Condensation Mechanism and Influencing Factor of Stability of Complicated Silicic Acid System

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DOI 10.1002/aic.12374

One complicated silicic acid system, containing Al^{3+}, Mg^{2+}, Fe^{2+}, and Fe^{3+}, is prepared through acidolysis of blast furnace slag. By investigating its gel time concerned with pH value, compared with that of ordinary silicic acid system, it is shown condensation reaction existing and efficiently controlling gelling characteristics of complicated silicic acid system by regulating pH values. The results are validated by FT-IR spectra analysis. With nonionic surfactant employed, the gel time is increased from 11 to 312 h, more suitable to control gel time than anionic surfactant. © 2010 American Institute of Chemical Engineers *AIChE J*, 57: 1339–1343, 2011

Keywords: complicated silicic acid system, condensation reaction, gel time, surfactant, pH value, blast furnace slag

Introduction

There have been some reports about condensation reaction and stability of silicic acid system, for example, Iler and other authors[1–4] studied the effect of pH value, salts added and concentration of silicic acid on condensation reaction of silicic acid. Xu[5] investigated the effect of particle diameter on stability of silicic acid system. But all those have not been concerned to complicated silicic acid system. Furthermore, there have been many reports about using siliceous minerals and waste to prepare fine siliceous chemical.[6–10] When those materials are dissolved in acid or alkali, complicated silicic acid system would be prepared. There have been many researches on the formation of silicic sol in a complex silicic acid system.[11–15] But there has not been any relative report on what to control gel time of such complicated silicic acid system. In the article, we studied the preparation of complicated silicic acid system via acid hydrolysis of blast furnace slag and proposed its condensation mechanism.

Materials and Methods

The complicated silicic acid system was prepared via acid hydrolysis of blast furnace slag with concentrated sulfuric acid. Blast furnace slag dissolved in sulfuric acid, CaO was removed as precipitate via filtering, and the filtrate was obtained including silicic acid and Al^{3+}, Mg^{2+}, and Fe ions forming complicated silicic acid. The pH value of system was regulated by adding slag and solution acidic hydrolysis.

Materials

The chemical analysis results of blast furnace slag, got from the First Iron General Works of Maanshan Iron & Steel Limited Company, were shown in Table 1. Concentrated sulfuric acid whose mass percent was 98% was purchased from Shanghai Reagent Co.

The sample solution includes SiO_2 of 100 mg/ml, Al^{3+} of 20 mg/ml, Mg^{2+} of 10 mg/ml, SO_4^{2-} of 160 mg/ml, a small

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Table 1. Chemical Composition of the Slag

Composition	SiO_2	CaO	Al_2O_3	TFe	MgO	S	TiO_2	other
Content (%)	31.86	40.02	14.77	0.322	9.05	0.92	1.17	1.88

quantity of Fe^{3+} ions and so on. The pH value of system is about 0.5.

The reagents OP 10, Tween-80, PEG2000, PVP, Sodium dodecyl benzene sulfonate (SDBS), Sodium hexame taphosphate (SHMP), and NNO Dispersant were all the analytical grade reagents and were purchased from Shanghai Reagent Co, without further purification. Double distilled water was used to prepare the solution in all experiments.

Methods

Preparation of Sample. Preparation of Investigated Solution. A certain amount of blast furnace slag was ground in particle size from 0.25 to 1.0 mm and some was prepared in acid-proof vessel. The mass ratio among blast furnace slag, water, and dilute sulfuric acid is 1:3.4:1.2. After dilute sulfuric acid cooled to room temperature, blast furnace slag was added into the vessel in mechanical rabble condition.

Control of pH Value. When acid hydrolysis reaction ended, the pH value of silicic acid system was about 0.5. At this time, blast furnace slag was added into the vessel to regulate pH value. Then, the silicic acid system was obtained by filtrating. The pH value range selected in this study was from 0.5 to 3.0.

To prepare the sample solution with surfactant, we dissolved the surfactant in water before the preparation of dilute sulfuric acid, and the other procedures were mentioned as above.

