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FACTORS INFLUENCING THE RATE OF SILICA GEL FORMATION
IN HIGH ACID-SALT SOLUTIONS

IDAHO NUCLEAR CORPORATION
NATIONAL REACTOR TESTING STATION
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FACTORS INFLUENCING THE RATE OF SILICA GEL FORMATION IN HIGH ACID-SALT SOLUTIONS

by

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A B S T R A C T

Means of influencing the rate of gelation of silicic acid in nitric acid-nitrate salt solutions or of controlling the gel were evaluated. The effect on gelation rate of acidity, salt concentration, silicic acid concentration, and temperature are given. A number of amines, functioning as hydrogen bonding agents, were relatively ineffective in altering gelation rate.

SUMMARY

The chemical or electrochemical dissolution of silicon-containing nuclear fuel alloys for reprocessing generates silicic acid in solution, which in turn polymerizes to polysilicic acid and may ultimately form a gel. The polymers and gels can lead to line plugging throughout the plant and emulsion stabilization in the solvent extraction columns of the reprocessing plant. Methods of control of this problem which were studied included preventing or slowing the polymerization, and using additives to accelerate the rate of polymerization so that the gel could be readily removed from solution. To study the effects of acid, temperature, salt concentration, and additives on this reaction, the gel times of solutions containing exaggerated concentrations of silicon were measured as a function of the variables. Finally, the effects were verified by measurements made with solutions of typical silicon concentrations. It was shown that by various mechanisms the presence of chemically inert solids or gelatin in the solution accelerated gel formation and would facilitate removal of the gel by centrifugation. Hydrogen bonding agents, which accelerated gelation in solutions of low electrolyte content, were not effective enough in the high salt, high acid solutions to be useful. Therefore, no new procedure was suggested by these studies which would satisfactorily coagulate the silica so that it would be effectively removed by filtration or sedimentation.

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FACTORS INFLUENCING THE RATE OF SILICA GEL FORMATION IN HIGH ACID-SALT SOLUTIONS

I. INTRODUCTION

The chemical or electrochemical dissolution of silicon-containing nuclear fuel alloys for reprocessing usually generates silicic acid in solution. In acid solutions this silicic acid polymerizes to polysilicic acid and eventually forms a gel. This silicic acid produced from dissolution of reactor fuels often leads to process difficulties in the plant streams at the Idaho Chemical Processing Plant. In the electrolytic dissolution process wherein stainless steel clad, uranium fuel is dissolved in nitric acid, the silica gel associates with grains of stainless steel dropped from the cladding and the resultant sludge deposits in the heat exchanger in the dissolver recycle loop and interferes with cooling of the dissolver solution⁽¹⁾. In the dissolution of aluminum alloy fuels in nitric acid, lower molecular weight silicic acid polymers act as emulsion stabilizers in the extraction columns, and sludges formed by the association of silicic acid with fine particles of metal in the dissolver form plugs in the process lines. The continuing occurrence of these problems indicates the need for understanding of the factors determining the rate of silica gel formation. Once the rate-determining factors are known, control of these sludge problems might be accomplished by methods such as preventing the gel from forming (slowing the rate of formation so that the material would be discharged from the system before a significant amount of gel was formed) or by speeding the formation and removing the gel before it could become troublesome in process equipment.

Silicon is present in most alloys either as an impurity remaining from the production of one or more of the metals in the alloy or intentionally added for metallurgical reasons⁽²⁾. Although elemental silicon is not known to be soluble in nitric acid, it apparently dissolves readily when it is present in an intermetallic compound in an alloy⁽²⁾. Any silicon which was contained in alloys which have been dissolved electrolytically appeared to dissolve completely. In the nitric acid process streams this dissolved silicon forms silicic acid and begins to polymerize at a rate dictated by the silicon concentration and the environment. To expedite the performance of the many experiments in this program and to give reproducible solutions, this dissolved silicon was simulated by the addition of sodium metasilicate stock solution to solutions containing acid and salts at concentrations of process interest.

