

SIMULATION OF SOIL REACTIONS: ALUMINIUM-IRON(III) HYDROXY SPECIES REACT WITH SILICA TO GIVE DEPOSITS ON PARTICLE SURFACES

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ABSTRACT: In solutions of three different, stable, Al-Fe(III) hydroxy species, reaction with silica particles for one month decreased the solution pH and gave deposits containing Fe, Al and Si over the surfaces of the particles, joining them together. Infrared difference spectroscopy showed the deposits to be similar to imogolite or feldspathoid phases, depending on the composition of the initial solution. Comparative SEM and EDXA elemental analysis profiles supported the conclusion that these laboratory products were similar to naturally occurring soil cementing agents. An explanation is given for the observed reactions and the formation of materials likely to act as cementing agents in soil.

Taylor (1988) reported that precipitated ferrihydrite reacted with soluble Al hydroxy phases at pH 4–4.2 to form soluble Al-Fe(III) hydroxy species. These solutions, stable at pH 4 even in the presence of 2 M NaCl, became unstable on contact with silica, precipitating Fe-rich phases which rapidly discoloured the silica surfaces and appeared to cause particle cementation.

Under field conditions complexes of poly-cations and amorphous silica have long been suspected as soil cementing agents and shown to be of significance in the formation of podzols (Farmer, 1979; Farmer *et al.*, 1980). In recent years, amorphous silica has been noted in duripans as a cementing agent (Flach *et al.*, 1974; Chartres 1985; Chadwick *et al.*, 1987), in fragipan (Bx) horizons (Steinhardt *et al.*, 1982; Norton *et al.*, 1984) and in hardsetting E horizons (Chartres & Fitzgerald, 1990). Brown & Mahler (1987) suggested that precipitation of amorphous silica increased the strength of plough pans in Idaho soils, while others have associated observed soil profile features with Fe, Al and Si in soluble mobile hydroxy complexes (Farmer 1979; Farmer & Fraser 1982; Farmer *et al.*, 1979, 1980; McBride *et al.*, 1984; Huang, 1988). We now further examine reactions of Al-Fe(III) hydroxy species with silica and attempt to relate them to the formation of cements in soils.

EXPERIMENTAL TECHNIQUES

Starting materials and procedure

Solutions containing Al-Fe(III) hydroxy species, stable at pH 4 for several months, were reacted with silica: amorphous Merck FO Optipur (Art. 11493), and the <2 µm fraction of acid-washed quartz. The three different Al-Fe solutions used are listed in Table 1 (A, B and

TABLE 1. Initial and final pH values and concentrations of Fe, Al and Si in Al-Fe(III) hydroxy solutions.

Sample no.	Silica type	Fe-Al hydroxy solution	pH		Elemental concentrations ¹ (mg/l)					
			Initial	Final	Al	Initial Fe	Si	Al	Final Fe	Si
1	Optipur	A ²	3.66	2.45	2075	500	0.5	1475	23.5	77.5
2	Optipur	B ³	7.60	5.87	58	30	5.2	20	11.5	62.5
3	Optipur	C ⁴	3.72	2.59	1475	400	1.75	850	50	62.5
4	Optipur	A ⁵	4.05	2.83	2075	500	0.5	850	75	72.5
5	Optipur	C ⁵	4.05	2.75	1475	400	1.75	700	70	70.0
6	NaOH-washed Optipur	A	3.66	3.27	2075	500	0.5	475	24.3	40.75
7	<2 µm acid washed quartz	A	3.66	3.70	2075	500	0.5	1400	392	<1.0
8	Optipur	H ₂ O ⁶	4.30	4.3	ND	ND	ND	ND	ND	50.0
9	Optipur	H ₂ O ⁷	4.20	4.57	ND	ND	ND	ND	ND	62.5
10	—	H ₂ O ⁷	4.20	4.57	ND	ND	ND	ND	ND	0.6

¹ Elemental concentrations refer to original 10 ml volumes.

² Fe-Al hydroxy cation solution formed during a reaction between a suspension of precipitated ferrihydrite and an aluminium nitrate solution at pH 4, February 1986 (original pH 4.3).

³ Supernatant solution above the <2 µm fraction of a Krasnozern soil (see Taylor, 1988).

⁴ Fe-Al hydroxy cation solution prepared February 1986, original pH 3.92 (see sample 1a Taylor, 1988).

⁵ The pH values of solutions A and C were adjusted up to pH 4.

⁶ Control experiment with Optipur silica in 30 ml acidified distilled water for 9 months.

⁷ Control and blank experiments in acidified distilled water for 1 month.

C). Solution A had been stored for ten months during which time the pH dropped from 4.3 to 3.66. Solution B, (Taylor, 1988) was a yellow supernatant solution from the <2 µm fraction of a krasnozern soil dispersed four years earlier and stored at 6°C. Solution C had already precipitated well-crystallized gibbsite during an earlier nine months' storage during which the pH dropped to 3.92 (sample 1A of Taylor, 1988). During the additional 14 months' storage prior to this work, the pH fell further to 3.72. For samples 4 and 5, Table 1, the pH of solutions A and C was adjusted to 4.05 before the addition of silica.

