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# Mechanism of dehydration and intumescence of soluble silicates

## Part I *Effect of silica to metal oxide molar ratio*

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The properties and structure of films prepared from solutions of potassium silicate were studied by thermal analysis, IR spectroscopy, and X-ray diffraction. Various $SiO_2$:$K_2O$ molar ratios from 2.55 to 4.72 were prepared and studied to determine the effect of molar ratio on the hygroscopic nature, solubility, and intumescence. The results provided insight into the physical structure, and mechanism of water absorption of the potassium silicate films. The molar ratio has a profound effect on the solubility, water absorption, and intumescence of the potassium silicate film. The primary mechanism of water absorption and retention is by ionic hydration. Decrease in the ionic hydration driving force as the molar ratio is increased results in decreasing solubility. Since intumescence results from the release of water vapour, the degree of intumescence decreases as the amount of ionically bonded water decreases with increase in molar ratio.

## 1. Introduction

There are numerous patents that include soluble silicates as the vehicle for fire protective coatings, owing to their property of intumescence (swelling) when exposed to flame. This intumescence results from the rapid liberation of water vapour upon exposure to high temperatures [1], thus, no noxious fumes are given off from the inorganic silicate-based coating. There are, however, drawbacks to such silicate-based coatings. The main drawbacks are their hygroscopic nature and poor water resistance.

Understanding the nature of the water retained in the silicate-based coatings, and what factors affect it, will help in the development of such coatings. This study concentrates on the affect that the silica to metal oxide ratio ($SiO_2$:$M_2O$) has on the water retained in the coating and how it and the silicate structure affects the intumescence.

To understand the hygroscopic nature, water solubility and intumescence of silicate-based coatings, it is necessary to first understand the chemical constitution of the silicate solution and how the coating exists in the ambient dried state. Work has been done by numerous scientists to determine the silicate constitution in solution and this is briefly summarized.

TGA (thermogravimetric analysis), DSC (differential scanning calorimetry), X-Ray diffraction and infrared spectroscopy give direct information on the nature of retained water and physical structure of the silicate material. In addition, water solubility, intumescence (i.e. upon exposure to flame), and water absorption plotted against relative humidity tests give indirect evidence of the physical structure and nature of water bonding in the silicate-based coatings.

## 2. Background

### 2.1. Soluble silicates in solution

Soluble silicates form various ionic species in solution and this can be illustrated by the solubility curve of Fig. 1 [2]. At low concentration (area A in Fig. 1) mononuclear $Si(OH)_4$ is in equilibrium with $(SiO(OH)_3)^-$ and $(SiO_2(OH)_2)^{-2}$ with the following dissociation constants at 25 °C

$$Si(OH)_4 \leftrightarrow (SiO(OH)_3)^- + H^+ \quad pK_1 = 9.46$$

$$(SiO(OH)_3)^- \leftrightarrow (SiO_2(OH)_2)^{-2} + H^+ \quad pK_2 = 12.56$$

In concentrated, highly alkaline solutions there is some indication of $(SiO_3(OH))^{-3}$ ions.

At higher concentrations (area B) the equilibria in solution become extremely complex as monomeric $Si(OH)_4$, and its ionic species, form siloxane (-Si–O-Si-) units. Iler [3] states that silicic acid ($Si(OH)_4$) has a strong tendency to polymerize in such a way that in the polymeric units there is a maximum

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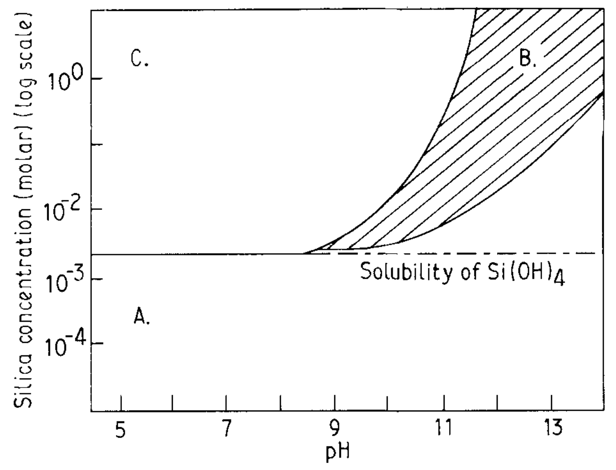

*Figure 1* Species in equilibrium with amorphous silica at 25 °C [2] (A mononuclear species, B polysilicate ions in solutions, C solution unstable with respect to amorphous silica).

of siloxane bonds and a minimum of uncondensed -SiOH, thus, as polymerization proceeds, condensation leads quickly to ring structures followed by the addition of monomer and other cyclic units to form larger three-dimensional spherical units. These condense to the most compact state with -Si(OH) and SiO$^-$ groups remaining on the outside. Such polymeric units can reach dimensions of from 1 to 2 nm in diameter. Work by Harris, Knight and Hull [4] shows evidence of a variety of polymeric species.

Polymerization in terms of the formation of siloxane bonds is a reversible process. The concentration of OH$^-$ that promotes ionization and condensation also promotes hydrolysis and depolymerization (i.e. dissolution), thus, monomeric Si(OH)$_4$ reaches an equilibrium state with the polymeric units. The size and concentration of polymeric units depends on the concentration of silica and the silica to metal oxide ratio. Increasing molar ratio results in a higher degree of polymerization (i.e. larger particle sizes) [3].

## 2.2. Effect of the silicate structure on intumescence

As discussed, the soluble silicate solution consists of polymeric silicate particles in equilibrium with monomeric silicate ions. It would be expected that upon drying, the cations in solution would act as cross-links between polymeric units through coordination with negatively charged polysilicate oxygen atoms (surface-Si-O$^-$ groups) [3, 5]. In the case of monovalent ions, such linkages would be broken due to dissociation upon submersion of such a sample in water, the rate of dissolution depending on the strength of cross-links between particles. In the case of multivalent cations, such as Ca$^{++}$, strong bonds link adjacent silicate particles and form insoluble precipitates when added to a silicate solution.