Because silica gel can be produced in many acid media used in fuel reprocessing, general studies of the effect of temperature and solution composition variables on the gelation rate were undertaken. Those factors which were shown to influence the gelation rates significantly were then further investigated at concentrations which were more closely related to specific process conditions.

II. EXPERIMENTAL APPROACH

1. BEHAVIOR OF DISSOLVED SILICON SPECIES

Silicate ions are soluble in alkaline solution, generally in the form of meta-silicate, SiO_3^{2-} , or orthosilicate, SiO_4^{4-} ; however, in acid the silicate ions protonate to form the corresponding silicic acid which then polymerizes to polysilicic acid⁽³⁾; aggregation or flocculation occurs as the silicic acid polymerizes, causing an increase in viscosity until a gel forms. The final gels obtained in this study were generally translucent and were rigid except for those produced in the very dilute silica systems in which only a fibrous or flocculant material separated from the solution. While it would have been most desirable to prepare the stock silicate solutions by the dissolution of an alloy containing silicon in a dissolvable form, this was not practical in the laboratory experiments. Dissolution of such alloys in nitric acid leads to the start of polymerization during the dissolution, and the preparation of a reproducible, stable stock solution of soluble silica by this means is impossible. Therefore, the soluble silica produced by alloy dissolution was simulated by use of sodium silicate solution. As soon as the latter was added to the acid media in the experiments, polymerization of the silicic acid began.

Several mechanisms for the formation of polysilicic acid and silica gels are discussed by Iler⁽³⁾. The time needed for the formation of this gel is highly dependent on several factors including temperature, pH, and concentration of silicon. The influence of these factors on the rate of gel formation has been investigated at low acid and salt concentrations⁽³⁾, but very little information is available on the relative importance of these variables in the region of high acid and salt concentrations.

The dependence of the gel time for silicic acid on silicon concentration observed here is shown in Figure 1. Across the concentration range shown in Figure 1, the gel time is inversely proportional to the silicon concentration raised to the 1.35 power. The expression:

$$T = \frac{1.9 \times 10^6}{C^{1.35}}$$

where T is gel time in minutes, and C is silicon concentration in mg/l, gives a reasonable correlation of the data. These results are discussed further in section 1.3.

The gel times at the nominal concentrations in current processes (Curve A, Figure 1) are comparable to process time cycles, that is, the recycle of solution in the electrolytic process and the storage of solutions in surge tanks between process operations in the aluminum process lead to contact times in the order of tens of hours. Reproduction of these very

long times was impractical in a laboratory program involving many experiments. In addition, before an extensive precipitate of silica gel (a line plug for example) can occur in process solutions, there must be a localized coagulation of polymerizing silicon up to a point where gel formation is possible. For these two reasons, most of the experimental work was done at concentrations of silicon about 100 times greater than those which are reported for the process flowsheets. The gel times for these solutions are shown in Curve B, Figure 1. Dilute silicon systems were investigated in detail for the effect of those concentration variables which showed the greatest promise in the high concentration studies.

Fig. 1 Effect of silicon concentration on gel time at 62°C.

2. AREAS OF INVESTIGATION

Two areas were investigated in this study. The first was a determination of the effects on gel time of the temperature and the concentrations of total silicon and metal salts plus the added effects of various dispersants and flocculants.

Iler has reported that various organic molecules are effective in "solubilizing" the precipitate formed between polysilic acid and gelatin by a hydrogen bonding mechanism⁽⁴⁾. This behavior suggests that the presence of some of these molecules in the dissolver systems could prevent sludge

formation by interfering with the polymerization of the polysilic acid. For this reason, the influence of various concentrations of added organic materials (referred to in this work as hydrogen bonding agents, HBA) was determined.

In the above-mentioned studies, the concentration of silica was kept 50 - 100 times higher than actual process concentrations in order that reasonable gel times might be observed. The second area of interest covered systems at or near actual process concentrations of dissolved silicon in which trends noted in the initial investigations were compared at these low total silicon concentrations. In these studies the possible usefulness of dispersants was also evaluated.