Generally, 1 g of silica was added to a stoppered Pyrex weighing bottle along with 10 ml of one of the above Al-Fe solutions whose pH, and Al, Fe and Si contents had been determined (Table 1). After periodic shaking for one month and centrifuging, the pH of the supernatant solutions was measured and, together with the first water washings, the solutions were made up to 25 ml for the determination of Al, Fe and Si. The residues were twice washed with water and once with ETOH, centrifuged and dried at 80°C. Exactly parallel treatments were given to two controls of Optipur silica in contact with distilled water at pH 4.2 for one month and nine months, respectively. A blank was run to check on the release of soluble silica from the glassware. In a further run Merck Optipur silica was washed with 1 M NaOH before contact with the Al-Fe solutions (Table 1).

Products of the reaction

After a preliminary examination by optical microscopy, the residues from reacted and control runs, (samples 5 and 9, Table 1) were carbon coated and examined by scanning electron microscopy (SEM) using a Cambridge Stereoscan 250, and elements were identified by energy dispersive X-ray analysis (EDXA).

Chemical analysis

Elemental concentrations in the various solids were measured by X-ray fluorescence spectroscopy (XRF) using the fusion method of Norrish & Hutton (1969), and in the reacting and final supernatant solutions by inductively coupled plasma (ICP) spectroscopy.

Infrared spectroscopy

Infrared (IR) spectra were recorded from 4000 to 400 cm^{-1} on a Digilab FTS 15/90 Fourier Transform Spectrometer with a Ge-coated KBr beamsplitter and a deuterated triglycine sulphate (DTGS) detector with a CsI window, and from 400–50 cm^{-1} with a 6.25 μm Mylar beamsplitter and a polythene window on the detector. Resolution was 2 cm^{-1} for 512 co-added scans. Samples of the unreacted and reacted quartz and silica and the evaporated sols (at 60°C) were prepared as pressed CsI disks from 3.0 mg sample, hand mixed with 500 mg of spectroscopic grade CsI, and pressed under 10 t.

The IR spectra of the solids formed during the reaction were obtained by scaled subtraction of the spectra of the solids and controls with exactly similar treatments. Various scaling factors were used to obtain optimal cancellation of peaks due to unreacted quartz or silica by complete reduction of the bands at 800 and 471 cm^{-1} in the mid- and far-IR range, respectively. The results are not sensitive to the choice of scaling factors as shown below (Fig. 7c). This technique is acceptable because wavelength calibrations are highly reproducible with this instrumentation. At the same time, subtraction spectra need careful interpretation since false turning points can be introduced, and groups of bands were used to overcome this problem. Due account was taken of other factors influencing difference spectra, including variations in band shape and the non-linearity of intensities, which are not believed to alter the present difference spectra. The essential bands used for interpretation were common in the samples examined and persisted as the scaling factors were varied. The resulting difference spectra represented the solid phases formed from reaction of the solutions with the silica or quartz surfaces, or of dissolved $\text{Si}(\text{OH})_4$ or its polymers deposited from solution. These spectra were plotted with smoothing to reduce digital noise, the resolution then being $\sim 8 \text{ cm}^{-1}$.

Natural samples

Soil samples showing fracture features were carefully removed in the field from the E horizon of an Aeris Albiqualf at Borambola and from the A horizon of a Calcic Palcustalf at Bruce Dale, both near Wagga Wagga in New South Wales (NSW), Australia. A field sample from a silica-indurated duripan at Fowlers Gap, western NSW, was also used. These samples were examined by SEM utilising EDXA. Five replicates of Borambola E horizon $< 2 \mu\text{m}$ fraction were also shaken overnight with deionized water, and Si, Al, Fe and Mn determined.

TABLE 2. Change in elemental concentrations of Al-Fe hydroxy solutions caused by reaction with silica.

Sample no.	10 ml solution composition changes (μ moles)			
	Fe	Al	Si	OH
1	-85.5	-222	27.4	-33.3
2	-3.3	-14	20.3	-0.0175
3	-62.7	-231	26.9	-23.8
4	-76.1	-454	25.6	-13.7
5	-77.0	-287	24.3	-16.7
6	-85.23	-593	14.3	-3.2
7	-19.3	-250	<0.2	0.183
8 ¹	ND	ND	17.8	
9 ²	ND	ND	22.3	0.36

¹ Control experiment with Optipur silica in 30 ml acidified distilled water for 9 months. [Si] measured after one month, and value represents the increased amount of Si in 10 ml volume.

² Control experiment in acidified distilled water. Changes in Si and OH measured after one month.

RESULTS

Chemical data

Table 1 summarizes the experimental details and includes the initial and final pH values and concentrations of Al, Fe and Si at the beginning and end of the experiments.

The results and changes in the supernatant solution concentrations (Table 2) show that the Al-Fe(III) species had consistently lower [Al], [Fe] and pH, and higher [Si] on contact with silica. Amorphous silica produced more pronounced changes in [Al] and [Fe] than quartz. The solution from the soil (sample 2), assumed to represent a natural Al-Fe hydroxy species, showed similar decreases. In contrast, the control experiments produced no drop in pH even after nine months, but amounts of silica were dissolved similar to those found with the reacted species.

Upon reaction, the silica grains of samples 1,3,4,5, and 6 became visibly yellow, Munsell notation 7.5YR (7/8-6/8), due to the precipitation of an Fe(III) phase shown by the decreases in [Fe] (Table 2). Sample 2 lost much less Fe, approximately 5% of the others, which was apparently insufficient to produce discoloration. Less Fe was also lost on reaction with quartz (sample 7).