As the SiO$_2$:M$_2$O molar ratio is increased (i.e. pH reduced) the polysilicate particles increase in size and the surface charge density decreases, thus the solution becomes more colloidal in nature. Such high molar ratio solutions would have a higher probability of forming -Si-O-Si- bonds between particles as the solution dries. This is the case with alkali stabilized colloidal silica (silica to metal oxide ratio of 25:1 and higher). As colloidal silica loses water upon drying, the colloidal particles have a greater probability of colliding due to Brownian motion and thus forming -Si-O-Si- bonds (see Iler [3] for a detailed explanation of the deposition of colloidal silica). Once dry, colloidal silica is insoluble and non-intumescent. Apparently, in addition to the water content, the strength of bonding in the coating network determines the degree of solubility and intumescence. Increasing the SiO$_2$:M$_2$O ratio of soluble silicates would be expected to result in stronger bonding thus providing greater water resistance and a lower degree of intumescence.

## 2.3. Nature of silicate bound water

The water contained by a room dried silicate sample can be considered to consist of "free" water, that removed by heating at 100 °C or desiccating at low relative humidity, and "bound" water [6]. The bound water is that given off at higher temperatures and includes; (1) physical adsorption of water by hydrogen bonding to surface silanol groups of silica particles (polysilicate ions), (2) ionic hydration (i.e. water molecules associated with each of the negatively and positively charged ionic species), and (3) water present as SiOH groups on the polysilicate ions which react at high temperatures to form siloxane bonds with the release of H$_2$O. Part of the bound water may also be given off at low temperature along with free water depending on the strength of bonding.

In the case of (1), work has been done on the hydration of silica gels and colloids to determine the degree and nature of hydration [6–8]. Iler [7] gives evidence of a monolayer of water hydrogen bonded to the surface silanol groups of colloidal particles, however, this was for the case of colloidal silica in which the pH was maintained at 9.0. Soluble silicate solutions are more complex with pH in the 11.5 to 12.0 range. The higher pH means that the polysilicate ions in soluble silicate solutions will have a lower degree of protonation (fewer -Si(OH) groups and more -SiO- groups). This will affect the extent and strength of water hydrogen bonded to the polysilicate ions.

In the case of ionic hydration (2), water molecules are associated with each of the potassium cations in the silicate solution. Different methods of analysis give roughly concordant values for the number of water molecules associated with each K$^+$ cation, and 2 is a generally accepted value [9, 10]. Upon drying, some of the water molecules associated with the K$^+$ cations would be replaced by cation–anion interactions. If there is not an excess of water, hydrates may form.

Hydrates have an orderly structure (i.e. are crystalline) and with several salts, there are various hydrates that may form. For example, copper sulphate can combine to form three different hydrates, trihydrate, pentahydrate and heptahydrate. The hydrate that forms depends on a number of factors with temperature and humidity being the most important.

A soluble silicate film is extremely complex and cannot be considered to be a true crystalline hydrate as in the case of copper sulphate. However, there are likely to be various potassium silicate salts contained within voids in the polysilicate chain which would probably be hydrated, or at high humidities, dissociated if an excess of water exists, also, potassium ions associated with polysilicate particles would be hydrated as in the case of silicate clays.

In the case of (3), conversion of polysilicate surface silanol groups to siloxane groups with the release of water starts to occur at temperatures greater than 200 °C [11, 12]. This reaction occurs between silanol groups on the same polysilicate particle as well as between neighbouring polysilicate particles. The silanol groups on polysilicate ions have an irregular arrangement and therefore formation of siloxane bonds with the release of water occurs gradually over a wide temperature range.

## 3. Experimental details

### 3.1. Preparation of silicate solutions

The soluble silicate investigated in this study was potassium silicate, chosen because of its high degree of intumescence. The potassium silicate solution used was PQ Corporation Kasil # 6. This has a molar ratio of 3.29 with 12.65% $K_2O$ and 26.50% $SiO_2$ in aqueous solution. From this starting solution, molar ratios of 2.55, 2.75, 3.00, 3.29, 3.64, 4.00, 4.35 and 4.72 were prepared. To decrease the molar ratio an appropriate amount of KOH (A.C.S. reagent) was added to the Kasil # 6 solution and allowed to stand for 3 to 4 h in sealed jars. Increasing the molar ratio was achieved by adding the appropriate amounts of Cabot Corporation Cab–O–Sil EH-5 fumed silica. This has a surface area of $380 \pm 30\ \mathrm{m^2\ g^{-1}}$ and a nominal particle diameter of 7 nm. Increasing amounts of water were added with increasing added silica to maintain an acceptable solids per cent in the 37 to 39% range. The samples were allowed to stand in sealed jars for 3 days to allow dissolution of the added silica. Three of the samples gelled (molar ratios 4.00, 4.35 and 4.72), however, heating these samples to 60 to 70 °C in an oven reduced the viscosity to the extent that they reverted back to a thick liquid.

### 3.2. TGA studies

Samples of each molar ratio were allowed to room dry for 1 week and the monolithic films were then sealed in plastic bags until testing. These samples were then thermogravimetrically analysed using a DuPont 951 Analyser. These TGA tests were conducted in the 25 to 900 °C range at a heating rate of $3\ {}^{\circ}\mathrm{C\ min^{-1}}$. The weight loss is a direct result of the evolution of water since no combustibles are present in the samples.

