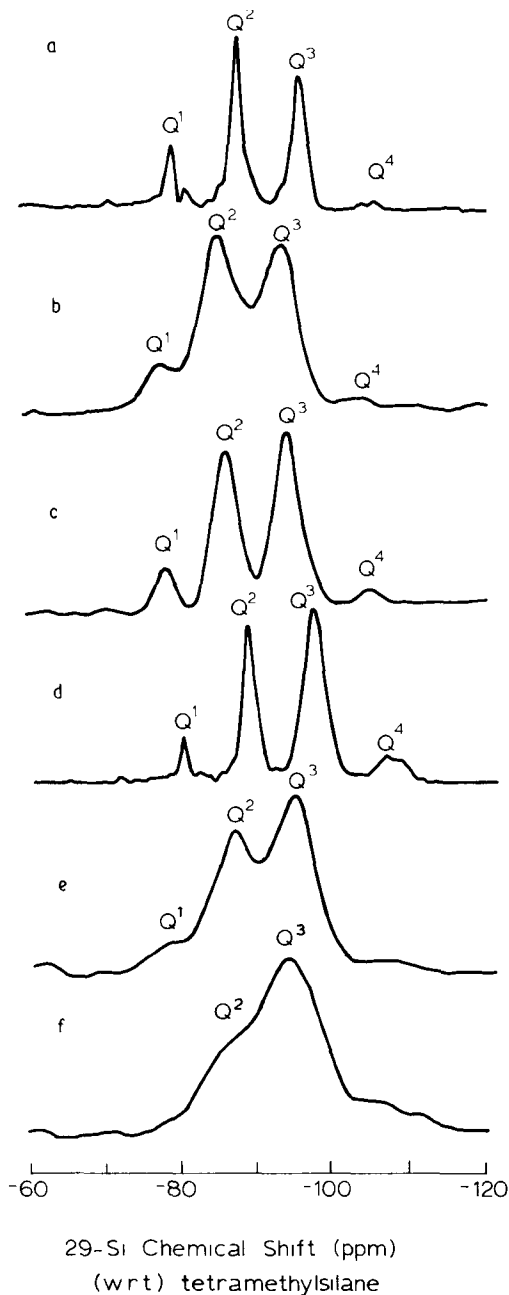


Figure 2 Solid-State ^{29}Si NMR spectra of ungasged and gas-treated sodium silicate NA56. (a) ungasged, undried; (b) ungasged, dried 110°C ; (c) CO_2 -gassed, dried 110°C ; (d) H_2S -gassed, undried; (e) H_2S -gassed, dried 110°C ; (f) SO_2 -gassed, dried 110°C .

to identify other polysulphide bands in the H_2S -gassed samples were inconclusive, because many of the diagnostic vibrations occur below 300 cm^{-1} ; a series of IR-active vibrations which occur in S_2^{2-} , S_4^{2-} , S_5^{2-} and S_6^{2-} [13, 15, 16] at 400 to 500 cm^{-1} is obscured in the present spectra by the O-Si-O bending band of the silicate. Nevertheless, the characteristic colour of the H_2S -gassed samples strongly suggests that polysulphide ion is produced concomitantly with the polymerization of the silicate. The ^{29}Si NMR spectrum of freshly-prepared H_2S -treated sodium silicate (Fig. 2d) is very similar to that of the undried, ungasged silicate (Fig. 2a), but contains a higher proportion of the more condensed Q^3 and Q^4 species. Drying at 110°C produces the characteristic broadening of the spectrum (Fig. 2e), which, however, retains a higher proportion of Q^3 species and less Q^1

than the corresponding ungasged dried sample (Fig. 2b). The NMR spectra produce no direct evidence for the presence of complexes in which sulphide is closely associated with the silicate groups.

3.2. The effect of gassing on the green strength of bonded mineral compacts

3.2.1. Gassing with CO_2

Fig. 3 shows the typical dependence of green strength on CO_2 gassing time for the ironsand-glass samples with the four sodium silicates, from which it is seen that the green strength increases sharply at short gassing times, eventually reaching constant strength.

Similar curves were found for all the other mineral mixes and sodium silicates gassed with CO_2 , but differences were recorded in the precise curve shapes, reflecting differences in the maximum green strength achieved and the gassing time needed to achieve maximum strength. The observed trends were as follows.