The XRF results for the Optipur silica and NaOH-washed Optipur silica before and after reaction with solution A are given in Table 3, the differences from 100% representing water content. The high Na in sample 6 was associated with the NaOH washing of the Optipur silica used in that experiment. In agreement with the results of Table 2, these XRF results for sample 6 showed a higher Al content than for sample 1, although the amounts of Fe were about the same.

The water extracts from the Borambola E horizon soil contained higher mean concentrations (mg/l) of Si (11.63) than Al (0.44), Fe (2.92) or Mn (3.39).

TABLE 3. X-ray fluorescence analysis (wt%) of Optipur silica before and after reaction with Al-Fe(III) hydroxy solution A.

Element	Optipur normal	Silica NaOH washed	Sample 1	Sample 6
Fe ₂ O ₃	0.03	0.04	0.63	0.68
MnO	0.00	0.00	0.01	0.01
CaO	0.00	0.01	0.00	0.01
K ₂ O	0.00	0.01	0.00	0.01
SiO ₂	93.56	89.38	84.97	83.13
Al ₂ O ₃	0.00	0.02	0.49	2.02
Na ₂ O	0.08	3.12	0.02	0.00
Total	93.67	92.58	86.12	85.86

Microscopic examination

Optical microscopy showed unreacted Optipur silica as partly translucent spheres varying in size and degree of agglomeration with small areas of white opaque material on the surface. After reaction, some of the spheres were yellow, probably due to precipitation of Fe compounds.

SEM results

Laboratory experiments. Back-scatter electron images of the water-treated Optipur silica control (sample 9, Table 1) showed loose powdery deposits of silica between weakly agglomerated spheres (Fig. 1). This deposit was removed by an NaOH wash (not shown) as well as by reaction with Al-Fe hydroxy species, as shown in Fig. 2. In contrast to the control, the EDXA profiles of the treated samples (sample 5, Table 1) showed that Fe and Al compounds were present on the surface of the silica spheres and in particulate deposits between them. Examination at various locations supported this result. Similar deposits were also found after reacting the NaOH-washed Optipur with the Al-Fe hydroxy species (sample 6, Table 1).

Field samples. Some morphological features of the silica-indurated natural hardpan sample from Fowler's Gap are shown in Fig. 3. Individual grains are embedded in a matrix, shown by thin section EM and EDXA (Chartres, 1985) to consist predominantly of amorphous silica along with small amounts of Fe, Al and Ti.

SEM images of siliceous zones in two soils with hard setting horizons are presented in Fig. 4. Fig. 4a shows the Brucedale A horizon soil particles to consist dominantly of clay minerals (labelled CM and identified by their platy morphology) that bridge quartz grains, silicified fungal hyphae (H) and amorphous silica and clay minerals (S) adhering to surfaces. Fig. 4b shows amorphous silica (from EDXA) replacing a rootlet or fungal hypha in E horizon material of the Borambola soil. Fig. 4c from the same horizon shows an inter-grain bridge of cemented fine particles and clay minerals, and EDXA on a small zone of this image (Fig. 4d) showed that silica and small amounts of Al and Fe were present.

IR analyses

Fig. 5a shows the mid-IR spectra of Optipur silica after reaction with solution A (samples 1 and 4) and solution C (samples 3 and 5), and also the spectra of the Optipur silica blank (sample 9, Table 1) having *exactly* the same treatment but with only water for the same period. Fig. 5b illustrates the resultant subtraction spectra representing the absorbances due to materials formed during the reaction.

Fig. 6 shows the far-IR spectra of NaOH-washed Optipur silica and solutions A and C,