### 3.3. DSC studies

Portions of samples prepared for the TGA studies were used for the DSC studies. Tests were performed on a Perkin Elmer DSC-2 in the 30 to 500 °C range and at a heating rate of $5\ {}^{\circ}\mathrm{C\ min^{-1}}$. Samples were contained in sealed aluminium sample dishes which were perforated with a pin to allow water vapour to escape. This was necessary since a build-up of vapour pressure would affect the temperature of onset of an endotherm.

### 3.4. Water absorption tests

The purpose of this test was to determine expansion due to water adsorption, and water retention of the potassium silicate coating at various relative humidities.

One coated aluminium sample and two petri dish samples of each molar ratio were prepared and allowed to room dry for a period of one week. These samples were placed in a humidity chamber at 22 °C and the relative humidity varied using sulphuric acid–water solutions in accordance with ASTM E104-85 [13].

The aluminium samples were coated to a dry film thickness of 0.5 to 1 mm to be used for expansion tests. The thickness of the room dried coating on each aluminium plate (3″ × 3″) was measured at three different marked locations using a digital micrometer accurate to 0.001 mm. Each subsequent measurement was taken at the same points to ensure consistency.

The petri dish samples were included in the test to give an indication of the amount of water retained as opposed to relative humidity. 5 g of each molar ratio solution was introduced into each petri dish and allowed to room dry for a period of one week before being placed into the humidity chamber.

The samples were tested at relative humidities of 5, 25, 57, 82 and 95% starting at 5% relative humidity. The samples were allowed to equilibrate before increasing the relative humidity. This was checked by weighing samples daily until the weight was constant.

### 3.5. Solubility tests

Solubility was determined by submerging petri dish (4 cm diameter) samples of each molar ratio in individual trays of 500 ml distilled water at 22 °C for 1 h. The water was stirred manually every 5 min. After one hour the samples were removed and allowed to dry overnight before weighing to determine weight loss.

### 3.6. Intumescence tests

Degree of intumescence was determined using the apparatus shown in Fig. 2. A bunsen burner supplied by a propane tank provided the flame to intumesce the coated aluminium samples. A pressure regulator and micrometer valve connected to the propane tank ensured a consistent heat flux for each of the tests and were set to give a temperature against time curve in accordance with ASTM E119 [14]. Coated aluminium samples from each molar ratio set were used in this test. These samples had been room dried for a period of one week.

Each sample was subjected to the flame test for a period of 5 min. The thickness of each coating was measured before and after the fire test to determine the

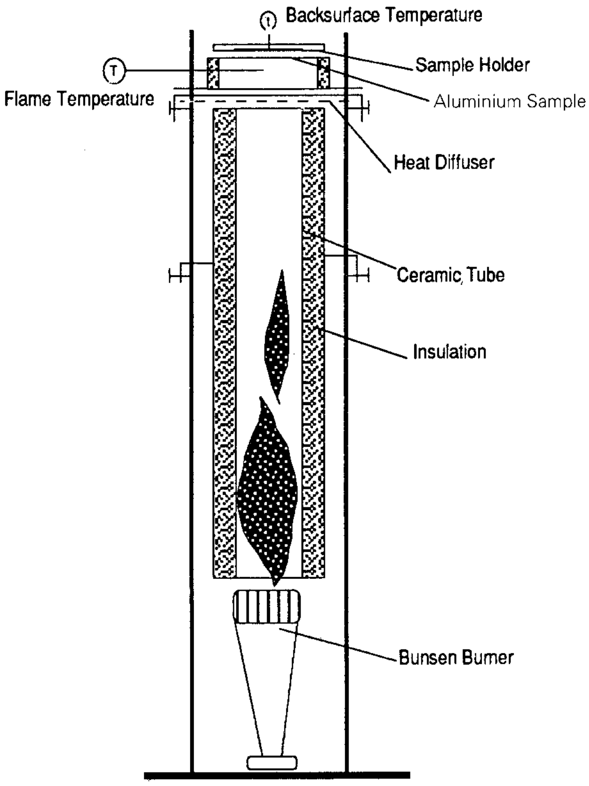

*Figure 2* Fire test apparatus.

degree of intumescence which was defined as the intumesced thickness divided by the initial thickness.

### 3.7. Infrared spectroscopy tests

Infrared spectroscopy was used to gain information on the nature of water retained in the silicate coating, and the structure of the silicate coating.

These tests were conducted in the 4000 to 600 $cm^{-1}$ region (2.5 to 15 μm). In this region lie the vibrational absorption bands of the –OH group attached either to silicon atoms or in the $H_2O$ molecules [8, 12, 15]. The stretching vibrations of both –SiOH and $H_2O$ lie near 3750 $cm^{-1}$ whereas, the deformation vibration of $H_2O$ lies near 1600 $cm^{-1}$.

In the 4000 to 600 $cm^{-1}$ range lie characteristic absorption bands of silicate structural groups. Alkali silicate glasses, fused silica, and silica gels have been studied extensively by IR and Raman spectroscopy and absorption bands have been assigned to the particular structural vibrations in the lattice [16–22]. No literature was found on films prepared from soluble silicates but the literature on glasses and silica gels was found to be applicable.

The strongest peak observed for siliceous materials is around 1100 $cm^{-1}$ and is attributed to the Si–O–Si stretching vibration. A band near 950 $cm^{-1}$ is particular to alkali silicates and intensifies with alkali oxide content. It generally has been attributed to the deformation vibration of non-bridging $SiO^-$ groups. A band near 800 $cm^{-1}$ is observed as a very weak band in vitreous silica and strong in quartz and other crystalline silicates. This has been ascribed to a O–Si–O bond bending mode.

Three molar ratio potassium silicate samples; 2.55, 3.29 and 4.72; were allowed to room dry for a period of one week and then sealed in plastic bags until tested. Each of the three samples were intumesced by placing them in a muffle furnace for 2 min at 500 °C. The intumesced structures included thin glassy bubbles which were removed and pressed between NaCl plates.