(a) CO_2 gassing time required to achieve maximum strength is independent of the mineral matter being bonded, but for each type of mineral matter, depends on the pH of the sodium silicate used (Fig. 4). As would be expected for a neutralization reaction being carried out with a constant flow rate of acidic gas, the more highly alkaline sodium silicates (those with the lower SiO_2 to Na_2O ratios) require longer times for complete neutralization. This is consistent with previous observations [3].

(b) The maximum strength achieved with CO_2 gassing varies both with the pH of the sodium silicate and with the mineral matter being bonded (Fig. 5).

Sodium silicates of highest pH (lowest SiO_2 to Na_2O ratios) produce the highest ultimate green strengths, again consistent with previous observations [3]. Ironsand bonds to a higher green strength than silica sand, but the addition of ground glass increases the green

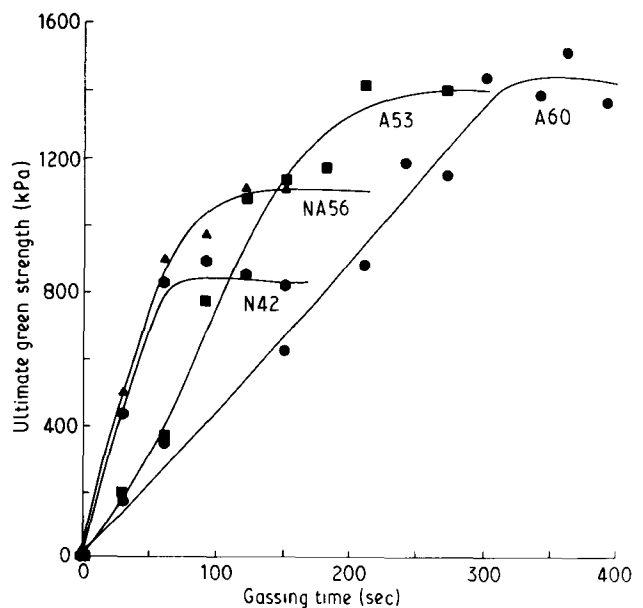


Figure 3 Dependence of green strength on CO_2 gassing time of ironsand/glass compacts bonded with various sodium silicates (\bullet A60, \blacksquare A53, \blacktriangle NA56, \blacklozenge N42).

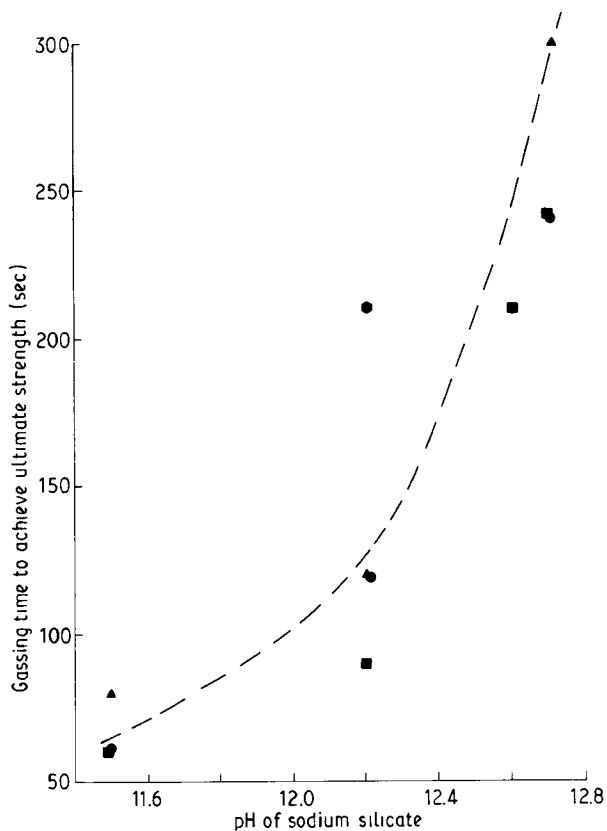


Figure 4 Dependence of the CO_2 -gassing time required to achieve ultimate green strength on the pH of the sodium silicate solution, for various mineral compacts. (● ironsand, ▲ ironsand and glass, ■ silica sand, ● silica sand and glass).

strength of both ironsand and silica sand samples (Fig. 5). These results suggest that the bonding mechanism involves interactions between the mineral grains and the gassed silicate, rather than depending on the cementing action of the hardened silicate phase alone. The previously reported deterioration of green