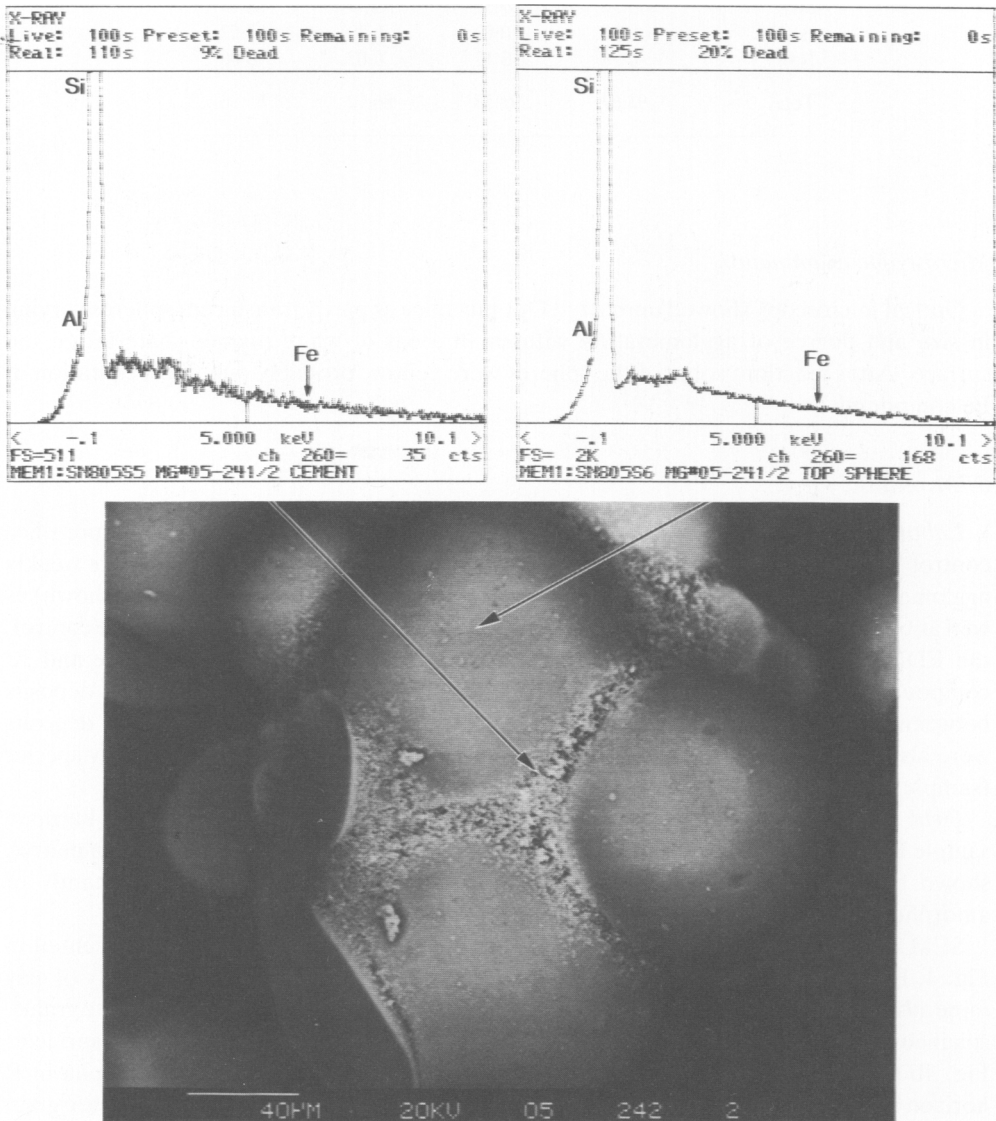


FIG. 1. EDXA plots and SEM back-scatter electron images showing the distribution of Fe and Al on control sample of Optipur silica.
Taylor, Raupach, Chantres, figure 1.

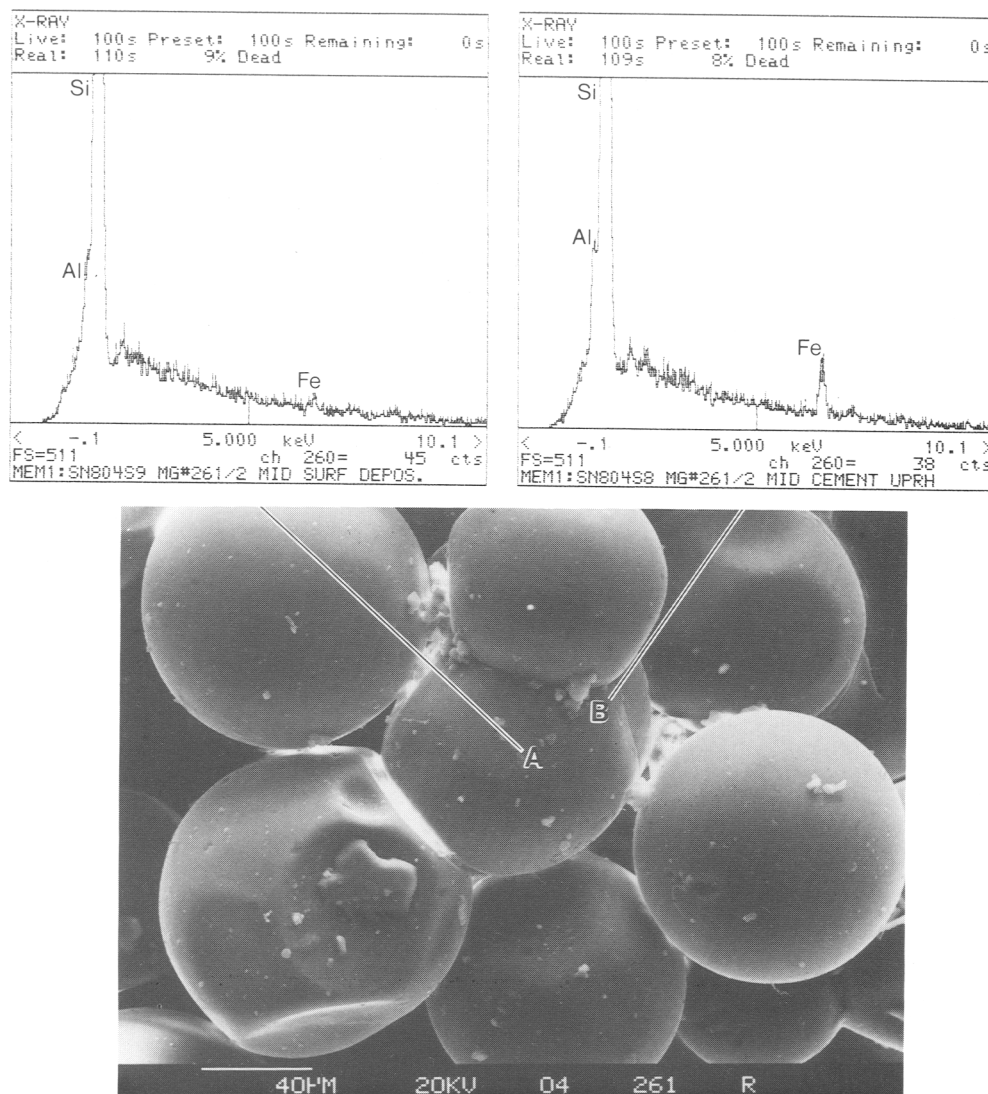


FIG. 2. EDXA plots and SEM back-scatter electron images showing areas of Fe and Al deposition in relation to surface morphology and zones of cementation of amorphous (Optipur) silica after reaction with Fe(III)-Al hydroxy cation solution C. Locations A and B used for EDXA scans are noted on the SEM image.

and also the spectrum of the product from sample 7 which is so similar to that of quartz that no deductions can be made from it.