In another series of tests, samples of 3.29 molar ratio potassium silicate were allowed to room dry for one week and then intumesced for 5 min at various temperatures.

### 3.8. X-Ray diffraction tests

X-ray diffraction was employed to study the silicate structure. Samples were ground and sifted through a 200 mesh sieve tray. A Phillips X-ray diffractometer was used with Cu $K_\alpha$ radiation providing a wavelength of 0.154 16 nm.

## 4. Results and discussion

### 4.1. Water absorption test results

The water content against relative humidity tests provided the data plotted in Fig. 3. The curves indicate the hygroscopic nature of potassium silicate especially above 57% relative humidity where the water absorbed increases dramatically. These curves are similar to absorption isotherms of water on silica powder [6] for which the absorption of water is due to hydrogen bonding with surface silanol groups (–SiOH), however, in our case the samples are in monolithic form as opposed to a powder and the extent to which water can be absorbed is limited by the rigidity of the silicate structure. Low molar ratio samples expand quite freely as shown in Fig. 4 whereas, higher molar ratio samples become increasingly rigid.

Ionic hydration should play an important role in the amount of water absorbed. The lower the molar ratio the higher the number of cations and anionic sites which can be associated with water molecules. This agrees with the pattern observed in Fig. 3. From the data plotted in Fig. 3, the number of moles of water per mole of $K^+$ can be calculated and these values are shown in Table I. These values include water present as water molecules and as –SiOH groups but molecular water is assumed to be predominant. The data agree with the hydration number of

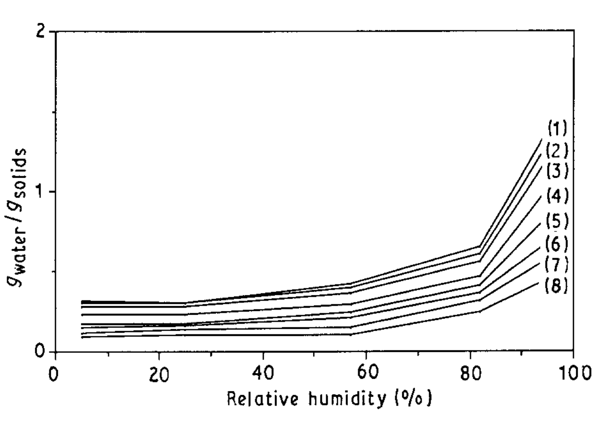

*Figure 3* Water content plotted against relative humidity (1, 2.55; 2, 2.75; 3, 3.00; 4, 3.29; 5, 3.64; 6, 4.00; 7, 4.35; 8, 4.72).

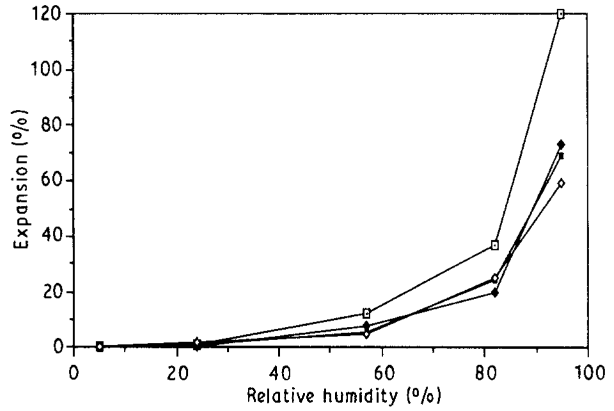

*Figure 4.* Per cent expansion plotted against relative humidity (□ 3.29, ◆ 3.64, ■ 4.00, ◇ 4.35).

$K^+$ in solution, generally accepted as two. These data provide some indication as to whether the $K^+$ cations are closely associated with the anionic sites. Cation–anion interactions will displace part of the associated water so that the number of water molecules would be expected to be two or less if stable hydrates form. At low relative humidity, the values are close to two or lower (varying with molar ratio) and the $K^+$ cations should be in close association with the anions. The number decreases with increasing $Si_2O:K_2O$ molar ratio as the particles become more colloidal in nature and the surface charge density of the polysilicate particles decreases. The decrease in surface charge density would reduce the repulsive force between silicate particles, thus changing the electrostatic equilibrium established between anion, cation and water molecules and allowing the particles to more closely approach each other, also, as the particles become more colloidal in nature there is a higher chance of siloxane bond formation between polysilicate particles. These factors results in a more rigid and brittle film as the molar ratio is increased.

At high relative humidities the moles of water per $K^+$ cation reach values as high as 9.38 and it would be expected that the cations are dissociated from the anionic sites. This increase in water content results in the samples becoming increasingly flexible.

The water contained in the potassium silicate samples is likely due to both ionic hydration, and by hydrogen bonding to polysilicate silanol groups by hydrogen bonding. The relative importance of ionic hydration as opposed to hydrogen bonding of water to silanol groups is clarified by thermal analysis.

