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# Influence of Temperature on Stability of Aqueous Alumina Slurry Containing Polyelectrolyte Dispersant

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***Abstract***

*Effects of temperature on the stability of aqueous alumina slurry dispersed with polyelectrolyte have been studied. An adsorption experiment was performed to investigate the mechanism of the temperature-dependent stability in the system. Viscosity measurement and sedimentation results show that temperature dramatically affects the stability of slurry. The adsorption of dispersant increases with increasing temperature and the stability is strongly dependent on the adsorption state. As temperature increases, more dispersant is needed to reach a new adsorption equilibrium. In low initial concentration of dispersant region, the dispersant is insufficient to satisfy the increasing adsorption as temperature increases. Consequently, the apparent 'coverage' declines and flocculation takes place. A stability map is established to indicate the effect of the temperature on the stability of this system. © 1996 Elsevier Science Limited.*

## Introduction

Polymers and polyelectrolytes have long been widely used in ceramic slurry processing for their distinctive advantages over inorganic agents,[1] especially for high-tech ceramics. Numerous studies have been published concerning the stability of suspension systems containing polymer or polyelectrolyte. In recent years satisfactory progress has been made on both empirical and fundamental study in this field.[1-4,14,15] The relationships among the stability, adsorption behaviour and several important parameters including pH, ionic strength, zpc, and the chemistry of the polyelectrolyte have been well discussed from different aspects for several typical systems in those previous studies.[4-9] However, little attention has been paid to the effects of temperature on the stability of a polymer-containing suspension and on its processing,[10,11] except a few empirical investigations which were reported on the effects of temperature on rheological behaviour of traditional clay slurry in the earlier part of this century.[12,13] It is well known that the stability mechanisms of such a suspension system are quite different from that of traditional slurry systems. Therefore, to acquire a better understanding of such systems, it is necessary to study every variable which may affect the surface chemistry of the polymer and the ceramic powder, their interactions and macroscopic behaviours of such a system, and to relate them to one another. The investigation of the effect of temperature on polymer-containing slurry behaviour will not only contribute to full control of processing and to the improvement of reliability of ceramic materials, but also may lead to a better understanding of the mechanisms of stability, for which many problems still remain unknown or not very clear because of the complexity of particle–polymer interactions and adsorption behaviours.[1,2,4,15]

Our previous studies[10,11] on the slurry dispersed with polyelectrolyte have shown that temperature can exert dramatic effects on the stability of the slurry, and consequently on the structure and density of the compact prepared from it. The present paper is an extension of that study and intended to clarify the mechanism of the extraordinary effect of temperature on stability of a slurry by means of an adsorption experiment and analysis.

## Experimental Procedures

### Materials

The alumina powder used throughout this study is commercially available AL-160SG-1 (Showadenko

Inc., Tokyo, Japan). It is 100% $\alpha$-$Al_2O_3$ with a purity better than 99·9% and a trace of $Na_2O$ less than 0·05 wt% according to the supplier's information. Its average particle diameter measured by a sedimentation method (CP-3, Shimazu Inc., Kyoto, Japan) was 0·56 $\mu$m and the mean specific surface area determined by BET technique (Micromet2300, Shimazu Inc., Kyoto, Japan) 3·1 $m^2/g$. The zero point charge (zpc) measured was pH 8 with a common electrophoretic mobility measuring device.

A commercial dispersant Seruna D-305 (Chukyoyushi Inc., Nagoya, Japan) was used, the main component of which is a type of ammonium polyacrylate according to the specification.

## Experimental method

*Slurry preparation*
Alumina powder (100 g) was gently poured into a flask containing 100 g aqueous solution of dispersant. The flask was immersed in water in a thermostatic bath and the mixture was stirred with a magnetic stirrer for 24 h. The stirring temperature range examined was 10–80°C. The slurries prepared were used for the following experiments.

*Viscosity measurement*
Viscosity of the slurries prepared above was measured with a conventional rotary viscometer (Visco-BL, Tokimec Inc., Tokyo, Japan) at 20°C.

*Sedimentation*
The slurries prepared at various temperatures were poured into graduated test tubes. The sediment heights were recorded after 15 days and photographs were taken at the same time.