III. EXPERIMENTAL PROCEDURE

1. PREPARATION OF REAGENT SOLUTIONS

Reagent solutions were prepared as follows. Concentrated (70%) nitric acid was used directly. The silicon stock solutions were prepared by dissolving 75 grams of $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ in distilled water and diluting to 250 milliliters.

A number of different silica stock solutions were prepared during the period of these experiments. Typical ones were selected for analysis as a check on the composition of the stock sodium silicate reagent. The total silicon concentration in these solutions was around thirty grams per liter. The gel time for a standard solution was checked frequently during the time a given stock was being used. No variation in the gel time was seen due to the age of the stock solution; however, a new stock solution was prepared if a precipitate was observed after a given solution had stood about two weeks.

A solution containing the major stainless steel cations in salt form and in the desired ratios of 71 iron-19 chromium-10 nickel was prepared by dissolving appropriate amounts of nitrate salts of iron, chromium, and nickel in distilled water. The concentration of the solution corresponded to 150 grams of dissolved stainless steel per liter.

2. HYDROGEN BONDING AGENT SOLUTIONS

The water-soluble organic compounds used were prepared to various concentrations by weighing the reagent and then diluting with distilled water to the required volume. These stock solutions were prepared up to concentrations of 250 g/l. Those organic compounds which were not soluble in water were pipetted directly into the acidified sample.

The organic compounds studied were triethanolamine, 2,3-butanedione, diethylenetriamine, quinoline, triethanolamine, diethylamine, pyridine, butylaminoethanol, and t-butyldiethanolamine.

3. GELATINS AND POLYMERS

Solutions of the various gelatins and polymers were made by dissolving a weighed amount of the gelatin in distilled water. The water soluble gelatins and polymers tested were: Jello K626004A and K325609, Knox gelatin, Polyhall 19, Polyhall 402, Polyhall 295, Aquafloc 403, Calgon coagulant aid 206, and Calgon coagulant aid WCL551. In addition, two industrial dispersants were tested, Nalco 344-L-8093R and Nalco 345-L41835.

The most soluble of the gelatins, Jello K626004A, could be prepared up to a concentration of 60 g/l and still be of low enough viscosity for pipetting.

4. PREPARATION OF SAMPLES

With the exception of samples prepared to pH 2.5, all reagents were pipetted directly into a 50 ml Erlenmeyer flask. The samples at pH 2.5 were prepared in 50 ml beakers by combining reagents and enough acid to give a pH of about 1.0 the pH was then adjusted to 2.5 by adding dilute NaOH dropwise and monitoring with a pH meter. The approach to pH 2.5 from the lower side was necessary to avoid the very rapid gelation which occurs at pH 5 to 7⁽³⁾. The sodium metasilicate solution was always the last reagent added to the solution since the silicate begins polymerizing immediately to polysilicic acid upon acidification. It was also found to be necessary to swirl the solution while adding the silicate, especially in concentrated solutions where silicate present in high local concentrations might precipitate.

All samples for which a gel time was observed were prepared to a total volume of approximately 10 ml. This volume was measured by pipetting the required amounts of reagents and water to give appropriate concentrations. The error due to differences in partial molar volumes among the reagents, and therefore in the total volume of the mixture of reagents, was assumed to be small and was ignored.

Immediately after preparation, each sample was immersed in a constant temperature ($\pm 1^\circ\text{C}$) water bath set for the desired temperature.

5. DETERMINATION OF GEL TIME

Although numerous factors influence the rate of polymerization of silica in a given system, the time to form a gel is quite reproducible^(4,5). Our preliminary investigations showed this gel time to be sufficiently dependent on solution composition to be a satisfactory gauge for measuring the relative effect of the various solution components. The gel time of each sample was taken as the time lapse between addition of the silicate to the sample and the initial appearance, after swirling the solution, of globules of silica gel on the side of the flask. The final firm gel formed after this time within 5% of the lapsed time. Reproducibility of gel time was approximately 3%, if caution was used in sample preparation, timing, and temperature control. As the complexity of the sample solution composition increased, gel times became less reproducible, probably due in part to random error in pipetting.