TABLE I Moles $H_2O$/moles $K^+$ calculated from water absorption tests

| Molar ratio | Moles $H_2O$/moles $K^+$ | | | | |
|---|---|---|---|---|---|
| | 5% r.h. | 25% r.h. | 57% r.h. | 82% r.h. | 97% r.h. |
| 2.55 | 2.06 | 2.06 | 2.89 | 4.45 | 9.38 |
| 2.75 | 2.21 | 2.17 | 2.85 | 4.38 | 9.29 |
| 3.00 | 2.13 | 2.09 | 2.74 | 4.22 | 9.09 |
| 3.29 | 1.84 | 1.88 | 2.35 | 3.81 | 8.24 |
| 3.64 | 1.50 | 1.59 | 2.13 | 3.67 | 7.49 |
| 4.00 | 1.48 | 1.59 | 2.06 | 3.54 | 6.72 |
| 4.35 | 1.32 | 1.43 | 1.60 | 3.26 | 6.07 |
| 4.72 | 1.09 | 1.21 | 1.28 | 2.81 | 5.11 |

## 4.2. TGA and DSC results

The TGA results shown in Fig. 5a indicate a linear drop in weight between the start of the runs and the points marked "A" which would correspond to evaporation of free water, and water physically adsorbed by hydrogen bonding to silanol groups. A rapid weight loss occurs in the region "A–B". This corresponds to a series of endothermic peaks observed in each of the DSC curves plotted in Fig. 5b. These peaks are likely to be due to various hydrated species (i.e. different forms of the silicate anion) present in the silicate samples. For each hydrated species, the water would be ionically associated with slightly different strengths depending on the electrostatic equilibrium determined by the size and charge [23] of the $K^+$ cation, the dipolar water molecule, and particular anionic silicate species present.

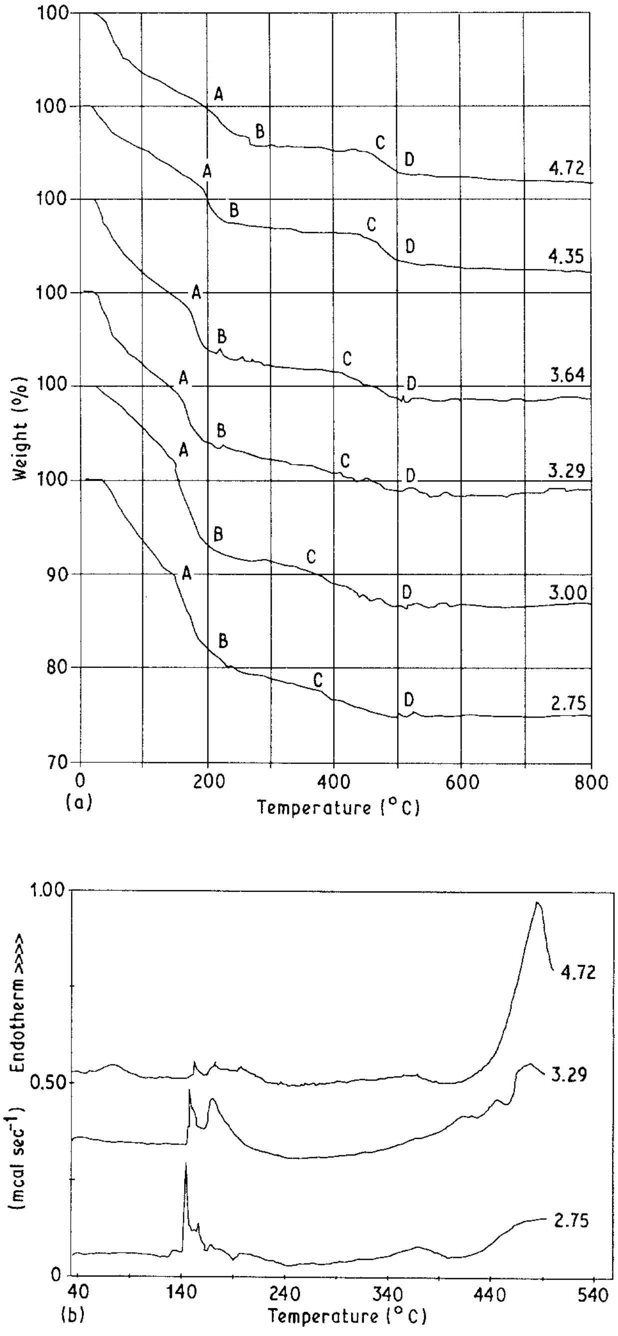

*Figure 5* (a) TGA results for various molar ratios, (b) DSC results for various molar ratios.

The rapid evolution of water vapour in the region "A–B" results in the initial intumescence of the sample. It can be observed that the water released in this region increases with decreasing molar ratio. This corresponds to a greater number of $K^+$ cations and silicate anions available for ionic association with water molecules as the molar ratio decreases.

After the initial rapid evolution of water vapour there is a more gradual decline in weight up to the points marked "C" on the TGA curves. This is believed to be due to dehydration of polysilicate silanol groups to siloxane with the release of water as is evident in this temperature range for powdered silica [11, 12].

A second rapid weight loss occurs in the region marked "C–D". This coincides with endothermic peaks in this temperature range (420 to 500 °C) as indicated in Fig. 5b. These high temperature endotherms are a result of the loss of strongly bonded water. A similar trend is observed in silicate minerals which in general lose ionically hydrated water in the 100 to 200 °C temperature range, and structural water (i.e. those present as –OH groups) in the 400 to 600 °C range [24, 25]. The release of structural water is likely the mechanism which produces the high temperature endotherms. In fact, X-ray diffraction indicated that $KHSi_2O_5$ was a significant component in the silicate matrix and this would be expected to give off structural water at an elevated temperature by the reaction

$$2KHSi_2O_5 \rightarrow K_2Si_4O_9 + H_2O$$

The release of structural water and the dehydration of polysilicate silanol groups is by the same mechanism, the dehydration of -Si(OH) groups. The loss of structural water that is evident in the TGA and DSC results occurs over a narrow temperature range as a result of the reaction of silanol groups in an orderly arrangement (i.e. belonging to $KHSi_2O_5$), whereas silanol groups of irregular polysilicate ions would react more gradually over a wider temperature range.

Table II gives an indication of the amount of water present as ionically bonded water molecules and as –SiOH groups, as calculated from the TGA results. Although the water present as –SiOH groups is not directly associated with the $K^+$ cations, it is written in terms of moles $H_2O$/moles $K^+$ for comparison purposes. The total bonded water shown in Table II is in close agreement with Table I for 5 and 25% relative humidity and indicates that at low relative humidity most of the water present in the silicate coating is strongly ionically bonded or present as SiOH groups.