Measurement of Gel Time. Stability of silicic acid system is characterized by gel time. In general, the gel time of silicic acid is considered the time from the beginning of silicic acid gelling to that silicic acid gel cannot flow when the test tube is inverse in thermostat water bath.[2] Considering the relationship between gel time and pH value of complicated silicic acid systems, it should be compared with that presented by Dai.[2] We took the time point that silicic acid gel could not flow when the container was inverse in thermostat water bath as the end of gel time.

Results and Discussion

Influence of pH value on gel time

Dai thought the most important factor influencing gel time of silicic acid system was pH value and presented the relationship between gel time and pH value. But there has not been any conclusion whether those results are appropriate for complicated silicic acid system. We studied the gel time–pH relationship of complicated silicic acid system and compared it with that of ordinary silicic acid system. To the ordinary silicic acid system, sulfuric acid is used as acidifier with molar concentration of SiO_2 1.65 mol/l and reaction temperature 25°C,[16] which are consistent with those of the complicated silicic acid system.

Figure 1 depicts gel time changing with different pH value for complicated silicic acid system changed and ordinary silicic acid system. Total trends of the two curves were basically identical. In strong acidic condition, gel time increases with the increase of pH value. When pH value is about 1.5, the gel time reaches the maximum. Then it decreases with the increase of pH value. Furthermore, condensation reaction occurs more easily to ordinary silicic acid system than to complicated silicic acid system, which indicates that some kinds of metal ions are introduced and prolong gel time of complicated silicic acid system. FT-IR spectra of the complicated silicic acid at different pH values were presented in Figure 2 to explore the action between metal ions and silicic acid.

The figure presents IR spectra of complicated silicic acid system under different pH values such as a: 0.5, b: 1.5, and c: 2.5. In the IR spectra diagram, the peaks at 3426 cm^{-1} and 1638 cm^{-1} originate from —OH dissymmetry stretching vibration and H—O—H bending vibration, 1138 cm^{-1} peak belonging to Si—O stretching vibration, 1091 cm^{-1} and 973 cm^{-1} peaks attributed to Si—O—Al vibration, 613 cm^{-1} peak caused by bending vibration of functional group of Al—OH.[17–20] MgO combining with silicic acid peak cannot be found in above picture.[21] Comparison with curve a, b, and c, with pH value increase, Si—O peak at 1138 cm^{-1} disappears and Si—O—Al peak at 973 cm^{-1} appears. It indicates that some aluminum ions combining with silicic acid forms aluminum–silicon polymer and its polymerization degree enhances with pH value increase.[1,22–23]

In a word, the variation of the characteristic peaks of Si—O—Al shows the complex reaction between silicic acid and aluminum. Then, we discuss the effect of metal ions on condensation reaction of complicated silicic acid system.

Condensation reaction of complicated silicic acid system

Gel time reaches the maximum when pH value is 1.5, and this pH value point is considered as the isoelectric point. On

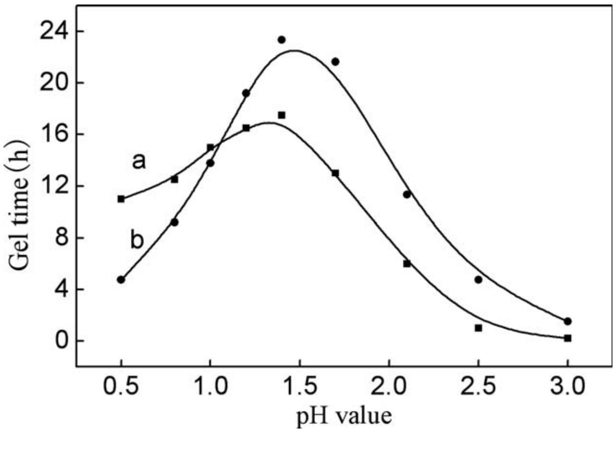

Figure 1. Relationship between gel time and pH value (a: complicated silicic acid. b: ordinary silicic acid).