The observed far-IR spectra of the materials used for Fig. 5 are shown in Fig. 7a; Fig. 7b illustrates subtraction spectra for this range, and Fig. 7c shows subtraction spectra for sample 5 using a range of scaling factors to demonstrate that the features of these spectra are not sensitive to the scaling factors chosen. Similar results were found in the mid-IR range.

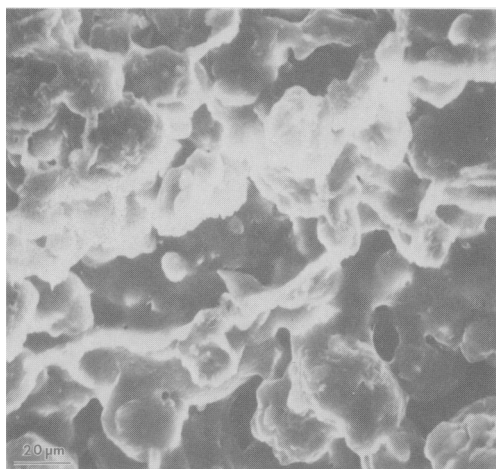


FIG. 3. SEM image from a silica-indurated duripan soil sample, treated with dilute HCl to remove carbonates, from Fowlers Gap, NSW. Amorphous silica has coated both quartz grains and clay minerals.

No essential changes in any of the above spectra, including the subtraction spectra, were shown on using other blanks, either sample 9 (Table 1), untreated Optipur silica, or the NaOH-washed material used in sample 6 (Table 1).

DISCUSSION

Soluble silica, from the powdered interstitial silica present in the Optipur silica (Fig. 1), is presumed to initiate the destabilisation of the otherwise stable hydroxy solutions which are reprecipitated as Al and Fe phases. Visual observation showed that the initial reactions were fast for Fe, and presumably also for Al, because the silica spheres became coloured within a few hours.

The pH of the control experiments (silica alone) did not change, but the pH drop was greater upon reaction than the decrease in pH during earlier prolonged storage of solutions A and C, and no gibbsite was formed. Two reactions may be responsible for this pH change. The one considered to be largely responsible is expressed by equation (1) which is associated with the satisfaction of the charge of the hydroxy cation by soluble silica. The other reaction arises from polymerization of soluble Al-Fe hydroxy species. Polymerization, which could lead to gibbsite, would be reversed in the presence of sufficient H^+ ions generated by the reaction of equation (1) and so account for the absence of gibbsite in the reaction products.



Equation (1) would give an Al or Al-Fe silicate phase which, along with polymerization products, could have cementing properties. Quartz was less reactive towards the soluble Al-Fe hydroxy species than amorphous Optipur silica, possibly due to its lower solubility. The lower Al/Fe ratios lost from solution at lower final pH values (Tables 1 and 2) could