*Adsorption measurement*
The amount of dispersant adsorbed on the surfaces of alumina particles was calculated by the difference between the initial concentration of dispersant solution and that of the supernatant of the slurry. The supernatants were obtained by centrifugation. The disperant concentrations of the supernatants were measured from their refractive index with a laser beam measuring system including a laser beam generator, a lens for converging the beam, a sample cell and a beam receiver. To minimize the interference caused by the fluctuation of ambient temperature, the sample cell was partitioned into two chambers, one of which was a reference chamber filled with distilled water and the other for the sample to be measured. The calibration indicated that the deflection of the beam on the receiver, $\Delta y$, was well linearly proportional to the concentration of the dispersant in the water solution. A accuracy better than 100 ppm was obtained with this measuring system.

*Others*
All slurries prepared at different conditions had almost the same pH value 9·2 ± 0·05 for this system, and no pH adjustment was made in the study. All concentrations mentioned in the text and figures were expressed in weight-percent solution base and the slurries had an identical solid loading of 50 wt%.

## Results

Figure 1 shows the relationship of viscosity and the initial concentration of dispersant at three different temperatures of preparation. At each temperature, the viscosity drops with increasing concentration of dispersant and reaches a minimum value. Three viscosity lines have different critical concentrations. The higher the temperature, the higher concentration of dispersant is needed to disperse the slurry.

Figure 2 shows the effect of temperature on the viscosity at two given concentrations, 0·4% and 1·0%. The viscosity for 0·4% increases rapidly as temperature exceeds 40°C; in contrast, that for 1·0% does not change appreciably with temperature. This indicates that the stability of a slurry can be strongly dependent on temperature and the sensitivity to temperature varies with its dispersant concentration.

Figure 3 shows the picture of gravitational sedimentation of slurries prepared at different temperatures with 0·4% dispersant. At low temperature (10°C, 20°C) the slurries are very stable with quite

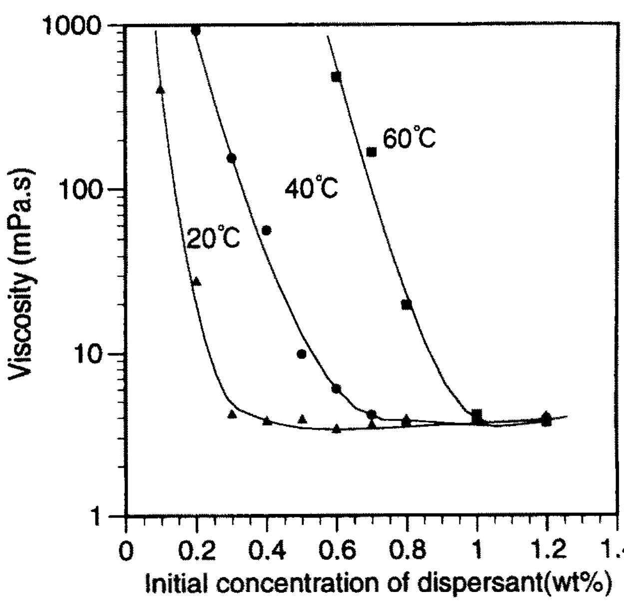


Fig. 1. Viscosity vs initial concentration of dispersant as a function of temperature.