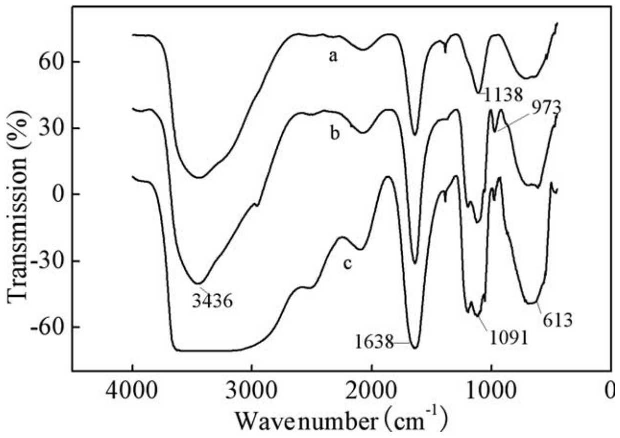

Figure 2. IR spectra of complicated silicic acid system under different pH values such as a: 0.5, b: 1.5, and c: 2.5.

left side of that point, the condensation equation of silicic acid can be written as[2]:

$$H_3A_m^+ + H_2A_n \rightarrow H_3A_{m+n}^+ + 2H_2O\,; \tag{1}$$

The rate of silicic acid condensation can be represented as:

$$v = k[H_3A_m^+]^x[H_2A_n]^y \tag{2}$$

A_m and A_n represent $[Si_m(OH)_{4m+2}]^{2-}$ and $[Si_n(OH)_{4n+2}]^{2-}$, respectively. k is reaction rate constant and is related to x and y which represent reaction order of each content, respectively.

There are two kinds of reaction between metal ions and silicic acid in the strong acidic conditions. On one hand, some monosilicic acid molecules react with Al^{3+} and Mg^{2+}.[21] In the meantime, the concentration of silicic acid molecule participating condensation reaction (1) and its reaction rate decreases. On the other hand, because of the high concentration 0.75 mol/l, aluminum ions will hydrolyze to form Al^{3+}—OH^- complex compound[24,25] and parts of silicic acid will react with aluminum to form aluminum–silicon polymer whose degree of polymerization is big enough to accelerate condensation of silicic acid. When pH value is 1.0, effects of the two actions reach a balance. When pH value is more than 1.0, the later action prevails gradually.

On the right side of isoelectric point, the condensation of silicic acid can be represented as:

$$HA_m^- + H_2A_n \rightarrow H_2A_{m+n} + OH^-. \tag{3}$$

The rate of silicic acid condensation can be represented as:

$$v = k[HA_m^-]^x[H_2A_n]^y \tag{4}$$

At this time, the concentration of silicic acid participating reaction (3) is reduced by the reaction of aluminum ions with silicic acid anions. For most of aluminum ions hydrolyzed forming complexes, the condensation reaction of complicated silicic acids with aluminum ions is still is higher than that of ordinary silicic acid system. The phenomenon is not consistent with the conclusion that metal ions will prevent condensation of silicic acid system in acidic conditions.[26]

The purpose of controlling gel time can be reached by regulating pH value. On the left of isoelectric point, the variation of pH value takes little effect on gel time. On the right of isoelectric point, gel time is sensitive to pH value. The maximum of gel time is only 16 h, so it is necessary to host for suitable surfactant to prolong the gel time.

Influence of additives on the gelling property of product

Surfactant is added before the acidic hydrolysis reaction happens. To focus on choosing suitable surfactant and discussing its mechanism of action, we put the influence of pH value on surfactant aside. The pH value of complicated silicic acid system by adding surfactant is regulated to 0.5 in the next experiment.

Anionic surfactant

The typical anionic surfactants SDBS, NNO, and SHMP are used, respectively, and the relationships between gel time and concentration of surfactants are shown in Figure 3.

The results indicate that gel time of complicated silicic acid system first decreases and then increases with concentration of surfactant increasing from 0 to about 0.5 g/l. SDBS used as surfactant, the gel time of complicate silicic acid system enhance greatly, the second NMO, and the worst SHMP. These anionic surfactants will ionize radical carrying negative charge to change zeta potential of silicic acid particle. The relationships between zeta potential and concentration of surfactant are shown in Figure 4.

