

## The Unexpected Behaviour of Potassium Aluminosilicate Solutions

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Potassium aluminosilicate solutions with low Si : Al ratios form gels more slowly with increasing KOH content but at higher Si : Al ratios the reverse is true; there are also significant differences in other solution properties.

Alkali silicate and aluminate solutions have been investigated by many methods, of which n.m.r. has been particularly useful.<sup>1</sup> Silicate solutions contain a mixture of species, the smaller (lower molecular weight) ones being favoured by higher alkalinity; aluminate solutions contain only  $\text{Al}(\text{OH})_4^-$ . When they are mixed together as for the synthesis of zeolites, sooner or later a gel generally forms. It is possible that the structure of the complex aluminosilicate anions believed to form in the solution determine which zeolite is eventually produced.<sup>2</sup> The existence of such complexes can be studied by n.m.r. and in order to do this the gel times of potassium aluminosilicate solutions were investigated so as to select compositions that would remain liquid during the experiment.

The relationship between gel time and composition was unexpected.

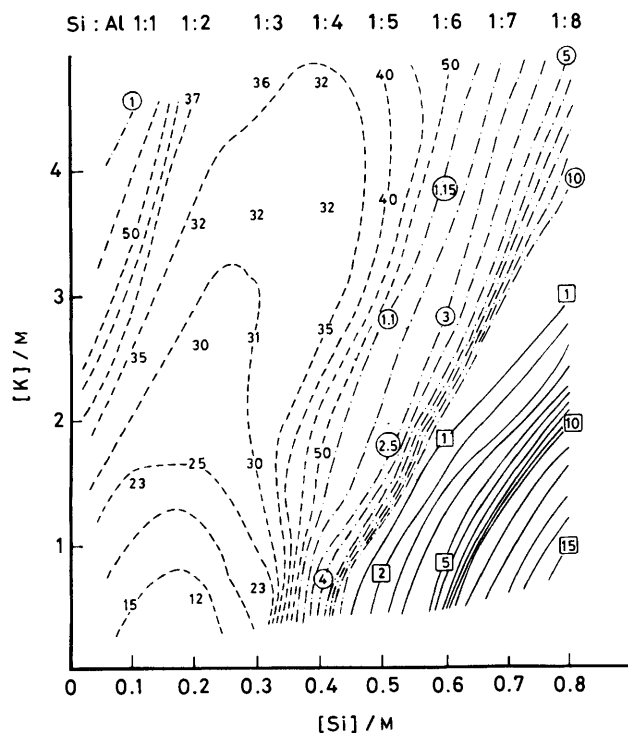
The test solutions (all 0.1 M with respect to Al) were prepared by rapid mixing of potassium aluminate and potassium silicate solutions. All the latter contained the same initial distribution of silicate species because their composition was kept constant at 1.0 M Si, 0.61 M K. The final alkali content was adjusted by changing the composition of the aluminate solutions, which invariably contained only  $\text{Al}(\text{OH})_4^-$ . Thus at the moment of mixing, the range of species introduced was in all cases similar.

The time from mixing to gel formation was noted, and the results obtained are shown in Figure 1. The mixtures show two

**Table 1.** Comparison of extremes of solution behaviour shown by the mixtures in Figure 1.

	Top left {high [K], low [Si]}	Bottom right {low [K], high [Si]}
Kinetics: gelation retarded by	{Increase in [KOH], {decrease in [Si].	{Decrease in [KOH], {increase in [Si].
<sup>27</sup> Al n.m.r. shows	Mainly Al(OH) <sub>4</sub> <sup>-</sup>	No Al(OH) <sub>4</sub> <sup>-</sup> ; all Al complexed by silicate
Light scattering	Initially low and steady, then rapid increase.	Higher initial values, followed by slow steady increase.
Conductivity	Initial rapid increase, decelerating steadily; no discontinuity at gelation.	Initial very rapid decrease, followed by slow, steady increase.
Zeolite produced at 95°C	Normally F (Al:Si = 1:1)	Normally W (Al:Si = 1:2.5) or L (Al:Si = 1:3)

In the 'valley', zeolite G (Al:Si = 1:2) is usually formed.



**Figure 1.** Gel time for 0.1 M Al potassium aluminosilicate solutions; [K] and [Si] given on axes. Figures represent the results of actual runs: numbers without circles or squares indicate times in minutes, those in circles times in hours, and those in squares times in days. Contours (approximate) follow a similar scheme; intervals: - - - - - 5 min, . . . . . 1 h, ——— 1 day.

extremes of behaviour; for compositions at the top left of Figure 1 (high K, low Si) increasing alkali retards gelation, as expected, but at the bottom right (low K, high Si) this trend is reversed with decreasing [KOH] retarding gelation (and this was totally unexpected). A region of minimum gel times separates the two types of behaviour. The contrast in behaviour is reflected in the results of investigations by other methods (Table 1); there is a profound difference in time-dependent behaviour in the two parts of the diagram.

Even at the lowest Si concentrations, enough silica is present for Al-O-Si complexes to form, but these are not observed in the most highly alkaline solutions. This suggests that Al(OH)<sub>4</sub><sup>-</sup> does not readily complex with small, highly charged, silicate groups such as HSiO<sub>4</sub><sup>3-</sup>. On the other hand, towards the bottom right of Figure 1, all the Al appears to be complexed by silicate; this may render it inert so that these solutions are slow to gel.

The presence of a reasonable number of uncomplexed aluminate ions and small but not too highly charged silicate ions may be pre-requirements for gel formation. This would explain the minimum in Figure 1. This idea is supported by the observation that if the compositions at the lower right of Figure 1 are made up by adding the additional alkali to the silicate (and thus reducing its degree of polymerisation) gelation occurs much more rapidly. Although detailed interpretation is not yet possible, these ideas are consistent with the properties listed in Table 1.

When the gels produced are crystallised, the zeolites formed do differ systematically across Figure 1; compositions at the top left normally yield zeolite F,<sup>3</sup> those at the bottom right W<sup>4</sup> or L,<sup>5</sup> and those across the middle G.<sup>4</sup> This need not, however, imply structural control by precursor species in the solution, since it could be merely a function of composition.

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