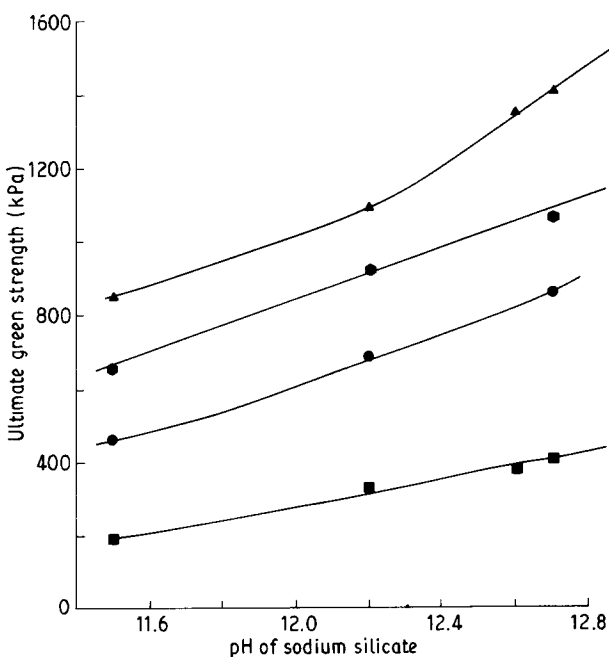


Figure 5 Dependence of ultimate green strength on the pH of the sodium silicate solution for various mineral compacts. (▲ ironsand and glass, ● ironsand, ● silica sand and glass, ■ silica sand).

strength with aging [3], especially in samples containing sodium silicates of high SiO_2 to Na_2O ratios was not investigated here; all the green strengths were measured immediately after sample fabrication.

3.2.2. Gassing with SO_2 and H_2S

Fig. 6 shows typical green strength curves for ironsand and sodium silicate NA56 gassed for varying times with SO_2 and H_2S , with the corresponding curve for CO_2 shown for comparison. The behaviour of SO_2 and H_2S -gassed samples is broadly similar to that of CO_2 , but the maximum strengths achieved with SO_2 and H_2S are lower than for the CO_2 -gassed samples.

Only one sodium silicate (NA56) was used in the experiments with SO_2 and H_2S ; the results obtained with the different mineral mixtures all followed the same trends, namely:

- in all cases, the maximum strengths followed the order $\text{CO}_2 > \text{H}_2\text{S} > \text{SO}_2$,
- in all cases, the CO_2 -gassed samples required the longest gassing times to achieve maximum strength, followed by SO_2 and H_2S ,
- as with CO_2 -gassed materials, the maximum strengths of the SO_2 and H_2S -gassed samples were recorded for the ironsand-glass mixtures, followed by ironsand alone, then silica sand-glass, with silica sand the weakest.

Neither the maximum strength nor the gassing time needed to achieve this maximum strength bears any apparent relationship to the dissociation constants of

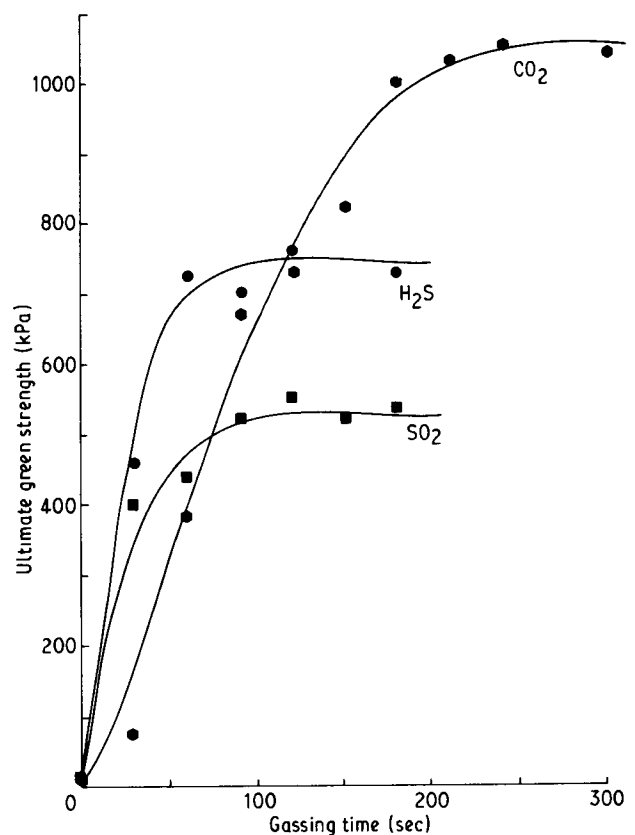


Figure 6 Comparison of gassing characteristics of CO_2 (●), SO_2 (■) and H_2S (●) in the development of green strength in ironsand bonded with sodium silicate NA56.