IV. RESULTS AND DISCUSSION

1. STUDIES AT HIGH SILICON CONCENTRATIONS

1.1 Dependence of Gel Time on Temperature

Gel time, t_g , is strongly dependent on the temperature of the solution, with t_g decreasing as temperature increases. Figure 2 shows the t_g vs. temperature curve for four solutions of varying composition. The curves are nonlinear over the temperature range investigated with gel times approaching the temperature axis asymptotically. The gel time will be expected to continue to decrease with temperature up to a temperature at which the gel melts.

Fig. 2 Temperature dependence of gel time.

- (a) 7.8M nitric acid, 4g silicon per liter.
- (b) 7.8M nitric acid, 5.5g silicon per liter.
- (c) 7.8M nitric acid, 4.4g silicon per liter, 15g stainless steel cations per liter.
- (d) 6.24M nitric acid, 5.5g silicon per liter, 15g stainless steel cations per liter.

Temperature dependence of gel time data has been used by Hurd (6) to calculate a quantity of energy, "Q", analogous to the heat of activation in ordinary chemical reactions. The derivation of the expression used to obtain "Q" will not be repeated here. However, the assumptions on which it is based, and the final result are important. The assumptions are as follows:

1. That we are dealing with a process which follows the laws of an ordinary chemical reaction so far as its velocity is concerned.
2. That the Arrhenius equation may be applied to our results.
3. That for a given run the time of gel measures the time when a certain fixed amount of the silica, in whatever form, in solution, has reacted. The final result, analogous to the Arrhenius equation, is:

$$\frac{d \ln t_g}{d 1/T} = \frac{"Q"}{R}$$

Therefore, the slope of a $\log t_g$ vs. $1/T$ curve can be used to obtain "Q". A curve of this type is shown in Figure 3. The "Q" calculated from the slope of this line obtained from a least squares fit of the data, is 9100 ± 300 calories. The error interval is based on experimental error in temperature and gel times and their affect on the slope of the line. Gel times were obtained over a temperature range of 0° to 80°C .

Although "Q" has been calculated for some of the strong acids at rather low concentrations (7) (pH 3-5) and also for somewhat higher acid concentrations (greater than 1 molar), no data were found for nitric acid in the high concentrations at which these studies were carried out. However, our result is comparable to those found by Hurd and co-workers, 9,000 calories and 11,000 calories, for H_2SO_4 and HCl , respectively, at acid concentrations greater than one molar.

Fig. 3
Determination of activation energy.

1.2 Dependence of Gel Time on Acid Concentration

Gel time is also highly dependent on the concentration of nitric acid. Figure 4 shows plots of t_g vs. molarity of acid over the concentration range typical of that used in the electrolytic dissolver. In Curve a, the concentrations of stainless steel salts and silicon were held constant at 6.0 g/liter and 4.4 g/liter, respectively. For Curve b, the silicon was at 6.3 g/liter with no added stainless steel salts. The curve once again is nonlinear with higher acid concentrations corresponding to lower values of t_g . There is no difference in the shapes of the curves due to the addition of stainless steel salts; the decrease in gel time expected due to the added silicon does occur.

1.3 Dependence of Gel Time on Silicon Concentration

As would be expected, the gel time is highly dependent on silicon concentration, or more correctly, on silicic acid concentration, with the gel time increasing rapidly at lower silicon concentrations. Figure 1 shows the plots of t_g vs. silicon concentration (gms/liter) to be nonlinear in the range studied. A kinetic rate expression has not yet been developed to fit this curve.

Fig. 4
Acid dependence of gel time.

- (a) Temperature: 62°C, 4.4 g silicon per liter, 6 gm stainless steel cations per liter.
(b) Temperature: 60°C, 6.2 g/liter silicon.