TABLE II Strongly bonded water calculated from TGA results. (a) Calculated from weight loss in the region A–B, (b) calculated from the region > B

| Molar ratio | Moles $H_2O$/moles $K^+$ | | |
|---|---|---|---|
| | (a) Ionically bonded water molecules | (b) Water present as –SiOH | Total |
| 2.75 | 0.89 | 0.57 | 1.46 |
| 3.00 | 0.89 | 0.63 | 1.52 |
| 3.29 | 0.55 | 0.55 | 1.10 |
| 3.64 | 0.57 | 0.56 | 1.13 |
| 4.35 | 0.52 | 0.77 | 1.29 |
| 4.72 | 0.50 | 0.77 | 1.27 |

## 4.3. X-Ray diffraction results

Several different molar ratio potassium silicate samples were heated from 35 to 425 °C at 5 °C min$^{-1}$. Each sample was analysed by X-ray diffraction and the results are shown in Fig. 6.

Due to the complex structure of soluble silicates, an amorphous structure was anticipated. This was the case for samples dried at ambient conditions and 5% relative humidity, however, a distinctly crystalline component was observed for the samples heated to 425 °C at 5 °C min$^{-1}$ as can be seen in Fig. 6. The signal was quite noisy and indicates $KHSi_2O_5$ crystalline regions [26] within the amorphous polysilicate matrix. The crystallinity was lowest for the low molar ratio samples.

The method of heating the samples affected the X-ray results obtained. A sample intumesced by placing it directly in a muffle furnace at 500 °C for 20 min showed no diffraction pattern. Another sample placed in an oven at 165 °C for 90 min showed a different diffraction pattern which corresponded to a polymorph of $KHSi_2O_5$ [27].

Samples of room dried potassium silicate were intumesced rapidly by placing them in a furnace maintained at temperatures of 450 and 500 °C for 25 and 45 min, respectively. These samples showed optimum intumesced structures, intumescing by a factor of about 25, however, samples intumesced at 520 and

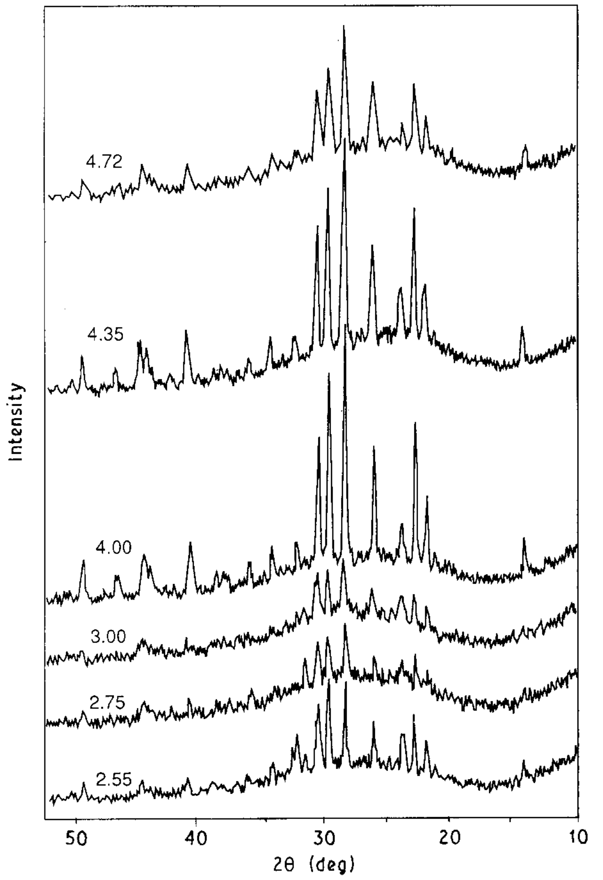

*Figure 6* X-Ray diffraction results for various molar ratio samples.

530 °C for 35 and 20 min, respectively, showed a significant amount of shrinkage (25%) as compared to the optimum structure for which no shrinkage was observed. These results correspond with the melting point of $KHSi_2O_5$ (515 °C[28]) and confirm the X-ray diffraction results indicating that $KHSi_2O_5$ is a significant component in the silicate matrix, however, although always present, only under certain heating conditions does it form an orderly structure and appear as an X-ray diffraction pattern.

The results agree with results obtained for alkali silicate glasses from which the soluble silicates are obtained by dissolution in water. At a molar ratio of 2, $(Si_2O_5)^{-2}$ sheets are present, but these are disordered in several ways as compared to the crystalline material and become more disordered as the molar ratio is decreased [2]. Apparently, the gradual heating of the potassium silicate samples resulted in crystalline regions whereas a rapid heating left the $KHSi_2O_5$ sheets in a disordered arrangement.

## 4.4. Infrared spectroscopy results

Three molar ratio potassium silicate samples (2.55, 3.29, and 4.72) were intumesced for 2 min in a muffle furnace maintained at 500 °C. Thin film, glassy bubbles were removed from the intumesced structures and sandwiched between NaCl plates. The samples were tested in the 4000 to 600 $cm^{-1}$ range using a single pass directly through the samples. The results are shown in Fig. 7.