At first, anionic surfactant neutralizes the positive charge on surface of complicated silicic acid particle, and the absolute value of zeta potential decreases. According to the DLVO theory, the electrostatic repulsion potential decreases

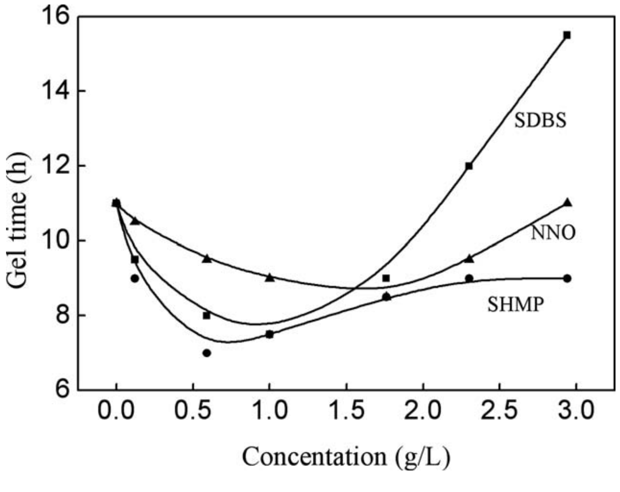

Figure 3. The gel time under the concentration of different anionic surfactants (NNO, SHMP, and SDBS).

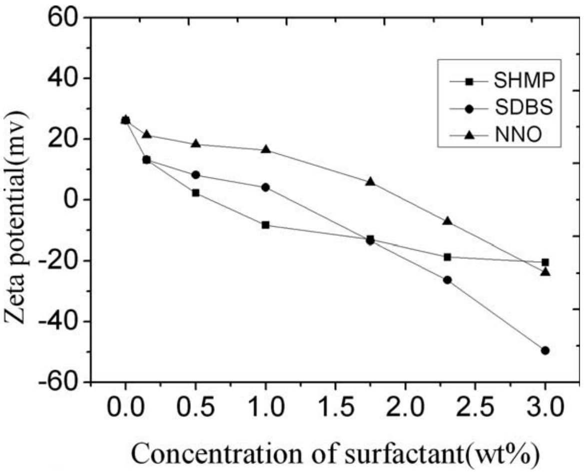

Figure 4. The zeta potential of complicated silicic acid under concentration of different anionic surfactants (NNO, SHMP, and SDBS).

with zeta potential and then the gel time decreases.[27–29] When the zeta potential reaches 0 mv, the gel time value is the shortest, because positive charge on particle surface is totally neutralized. With more surfactant, the silicic acid particle will carry negative charge. The absolute value of zeta potential will increase with concentration of surfactant increasing. Then the gel time increases with electrostatic repulsion potential increasing. The results show that the maximum of gel time is only 16 h when concentration of surfactant is 3%.

Nonionic surfactants

Because of the poor contribution of anionic surfactant to gel time of complicated silicic acid, nonionic surfactants are used in the next experiment. Relationships between gel time and concentration of nonionic surfactants are shown in Figure 5.

Comparison of Figure 5 with Figure 3 shows that the effect of nonionic surfactant is several times and even several decuple times better than that of anionic surfactant, and the gel time always increase with the increasing concentration. The comparison of the four curves in Figure 5 indicates that the chemical structure and molecule mass of nonionic surfactants dominate gelling property of complicated silicic acid.

For instance, OP-10 owns a hydrophilic group composed of PEO chain containing ten PEO periods and Tween-80 has three hydrophilic groups containing PEO chain and a hydrophobic group linking PEO chain. Furthermore, steric hindrance made by the heptadecyl of Tween-80, hydrophobic group, is stronger than that made by the octyl of OP-10 and complex reticular structure can reinforce steric hindrance by molecular chain winding with each other due to complex structure of Tween-80. Consequently, Tween-80 is more easily adsorbed on surface of silicic acid particle than OP-10 and takes better effect than OP-10 with the same concentration.

In addition, the hindrance of flexural large molecule formed by dissociation of PEG2000 in water is stronger than that of simple linear structure of PVP and the molecular weight of PEG2000 is less than that of PVP so PEG2000 can form gel more difficult than PVP. For hydrogen bond adsorption is formed by the reaction of oxygen atom within the lactam group of PVP with the hydroxyl group on surface of silicic acid particle, which will influence condensation of particles caused by condensation of hydroxyl group on the particle surface.[30,31] While PEG2000 has only two kinds of hydrophilic group, ether link or hydroxyl group. The link can easily take homonymy particle affinity interaction with oxygenous colloidal particle, so PEG2000 is more easily adsorbed on surface of silicic acid particle than PVP.