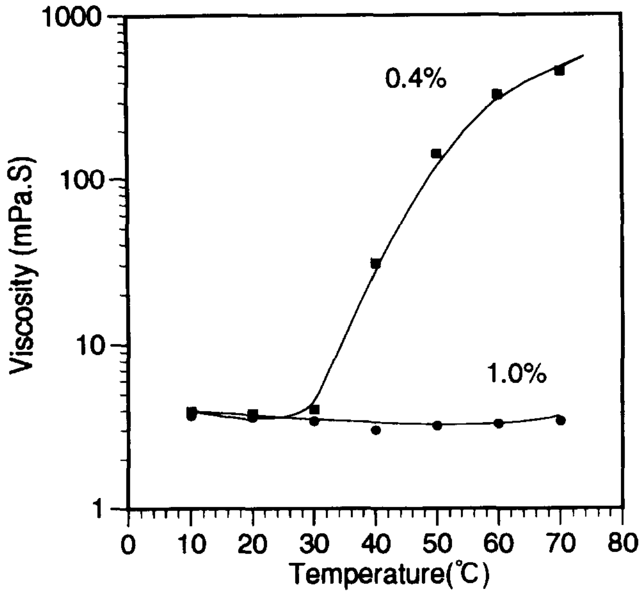


**Fig. 2.** Effect of temperature on the viscosity (initial concentration 0·4%).

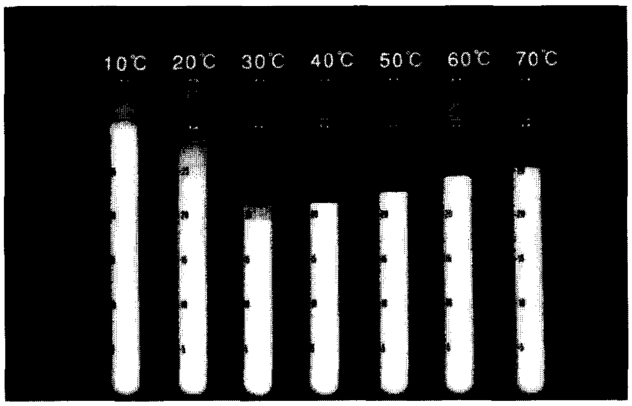


**Fig. 3.** Sedimentation of the slurries mixed at various temperatures. Period: 15 days, initial concentration: 0·4%, solid loading: 50 wt%.

turbid upper liquids and no clear boundary can be identified between the sediments and the upper liquids, while at higher temperatures, 30–70°C, the upper liquids are very clear and the sediment boundaries are sharp. The picture also shows clearly that the heights of the sediments for 30–70°C increases as temperature increases. This indicates that the slurry shifts from a stable state to an unstable one with increasing temperature at this concentration. The degree of flocculation enhances with increasing temperature too.

Figure 4 shows the result of the adsorption experiment at three different temperatures. Adsorption increases with increasing initial concentration and finally reaches its saturation limit (plateau level) for each temperature. The diagonal line in the figure represents total amount of dispersant added, that is, the adsorption amount plus that of free dispersant remaining in the solution. Referring to it, the amount of free dispersant can be easily read. The figure shows that free dispersant molecules are always present in the slurries, even for those with very low initial concentration. The three isotherms of adsorption apparently fit Langmuir type if they are plotted alternately with equilibrium concentration as the horizontal axis. The figure also shows that the adsorption of the dispersant increases with an increase in temperature throughout the concentration range examined. The saturation limits of adsorption are about 360, 480, and 640 mg/100 g alumina for 20°C, 40°C and 60°C, respectively.

Figure 5 shows the relationship between adsorption saturation limit and temperature. The adsorption saturation limit is almost linearly proportional to temperature and increases by more than 100% from 10 to 70°C.

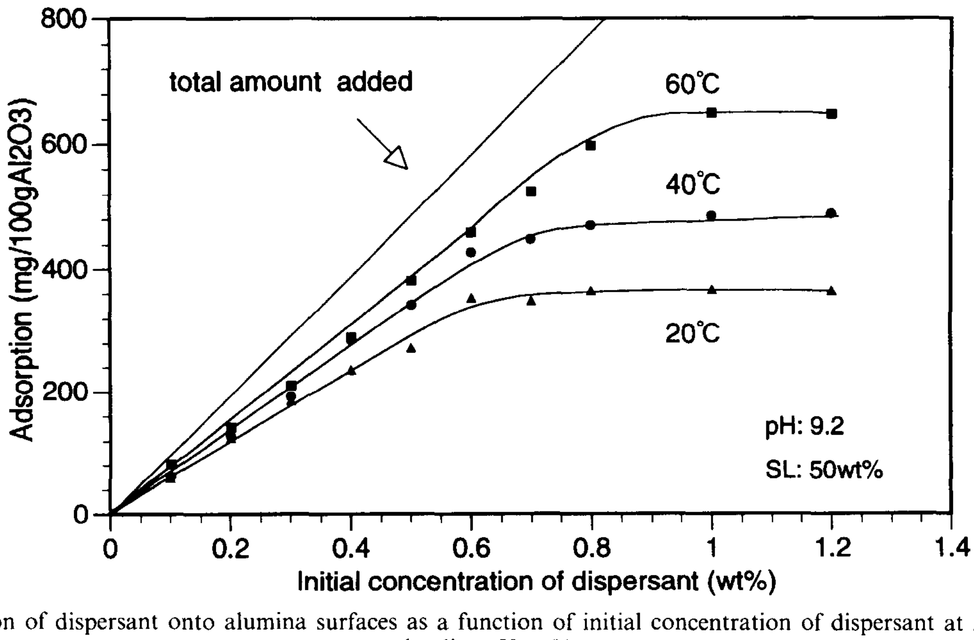


**Fig. 4.** Adsorption of dispersant onto alumina surfaces as a function of initial concentration of dispersant at 20, 40, 60°C solid loading: 50 wt%.