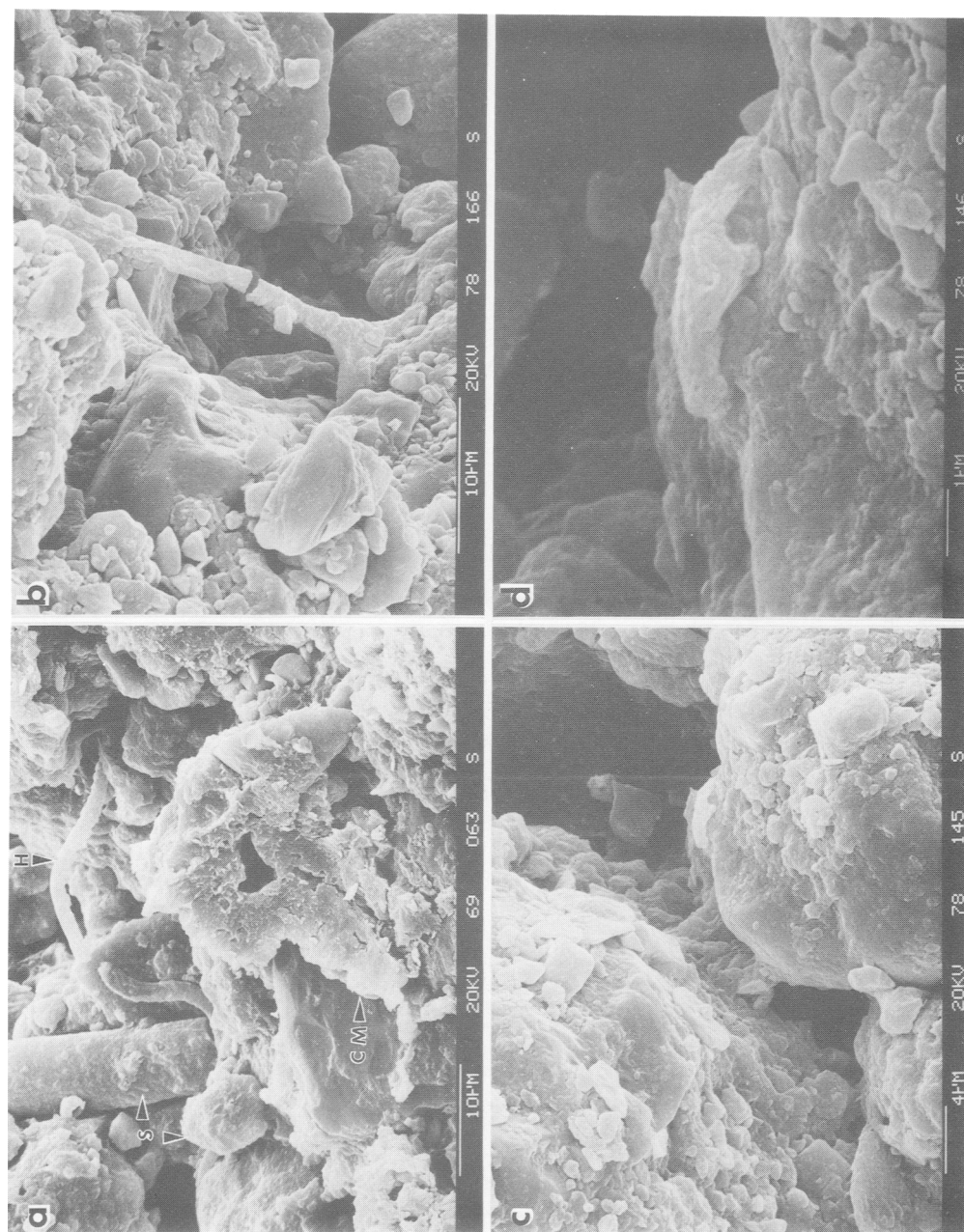


FIG. 4. SEM images showing morphological features of: (a) soil sample from Bruccedale A horizon; (b) Borombola E horizon sample showing rootlet or fungal hyphae replaced predominantly by amorphous silica; (c) inter-grain bridging in Borombola E horizon; (d) enlargement of section of micrograph (C).

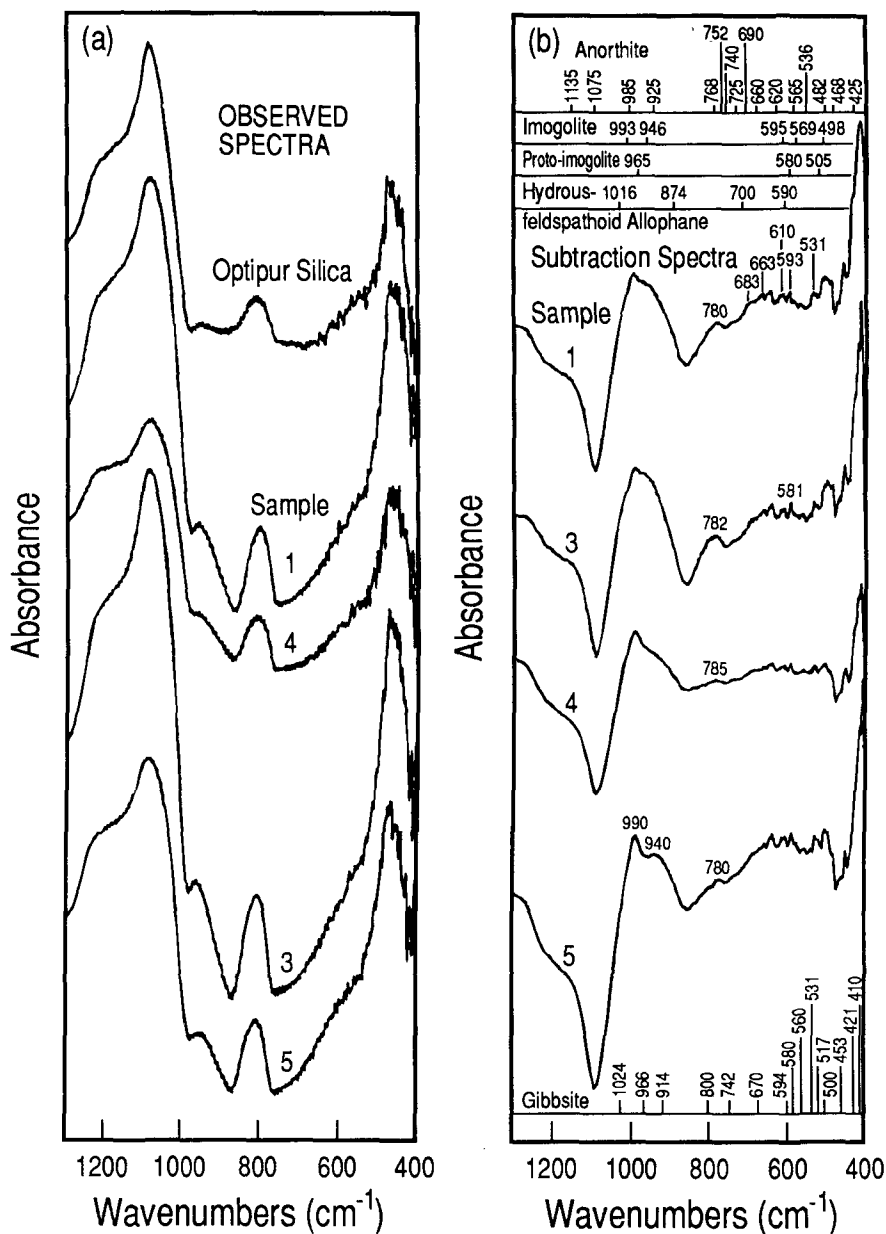


FIG. 5. IR spectra (mid-IR range) of Optipur silica (samples 1,3,4 and 5) and of the solid phase material formed in the presence of Optipur silica with different Fe(III)-Al solutions A and C; (b) subtraction spectra of the solid phases formed. References for the frequencies for the bar charts: for imogolite, proto-imogolite and hydrous feldspathoid allophane, Russell (1988); for anorthite, Liese (1975), Kovach *et al.* (1975); and for gibbsite, unpublished data of one of the authors (MR).