The results show that nonionic surfactant will form steric hindrance by dissociating long chain molecule instead of ionizing to influence surface potential of silicic acid particle.[32–34] The trend of gel time is owing to increase coating effect with the increase of the concentration of surfactant. Comparison of Figures 3 and 5 reveal that nonionic surfactant with steric hindrance effect is more suitable to disperse complicated silicic acid system than anionic surfactant with electrostatic stabilization.

Figure 5a presents, in the presence of small molecule nonionic surfactant, the gel time range of complicated silicic acid is narrow. For example, Tween-80 makes the gel time of complicated silicic acid sensitive to its concentration while OP-10 takes effect slowly over a wide range of its

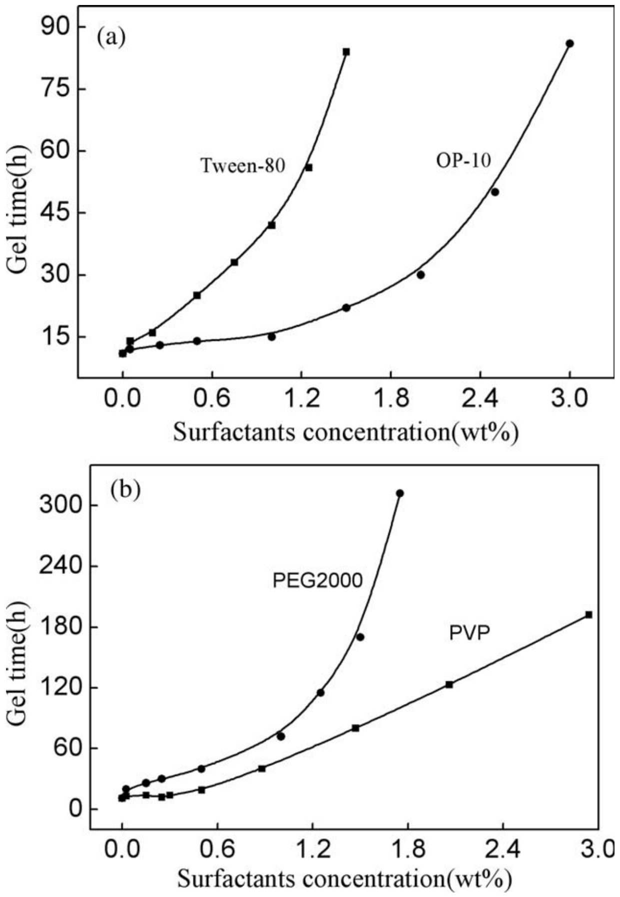

Figure 5. Change of gel time with concentration of nonionic surfactants (a: small molecule nonionic surfactants. b: big molecule nonionic surfactants).

concentration. In Figure 5b, big molecule nonionic surfactants employed the gel time range of complicated silicic acid, and its gel time is broad. PEG2000 takes effect gently at first and then it makes gel time sensitive to its concentration. The effect of PVP is in a linear relationship with its concentration. In a word, the molecule mass of nonionic surfactants is one main factor in controlling the gel time of complicated silicic acid system.

Conclusions

In this study, we propose the condensation reaction of complicated silicic acid system and find the method to control its gel time.

1. The relationship of gel time with pH value of complicated silicic acid system is identical with that of ordinary silicic acid system. Metal ions play dual roles on condensation—hindrance and promotion. When pH value is 0.5–1.0, the hindrance role dominates. When pH value is more than 1.0, the promotion role dominates. It is determined by different condensation of metal ions with silicic acid and poly silicic acid.
2. The predominant factor of surfactant on gel time is the chemical structure of surfactants. Nonionic surfactant with steric effect is more suitable to control gel time than anionic surfactant with electrostatic effect.
3. pH values and surfactants, especially nonionic surfactants, can be used to efficiently control gel time of complicated silicic acid system. For instance, its gel time is prolonged to 312 h by using PEG2000 at 1.7% mass concentration.

Acknowledgments

The authors are grateful to Anhui Provincial International Cooperation Project (09080703019) and Innovative Research Team in support of the work of their group.

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Manuscript received Nov. 25, 2009, and revision received Jun. 29, 2010.