All the samples show a broad band in the 1100 to 1000 $cm^{-1}$ region. This band corresponds to the Si–O–Si stretching frequency. The broadness of this band indicates an irregular structure which is expected in the soluble silicate matrix. The 2.55 molar ratio sample shows a connected band at about 967 $cm^{-1}$, likely corresponding to the vibration of non-bridging $SiO^-$ groups. The number of such groups decreases with increasing $SiO_2:K_2O$ molar ratio as the degree of polymerization increases in the silicate structure. This is the observed pattern as the band diminishes with increasing molar ratio indicating fewer $SiO^-$ groups. A peak at about 620 $cm^{-1}$ in the 2.55 and 3.29 molar ratio samples is ascribed to a bending mode of $SiO^-$ [19]. This peak reportedly becomes less intense and shifts to lower wavelengths as the $SiO_2:K_2O$ molar ratio increases. This shift is observed in the 4.72 molar ratio sample for which the peak is out of range below 600 $cm^{-1}$.

There is not a significant difference in the 800 $cm^{-1}$ O–Si–O bond bending band for the three samples. A band at 1440 $cm^{-1}$ for the 2.55 and 3.29 molar ratio samples is another band which has been observed in alkali silicate glasses [29]. This corresponds to a sharp band observed with sodium orthosilicate ($Na_4SiO_4$) [30] in which the free silicate ion ($SiO_4^{-4}$) is present. This band is sharpest for the 2.55 molar ratio sample for which the largest number of free silicate ions (i.e. monomeric silicate) would be expected.

Fig. 8 shows the effect of temperature on 3.29 molar ratio potassium silicate samples. Curve 1 corresponds to a thin film of potassium silicate dried on an AgCl plate for 22 h. A very broad band is evident in the 2500 to 3800 $cm^{-1}$ region which results from the superposition of stretching vibrational bands of –OH groups in –SiOH and water. The broadness of this band indicates the irregular pattern of –SiOH groups. This broad band is also evident in the curve corresponding to

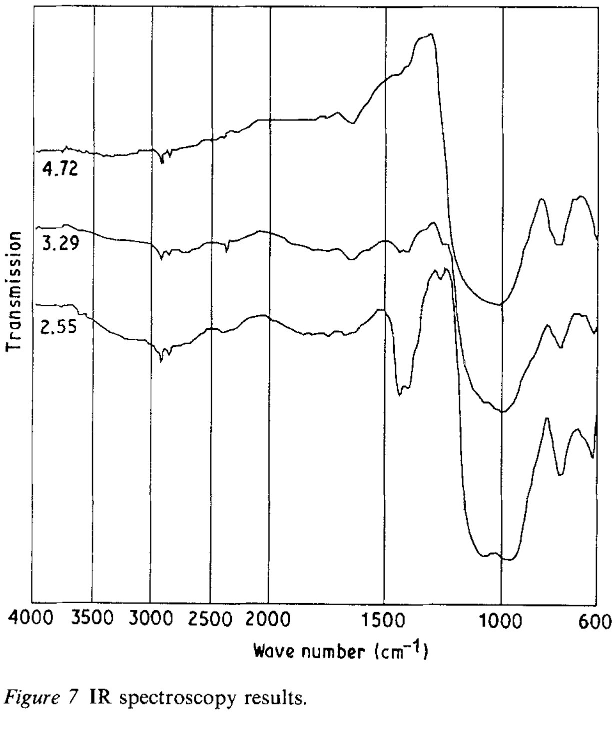

*Figure 7* IR spectroscopy results.

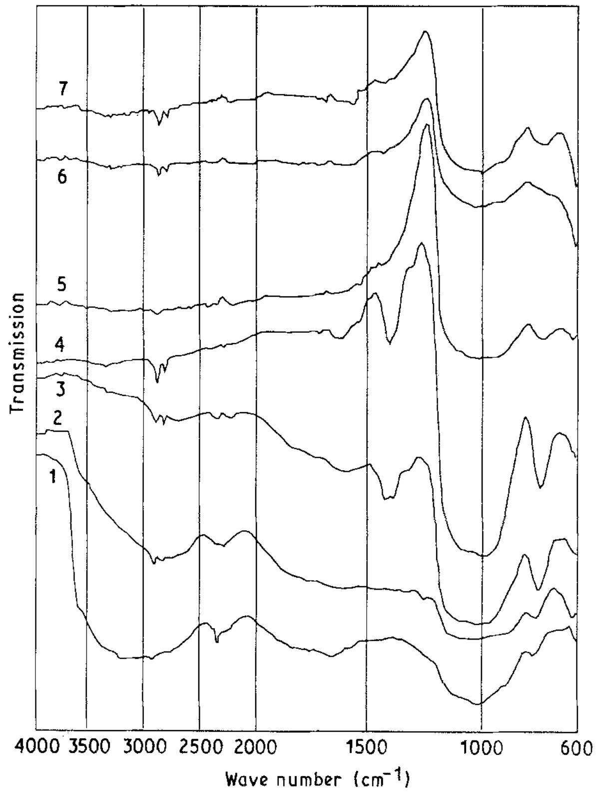

*Figure 8* IR spectroscopy results. Curve (1) thin film dried on AgCl plate for 22 h, other samples intumesced for 5 min at the following temperatures and placed between NaCl plates, (2) 300 °C, (3) 400 °C, (4) 500 °C, (5) 600 °C, (6) 800 °C, (7) 980 °C.

intumescing the sample at 300 °C for 5 min but is less intense. A broad band at around 1630 cm$^{-1}$ in most of the samples is just barely evident and is due to the deformation vibration of $H_2O$, but with a higher-order $SiO_2$ network vibration superimposed [8], thus it does not give definite indication of the presence of water, and is present even when the sample has been melted at 980 °C.

There is not enough information contained in the results to distinguish absorbed water from –SiOH groups, but it is evident that the sample intumesced at 500 °C for 5 min shows no evidence of either, therefore, any –SiOH groups that were present must have dehydrated to form –Si–O–Si– bonds by this temperature.