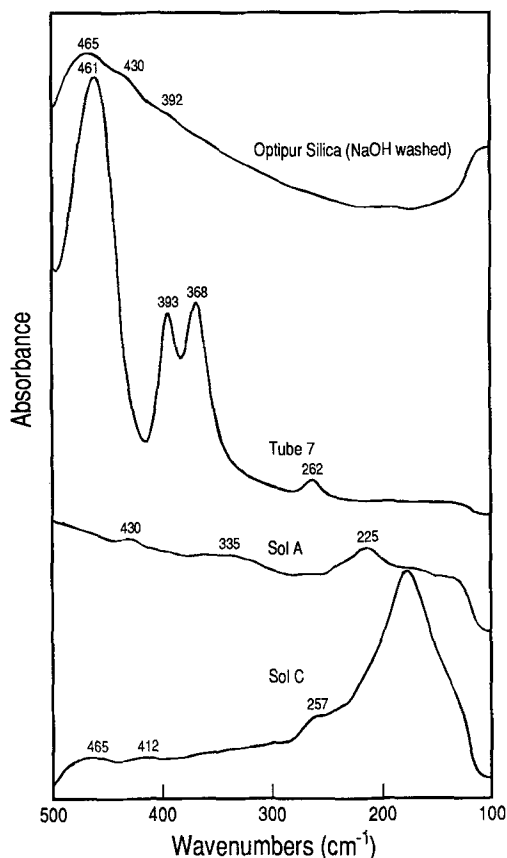


Fig. 6. IR spectra (far-IR range) of selected starting materials, quartz, and evaporated solutions A and C.

arise from a further dissolution of Al ions from the initial precipitated reaction products by the H^+ ions produced in reaction (1). The Al ions so formed could then react with dissolved silica or silica surfaces to give further solid phase material.

The IR spectra of samples 3 and 5 resembled each other as did those of samples 1 and 4 (Fig. 5a) presumably due to their common starting materials. The spectrum of the residue from evaporation of solution A was similar to that of an Fe oxyhydroxide phase, whereas that from C (Fig. 6) resembled gibbsite. This is, to some extent, in keeping with the earlier observed precipitation of gibbsite from solution C during storage (Taylor, 1988).

The new phases formed are not very well defined and only limited information can be deduced from the IR spectra. Even so, the results are definite and it is important to note that these spectra, particularly those for the far-IR, are in good agreement with other results obtained in our work on the IR spectra of poorly crystalline materials which act as cementing agents in soils (Chartres *et al.*, 1990). There was no definite IR evidence that the reaction products contained ferrihydrite.

From Fig. 5a and 7a the Optipur silica blank (sample 9, Table 1) gave mid-IR absorbance maxima at c. 1090, 960, 800, 460 and 390 cm^{-1} whereas the treated samples had maxima at