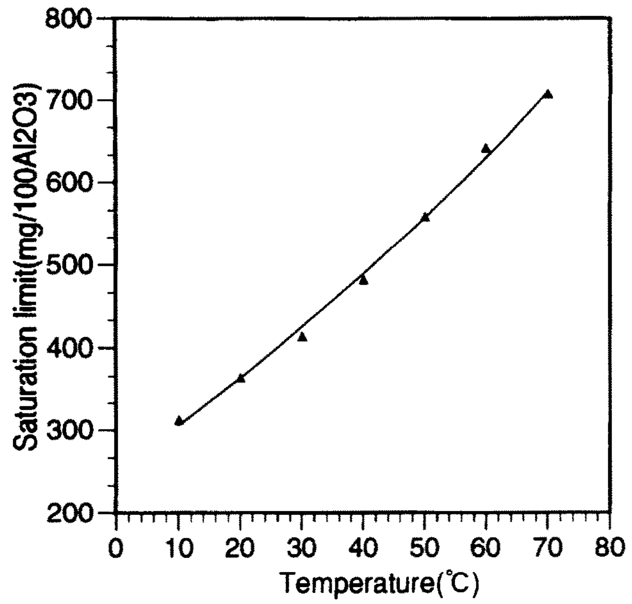


**Fig. 5.** Adsorption saturation limit as a function of temperature.

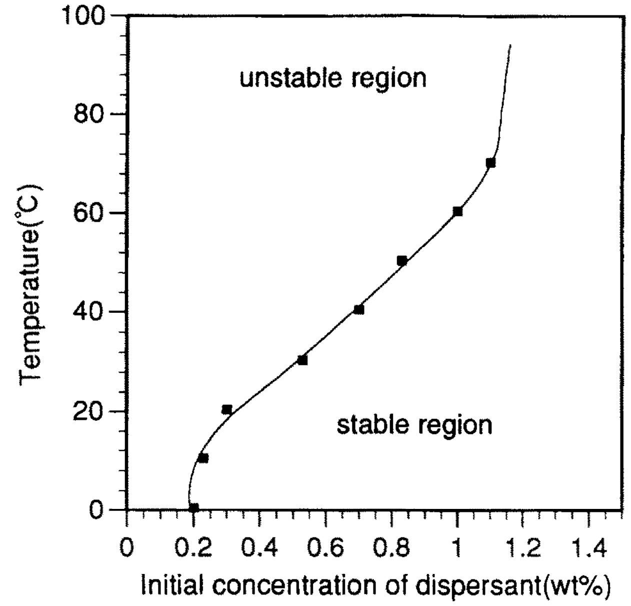


**Fig. 6.** Stability map for $\alpha$-$Al_2O_3$ suspension containing polyelectrolyte dispersant. Squares represent data based on viscosity vs initial concentration relation at various temperatures. See text for description of two regions. pH 9·2, solid loading: 50 wt%.

## Discussion

### Temperature effects on stability

The results from both viscosity measurements and sedimentation shown in Figs 1, 2, and 3 clearly demonstrate that temperature exerts a significant effect on the stability of this system. These results are consistent with each other and with those of our earlier reports.[10,11] This temperature effect is not only of significance for processing but also implies that temperature plays an important role in the interactions between polyelectrolyte and alumina particles. Further explanation on this will be given in the later discussion on the correlation of adsorption and stability.

The present study also found that the effect of temperature on the stability varies with dispersant concentration. As shown in Fig. 2, for different initial concentrations the influence of temperature on the viscosity can change greatly. This means that temperature effect and concentration effect on the stability depend on each other.

In order to clarify these relationships, a stability map for this system was established as shown in Fig. 6. This map is based on the data derived from Figs 1, 2 and other additional data of viscosity vs concentration as a function of temperature. There are two regions in the map, stable and unstable, corresponding to dispersed and flocculated state. With this map, one can clearly see the correlation between the influence of temperature and that of dispersant concentration on the stability over all the temperature and concentration ranges examined. The lower the concentration, the more sensitive the stability of the slurry is to temperature. When dispersant concentration is higher than 1%, the stability of the slurry is not affected by temperature.