The spectra in the 1500 to 600 cm$^{-1}$ range undergoes significant change between 500 and 600 °C. As discussed previously, the melting point of $KHSi_2O_5$ is 515 °C and above this temperature significant shrinkage of the intumesced structure occurs. The change in the spectra may correspond to a change to a more vitreous state in the samples. This is consistent with the observed decrease in the 800 cm$^{-1}$ band which is strongest for crystalline silicates and weakest for vitreous silica.

## 4.5. Effect of molar ratio on the intumescence

Solubility, and degree of intumescence, against molar ratio data appear to be correlated as shown in Figs 9 and 10. The exception to this is for the degree of intumescence of the three lowest molar ratio samples of 2.55, 2,75 and 3.00. This may be due to insufficient silica content necessary to produce a thicker intumesced structure. The highest degree of intumescence occurs at a molar ratio of 3.29 after which the intumescence begins to drop. The solubility decreases continually from lowest molar ratio to highest molar ratio.

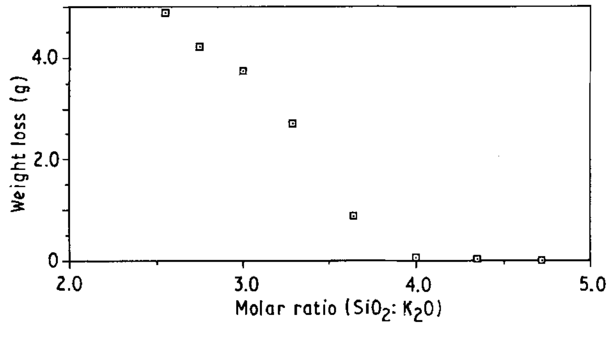

*Figure 9* Solubility plotted against molar ratio.

As the molar ratio increases, the amount of water ionically bound in the matrix decreases. Since the release of water vapour is the driving force for intumescence, the decrease in water content explains the decrease in intumescence. Solubility also decreases since the polysilicate particles increase in size and the surface charge density decreases along with the number of cations, thus, the driving force for hydration and dissolution of the silicate film decreases, also, as the molar ratio increases, there is a greater probability of siloxane bond formation between particles upon drying.

## 4.6. Effect of water content on the intumescence

Since the rapid evolution of water vapour from the silicate matrix is the driving force for intumescence, water content should have a major influence on the degree of intumescence. Several aluminium samples were coated with a 3.29 molar ratio potassium silicate solution and allowed to room dry for a period of one week. Samples were then placed in humidity chambers with relative humidities of 5, 57, 82 and 95% at 22 °C. These samples were allowed to equilibrate and were then tested for degree of intumescence. The data are plotted in Fig. 11.

From Fig. 11 it is seen that water content has a significant effect on the degree of intumescence. Samples maintained at a relative humidity of 95% and then tested gave a high degree of intumescence, however, these samples were hollow with thin crusts and would provide poor fire protection. All other samples had solid foam structures. There is little difference in the intumesced structure or degree of intumescence for samples maintained at 57 and 82% relative humidity whereas samples dried at 5% relative humidity had insufficient water content to provide a high degree of intumescence.

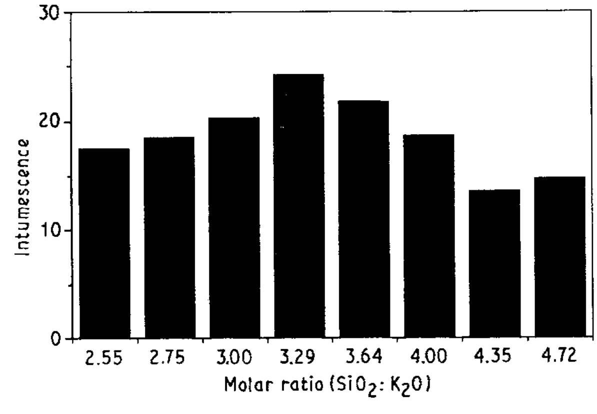

*Figure 10* Degree of intumescence plotted against molar ratio.

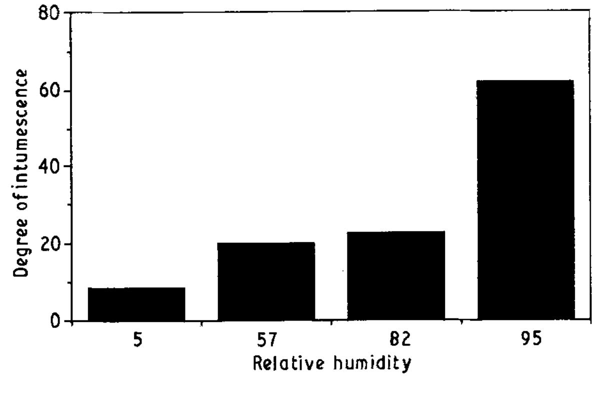

*Figure 11* Degree of intumescence plotted against relative humidity.

## 5. Summary and conclusions

Potassium silicate becomes increasingly hygroscopic as the silica:potassium oxide ratio decreases. The hygroscopic nature of each of the molar ratio samples tested was especially apparent above 57% relative humidity where the amount of water absorbed increased dramatically.

Low molar ratio samples expanded freely as water was absorbed whereas higher molar ratio samples became increasingly rigid and resistant to expansion. The lower degree of expansion is likely due to the smaller driving force of ionic hydration with increasing molar ratio. Formation of siloxane bonds between polysilicate particles may also be involved.

The amount of water contained in the dried sample has a significant effect on the intumescence. In addition the rigidity of the structure effects the onset and degree of intumescence. Both of these results are consistent with the mechanism of intumescence; the rapid evolution of water vapour which forces the silicate matrix apart.

$KHSi_2O_5$ sheets are present within the polysilicate matrix and under gradual heating conditions appear as an orderly structure as evidenced by an X-ray diffraction pattern. $KHSi_2O_5$ has a melting point of 515 °C and above this temperature significant shrinkage of the intumesced structure occurs.

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