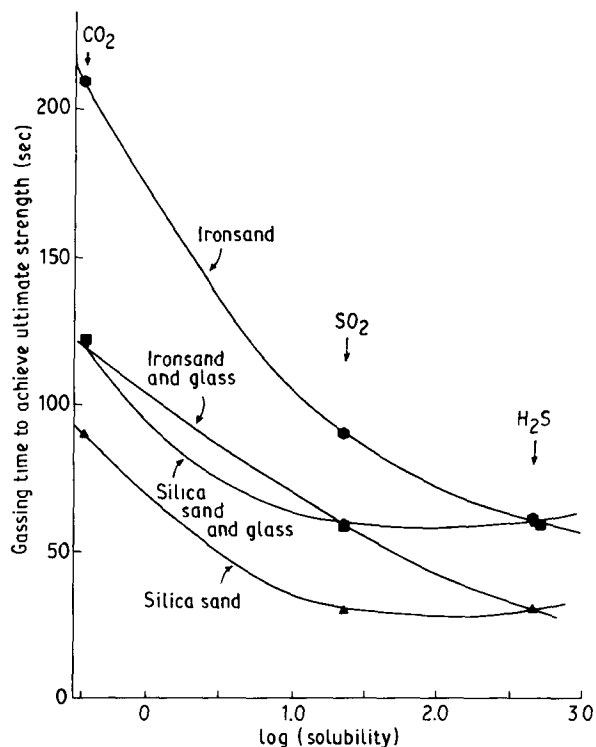


Figure 7 Dependence of gassing time to achieve ultimate green strength on the solubility of the gas in water, for various mineral compacts bonded with sodium silicate NA56. (●) ironsand, (▲) silica sand, (■) silica sand and glass, (●) ironsand and glass.

aqueous solutions of CO_2 , SO_2 or H_2S , as might be expected if the gassing process was a simple acid neutralization phenomenon. A relationship was, however, observed between the gassing time for maximum strength and the solubilities of these gases in water (Fig. 7), the least soluble gas (CO_2) requiring the longest gassing time, and the most soluble (H_2S) requiring the shortest time. (Note that Fig. 7 is based on the available solubility data at 0°C [17], whereas the experiments were carried out at room temperature; the trend is nevertheless illustrated.) These results, therefore, suggest that several factors contribute to the development of strength in the gas-silicate bonding process. The initial stage apparently involves solution of the acidic gas in the water present (with relatively insoluble gases this is a slow step), followed by immediate reaction of the resulting hydronium ions with the sodium silicate to form silicic acid and other neutralization products. The setting reaction proper probably involves both dehydration and the formation of polymeric silica species, which interact chemically with the mineral grains being bonded. The nature of these interactions appears quite complex, being also influenced by the nature of the other products of the gas-sodium silicate reaction.

4. Conclusions

The conclusions are as follows.

(1) In the process of bonding particulate mineral matter by sodium silicate, the attainment of green (unfired) strength is accelerated by treatment with acidic gases such as CO_2 , SO_2 and H_2S . Alkaline and neutral gases have no such beneficial effect.

(2) The development of green strength in a silicate-bonded mineral compact increases with the time of exposure to the gas, up to a maximum value which depends on the Si to Na ratio of the sodium silicate (i.e. its pH), the chemical nature of the mineral matter being bonded, and the gas used.

(3) The gassing time required to achieve maximum strength (i.e. the amount of gas required) depends on the pH of the sodium silicate and the solubility of the gas in water, but is independent of the mineral matter being bonded.

(4) The reaction between the acidic gases and sodium silicate solution forms polymeric silica species and various neutralization products (NaHCO_3 and Na_2CO_3 with CO_2 , Na_2SO_3 with SO_2 and sodium polysulphides with H_2S). Solid-state ^{29}Si NMR spectroscopy suggests that the polymerized silica species formed by gassing with CO_2 are less highly condensed than the products of gassing with H_2S or SO_2 , the latter being the most highly condensed. All of the present silicas have ^{29}Si NMR spectra totally dissimilar to silica gel. The solid reaction products then interact in a complex manner with the surfaces of the mineral particles being bonded.

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