### Temperature-dependent adsorption and its effect on stability

*Effect of temperature on adsorption*

Generally the adsorption of polyelectrolyte dispersant on ceramic particles is governed by several well known parameters including pH, ionic strength, zpc of the particle and the surface chemistry of the polyelectrolyte as mentioned above.[5-9,16] However, the adsorption experiment in the present study revealed that the adsorption of the dispersant on the surfaces of alumina particles is greatly dependent on temperature as well. The adsorption increases with increasing temperature over all the concentration range examined and the saturation limit is approximately proportional to temperature as shown in the experimental results. This temperature-dependent adsorption behavior has a profound influence on the stability of the suspension and is responsible for the extraordinary results shown in Figs 1, 2, and 3. The mechanism of the influence of temperature on the stability of this system stems from its temperature-dependent adsorption.

*Relation between coverage and stability*

It has been known that the stability of slurry dispersed with polyelectrolyte depends not on absolute adsorption amount but largely on or whether the adsorption is saturated or not, and in most cases saturation adsorption (coverage = 100%) is needed to achieve the dispersed state.[2,4-9] Notice that coverage here is only an apparent one referring to the ratio of the adsorption amount to its saturation limit of adsorption. However, it is easily seen by comparing Figs 1 and 4 that for this system the slurry can be dispersed at a lower concentration where the adsorption does not reach its saturation limit yet. The discrepancy can be explained that the affinity of adsorption decreases because of a higher pH (9·2) of the slurry and a lower zpc (pH 7·9) of the alumina powder used. Under this condition, alumina particles and dispersant molecules are identically charged with negative charges. Hence a strong electrostatic repulsion between them results. This repulsion hinders the adsorption and at the same time it provides an additional force to disperse the particles partly covered with dispersant molecules.

*Mechanism of temperature effects on stability*

As shown in Figs 4 and 5, when temperature increases, the saturation limit of adsorption increases accordingly, and more polymer is required to reach a new equilibrium level of adsorption. If the initial concentration is relatively low, free polymer is insufficient to satisfy the increasing adsorption level, hence the unsaturation adsorption or poor coverage will result. That means the transition of the adsorption state from a saturation to an unsaturation or from a higher coverage to a lower one will happen at the low dispersant concentration region. As mentioned above, this transition of adsorption state may cause change of the stability of slurry, i.e. from a stable state to an unstable one. This can be clearly seen from Fig. 2 where the viscosity shows a strong dependence on the temperature in a slurry with low concentration (0·4%), while the slurry with a high concentration (1·0%) does not show temperature dependence. For a slurry with higher dispersant concentration, sufficient polymer is present and able to match the increasing adsorption to a new saturation limit to maintain 100% adsorption state, and consequently the stable state will not change with temperature. The stable map of Fig. 6 also evidently supports the above explanation. The map shows that the lower the initial concentration, the lower transition temperature for stability is, in other words, the more sensitive the stability is to temperature. Another investigation of the authors on a similar aqueous alumina suspension system containing polyacrylic acid proves the same mechanism for temperature effect on the stability of the slurry.

The understanding of the mechanism of the extraordinary temperature effect on the stability of the slurries containing polymeric dispersant may benefit ceramic suspension processing, such as optimum dosage, temperature controlling and so on. In the light of the temperature sensitivity in the low dispersant concentration region for such systems, it is necessary to provide an excess amount of dispersant to the slurry to ensure its stability as temperature fluctuation might be involved during the processing. For the same reason, a low processing temperature may be preferable.

The reason why the adsorption increases with increasing temperature in such a system is not yet very clear. However, it has been found in our study on similar systems that there is an additional attractive interaction between the alumina particles and the polyelectrolyte molecules apart from electrostatic interaction and van der Waals force. This additional interaction seems to be the so called hydrophobic interaction and is thought to play an important role in the unusual adsorption behavior in such a system.

## Summary

The viscosity of aqueous alumina slurry dispersed with polyelectrolyte increases significantly as temperature increases in the low dispersant concentration region, and the sedimentation height of the slurry increases accordingly. The stability of the slurry with low dispersant concentration changes with increasing temperature from a stable state to an unstable one, while that with a relatively higher concentration does not. The higher the temperature, the more dispersant is needed to maintain the dispersed state of the slurry.

The adsorption of dispersant increases with an increase in temperature. The adsorption saturation limit (plateau level) increases almost linearly with temperature. The increase of adsorption with temperature is responsible for the temperature-dependent stability of this system. At a relatively lower initial concentration in the slurry, the dispersant is insufficient to satisfy the increasing adsorption as temperature increases. Therefore, unsaturation adsorption or poor coverage results, and consequently the slurry will shift from a stable state to an unstable one.

The stability map provides a clear view of the correlation of the effect of temperature and concentration on the stability of the system.

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