1.4 Dependence of Gel Time on the Concentration of Metal Salts

Stainless steel cations were shown to have little effect on the gel time at higher acid concentrations. In a solution 7.8M nitric acid, and approximately 4 g/l silicon, only a two-minute difference in gel time was observed in a total gel time of around 12 minutes over the concentration range of 0 to 15 grams stainless steel/liter. Although this represents approximately a 16 percent decrease in gel time, the effect is still relatively small when compared to the changes caused by varying silicon concentration.

1.5 Effect of Hydrogen Bonding Agents on Gel Time

The varied effect of organic hydrogen bonding agents is shown in Figure 5. Most of these materials increase the gel time by less than a factor of two in concentrations up to 100 grams of hydrogen bonding agent per liter. Since most of the compounds tested are bases, some of

Fig. 5
Effect of hydrogen bonding agents on gel time.

Stainless steel system: 6.24 molar nitric acid, 6 g/l silicon, temperature: 62°C

the action of these materials can be attributed to partial neutralization of the acid; this will be offset to some extent by the salt effect of the organic material. The amounts of organic material added here are quite large compared to the range of concentrations studied for salt effect due to stainless steel ions.

Comparison of Curve b in Figure 3 with Figure 5 for dependence of t_g on acid concentration and on hydrogen bonding agent concentration shows that the effect of two of these materials, pyridine and diethylamine, is considerably greater than would be expected for acid neutralization alone. When the effect of the acid neutralization is subtracted out, both diethylamine and pyridine, at concentrations of 100 g/l approximately triple the gel time for a solution containing silicon at 6 g/liter.

The effects of hydrogen bonding agents on gel times were examined at pH 2.5. At this pH it was necessary to use higher silicon concentrations than were used in the earlier studies in order to get gel times that were reasonable in length. These results showed that pyridine

and diethylamine shortened rather than lengthened the gel times. In a solution containing 18 grams of silicon per liter, a concentration of 52 grams of diethylamine per liter reduced the gel time from 116 minutes to 104 minutes. A concentration of 52 grams of pyridine per liter reduced the gel time from 116 minutes to 59 minutes.

The polymerization rate of silica is reported to be at a minimum in the region of pH 2.4⁽³⁾. At high pH the polymerization is catalyzed by OH⁻ ions; at lower pH, H⁺ ions catalyze the reaction. The polymerization of silicic acid can be catalyzed by other ions as well. This catalyzing effect of fluoride, hydroxide, and hydrogen ions has been attributed to the expansion of the coordination sphere of the silicon to six members⁽³⁾. The organic materials used in these tests could act in this manner through the hydrogen bonding sites available in the molecules. At pH 2 to 3, where the gel time is a maximum, the added organic molecule can act as a catalyst to accelerate the polymerization of the silica.

Thus, although it was shown that the hydrogen bonding agents did influence the gelation rate for silicic acid, the nature of this influence was acid-dependent, and the total effect was too small to be of process use.

1.6 Effect of Gelatins and Polymers on Gel Time

The gelatins and polymers are expected to interact with the polysilicic acid in much the same way as do the organic molecules, that is, forming hydrogen bonds with the acid. However, in this case, high molecular weight proteins of the gelatin are surrounded with silicic acid rather than vice-versa, and, therefore, they act as giant polysilicic acid molecules⁽⁴⁾. This process would then logically decrease gel time since the silicic acid is bonded together more rapidly and could provide a mechanism for silica removal. Most of the gelatins and polymers which were tested in concentration ranges feasible for use in the electrolytic dissolver showed no significant effect on the gel time in 7.8M nitric acid. Rapid flocculation or precipitation was seen with only two of the tested materials. A slight precipitate formed when the silicate solution was added to the acid-Polyhall 19-stainless steel solution. The nature of this precipitate was not investigated because the Polyhall 19 did not significantly affect the gel time. The Aquafloc 403 precipitated when added to acid without silica present and therefore was useless in this application.