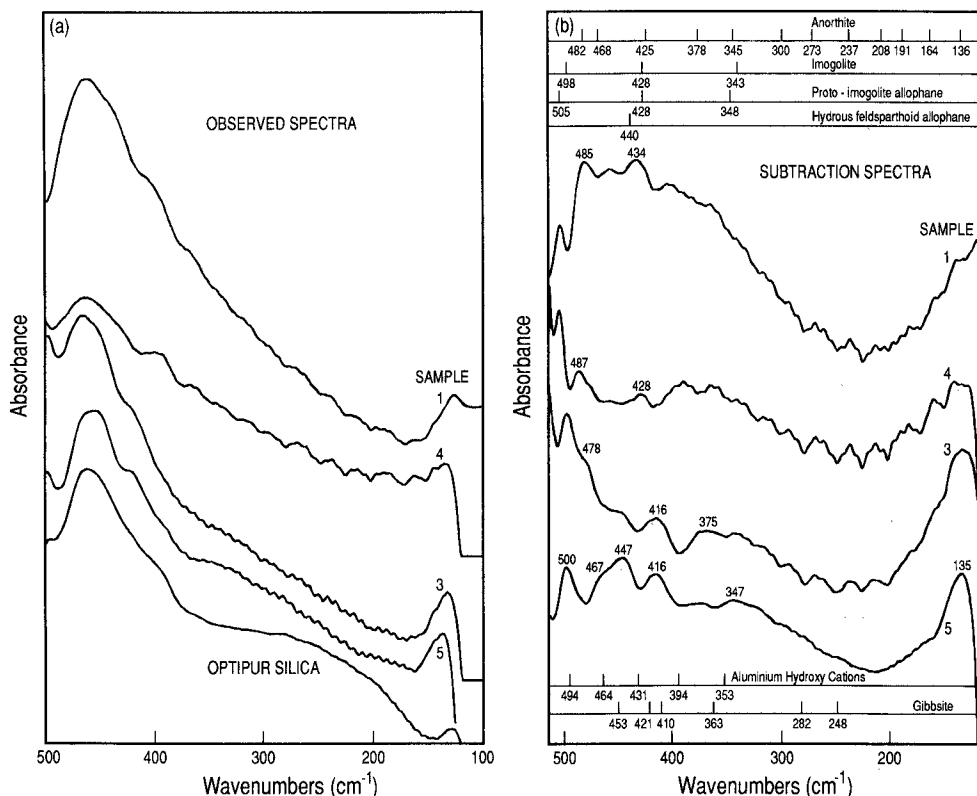


FIG. 7. (a) IR residual spectra (far-IR range) of Optipur silica and the solid phases formed in the presence of Optipur silica with solutions A and C; (b) subtraction spectra of the solid phases formed.

c. 1085, 960, 800 and 512 cm⁻¹ for samples 1 and 4, and at 1095, 955, 805 and 470 cm⁻¹ for samples 3 and 5. As explained, the silica bands near 800 and 470 cm⁻¹ were subtracted out so that the minima in Fig. 5b are absorbances due to Optipur silica, whereas maxima are due to the absorbances from the reaction products. The minimum at 1090 cm⁻¹ is due to silica in the starting material. The minimum at c. 850 cm⁻¹ is probably real in the spectra of the products. Although there is no major band at 850 cm⁻¹ in quartz or in any of their analogues, this has been related to "gaps" in a continuously connected SiO₂ network by Bell (1972) who predicted bands at c. 1050, 750, 550 and 400 cm⁻¹ for linked silica tetrahedra. This compares with our observed bands at c. 780, 550, and 420 cm⁻¹. Since there is no band at 850 cm⁻¹ the solid reaction product phases appear to contain linked rather than disconnected silica tetrahedra.

The main bands appearing in the IR spectra of samples 1 and 4 are near to those of imogolite, proto-imogolite and some feldspar materials (see Fig. 7b), supporting the idea that new phases are formed. Samples 3 and 5 gave bands at c. 940 447 and 416 cm⁻¹ that possibly indicate a tendency towards an Al-rich product, although the 940 cm⁻¹ band present in the spectra of both the controls and the reaction products has been associated with Si-OH bonds. Reference frequencies for the Al hydroxy cations (Fig. 7b) have been taken from the subtracted spectra for Al-pillared and untreated bentonites using unpublished results obtained by one of us (MR) in this laboratory.

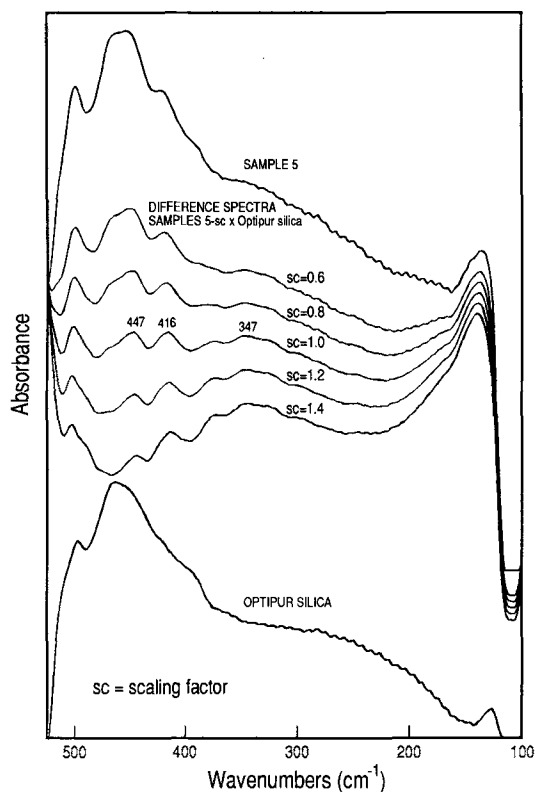


FIG. 7(c). Examples of IR subtraction spectra for sample 5 using various scaling factors. References as for Fig. 5.

The mid- and far-IR spectra of the solid phases formed on reaction (Fig. 5b and 7b) were in reasonable agreement with the conclusion that those formed from solution A were imogolite- and feldspathoid allophane-based, whereas those formed from solution C were more Al-based.

The association of Fe, Al and Ti with the amorphous silica cementing agent in the duripan sample agrees well with the above results. The results on the Brucedale and Borambola soils show that material had been precipitated or deposited on the surfaces of quartz and clay particles (Fig. 4) coating voids and, together with clay minerals, forming inter-grain bridges. EDXA suggests that these precipitated materials contain high proportions of amorphous silica, and Fe, Al and Ti. These coatings are difficult to analyse in the presence of varying amounts of silica but it can be realistically inferred from IR difference spectra (Chartres *et al.*, 1990) and EDXA elemental analysis that they resemble those formed in our experiments.

CONCLUSIONS

The reaction of soluble Al-Fe hydroxy species with silica particles produces deposits with potential cementing properties. This observation is supported by solution chemistry, IR

spectroscopy and EDXA spectra. This reaction resulted in a pH decrease, and the deposits formed contained Al, Fe and silica. IR difference spectroscopy showed these deposits to resemble imogolite and feldspathoid phases and some soil cementing materials. This suggests that similar reactions to those investigated here may occur in soil systems and be responsible for some morphological features.

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