Because of its greater solubility in water, the low temperature, Jello K626004A, gelatin could be studied at higher concentrations, but at concentrations as high as 13.5 g/l this gelatin only decreased the gel time by approximately 4 minutes in a total time of about 25 minutes. None of these tests indicate that a useful dispersion or precipitation of the silica gel can be obtained with any of these materials.

The two Calgon polymers, Coagulant Aid 226 and Coagulant Aid WCL 551 did show a significant effect on gel time. These results are shown in Figure 6, which also gives the condition and concentrations

of the runs. There also appeared to be a noticeable effect on the physical nature of the gels formed when either of these two polymers was present. The gels formed seemed more like a syrup than a normal gel; this characteristic made the gel point difficult to determine and the gel times were therefore less reproducible. It did not appear that this form of the gel would be useful for silicon removal by precipitation.

2. STUDIES AT NORMAL (LOW) SILICON CONCENTRATION

2.1 Introduction

Results of studies made at silicon concentrations on the order of that found in the electrolytic dissolver (60 mg/l) showed that after a sufficient period of time (sometimes several days) a silica gel will form at this low concentration. The gel formed in the solution has a fibrous or webby appearance. Vigorous stirring will break up this web, but on standing, it will once again associate.

2.2 Dependence of Gel Time on Silicon Concentration

Even in this low concentration range of silicon, the gel time, at 61 - 62°C, was highly dependent on the silicon concentration. A solution of 8.0M nitric acid, and 300 mg of silicon per liter formed a gel in less than 18 hours; a solution of 8.0M nitric acid and 150 mg of silicon per liter formed a gel between 30 and 48 hours; and a solution containing only 75 mg of silicon per liter and 7.0M nitric acid took from 72 to 96 hours to gel.

2.3 Effects of Hydrogen Bonding Agents on Gel Time

The two most effective hydrogen bonding agents, pyridine and diethylamine, showed little if any effect on gel time in this concentration range. Even at concentrations of hydrogen bonding agent as high as 100 g/l or roughly 300 times the silicon concentration, there was no detectable effect. Apparently the polymerization process is so slow at these concentrations that the hydrogen bonding agents can be displaced during gel formation without significantly influencing the gel time.

Fig. 6 Effect of calgon coagulant aids on gel time.

(a) Calgon coagulant aid 226;
4 gm silicon/l, 6.25M nitric acid,
temperature: 54°C.

(b) Calgon coagulant aid WCL 551;
4 gm silicon/l, 6.24M nitric acid,
temperature: 54°C.

2.4 Effect of Stainless Steel Particles on Gel Time

Metal particles present in the silicic acid solution are incorporated in the gel phase and appeared to influence the gel time. The incorporation of the solids depends on two factors; most important is the amount of agitation of the solution which occurs during the gel formation; the second variable is the length of time during which gelation occurs; the longer the gel time, the greater the amount of solids that may become incorporated in the gel. In dilute solutions of silicon, the presence of solids decreased the gel time; solutions of 8.0M HNO_3 and 75 mg of silicon per liter with solids present gelled in about 90 hours while the same solution required 115 hours to gel without solids. These results indicate that the particles aided the gelling process by providing surface area for coagulation of particles. This mechanism can not be established clearly in this system but appears to be a significant part of the sludge formation mechanism.

V. PROCESS APPLICATIONS AND CONCLUSIONS

The results obtained in these studies have the following implications in the electrolytic dissolution system:

(1) The effect of the stainless steel solids on gel time demonstrates that the sludge formation rate would be reduced by decreasing the amount of this suspended material which is circulating with the aging silicon solution.

(2) The hydrogen bonding agents which could be expected to aid in the management of this sludge were not useful in the high-acid, high-salt solutions.

(3) No procedure was suggested by these studies which would satisfactorily coagulate or otherwise convert the silica so that it would be effectively removed by filtration or sedimentation.

It was concluded that gel time measurements were a reproducible means of studying the rate of polymerization of silica in process solutions, and it was shown that the gel time was strongly influenced by acidity, temperature, salt concentration, silicon concentration, and the presence of metal particles.

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