Effects of eluted metal ions on the properties of ceramic slurry and slip-casted green bodies

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ABSTRACT

The characteristics of ceramics produced by wet forming are determined by the particle dispersion in the utilized slurry, obtained by mixing ceramic powder and a solvent. Evaluation and control of the particle dispersion is thus important. In the case of ceramic powder containing a sintering aid, metal ions may be eluted from the particles during preparation of the aqueous slurry. It remains unclear, however, how the metal ions affect the particle dispersion and the green body characteristics. Hence, in the present study, Mg2+, Al3+, and Ca2+ ions were added to common water-based alumina slurries, and their effects on the slurry and green body characteristics were investigated. It was found that the presence of about 10 mM of metal ions caused agglomeration of the slurry particles and decreased the green body packing fraction. The effects were particularly significant for small amounts of the added dispersant. When the dispersant dosage exceeded a certain level, the added metal ions produced no observable change in the slurry or green body characteristics. In addition, higher-valence metal ions were found to decrease the maximum green body packing fraction and increase the dispersant dosage required to reach the maximum packing fraction.

1. Introduction

The slurry utilized in the ceramic wet-forming process is generally prepared by mixing ceramic powder, a solvent, and additives such as a dispersant and binder. The slurry is formed into the desired shape and then dried and sintered to obtain the final product. The characteristics of the product depend on the dispersion or aggregation state of the slurry particles, with good dispersion producing a high-density product and aggregation producing a low-density product. The dispersion state is controlled by the addition of a polyelectrolyte. Previous studies have revealed that with increases in the polyelectrolyte dosage, the dispersion state of the slurry particles changes from network formation to good dispersion and then to aggregation [1–4]. Addition of an appropriate amount of polyelectrolyte is thus important. One of the most important factors affecting the particle dispersion in slurry when a polyelectrolyte is added is the amount of the polyelectrolyte adsorbed on the particle surface. Several researchers have discussed this factor and its specific relationship with the particle dispersion in slurry. Wada et al. [5,6] investigated the relationship between the amount of polyelectrolyte adsorbed, the type of dispersant, and the particle dispersion state in slurry. Zhang et al. [7] investigated the effect of the solvent composition, while Wu et al. [8–12] examined the effect of a slurry’s pH. In addition, Unuma et al. [13–15] considered the specific effect of the particle volume concentration in the slurry, while Davies et al. [16–18] investigated the effect of the green body density.

Further, metal ions may be eluted from the particles during the preparation of an aqueous slurry. This has also been found to impact the amount of polyelectrolyte adsorbed. Ringenbach et al. [19] added a polyacrylic acid (PAA) and AlCl₃ to an aqueous α-alumina slurry, and found that the amount of PAA adsorbed was increased by the presence of the Al³⁺ ions. Sun et al. [20] also added PAA to an aqueous α-alumina slurry and measured the amounts of PAA adsorbed in the presence of various concentrations of NaCl or MgCl₂. They found that the amount of PAA adsorbed varied with both the ion species and the concentration. Dupont et al. [21] added PAA and Ca(NO₃)₂ to aqueous alumina slurries with different pH values and observed that the presence of Ca²⁺ ions increased the amount of PAA adsorbed only slightly under acidic conditions, but increased it significantly under alkaline conditions. Vermohlen et al. [22] added PAA with various molecular weights and NaCl or CaCl₂ to an aqueous alumina slurry and found that the amount of PAA adsorbed was higher in the presence of the divalent Ca²⁺ ions than with the
monovalent Na⁺ ions. Deliormanli et al. [23] added PAA and MgCl₂ to slurry containing lead magnesium niobate (PMN) particles and observed that the presence of MgCl₂ almost doubled the amount of PAA adsorbed. Ohtsuka et al. [24] prepared an aqueous alumina slurry using alumina particles containing 0.1 wt% MgO as a sintering aid, and found that the amount of PAA adsorbed was maximized by the elution of Mg²⁺ from the MgO. Kiguchi et al. [25] added a polycarboxylic acid ammonium (PCA) aqueous solution containing MgCl₂ to an aqueous alumina slurry and found that the amount of PCA adsorbed increased with increases in the dosage of the MgCl₂ additive. Satone et al. [26] added PCA solutions containing different metal chlorides (MgCl₂, AlCl₃, CaCl₂, and BaCl₂, respectively) to slurry samples containing zinc oxide and titanium oxide particles and examined the resultant rheological characteristics. They found that the slurry particle agglomeration and yield stress increased with increases in the valence and radius of the metal ions eluted from the chlorides.

As noted above, many studies have been conducted on the influence of eluted metal ions on the amount of polyelectrolyte adsorbed. It remains unclear, however, how the amount of polyelectrolyte adsorbed affects the dispersion of the slurry particles. Furthermore, there has been no investigation of the effects of the green body characteristics of changes in the amount of polyelectrolyte adsorbed due to metal ion elution and variations in the slurry characteristics. In the present study, therefore, we prepared aqueous alumina slurry samples using two different types of alumina particles and measured the amounts of metal ions eluted. We subsequently added MgCl₂ and AlCl₃ to the slurry samples and investigated the respective effects on the elution of metal ions, the amounts of polyelectrolyte adsorbed, the dispersion of the slurry particles, and the characteristics of the green bodies.

Table 1. Chemical compositions (wt%) of the alumina powders provided by the manufacturer.

|        | Al₂O₃ | Fe₂O₃ | SiO₂ | Na₂O | MgO | H₂O | L.O.I |
|--------|-------|-------|------|------|-----|-----|------|
| AES-12 | 99.9  | 0.01  | 0.06 | 0.04 | 0.01| 0.01| 0.01 |
| AES-11E| 99.8  | 0.01  | 0.06 | 0.04 | 0.1 | 0.02| 0.01 |
| L.O.I (Loss of ignition) |

2. Experimental

2.1. Measurement of the metal ion concentration

A desktop inductively coupled plasma (ICP) emission spectrometer (SPS7800, SII, Japan) was used to measure the concentrations of metal ions eluted from the alumina particles. Two different alumina powder samples were investigated, with the first containing no sintering aid (AES-12, d₅₀ = 0.44 µm, Sumitomo Chemical, Japan), and the second with MgO added as a sintering aid (AES-11E, d₅₀ = 0.48 µm, Sumitomo Chemical, Japan). The chemical compositions of the two alumina samples are presented in Table 1.

Deionized water was used as the dispersion medium, and polycarboxylic acid ammonium (PCA) (Celuna D-305, Chukyo Yushi, Japan) as the dispersant. Different amounts of PCA, 0, 1.0, 3.6, 8.0, 12.0 mg per gram of alumina, respectively, were considered, with the alumina particle concentration was adjusted to 40 vol%. But, no slurry could be prepared without the addition of PCA when the alumina particle concentration adjusted to 40 vol%. So it was adjusted to 5 and 10 vol% only when prepared without the addition of PCA. The slurry samples were prepared by adding PCA (0, 1.0, 3.6, 8.0, 12.0 mg·g⁻¹ Al₂O₃) to deionized water and stirring with a stirrer for 15 min, followed by ultrasonic bathing for another 15 min. Alumina powder was then added to each PCA solution to achieve an alumina particle concentration of 40 vol%, followed by ball milling for 1 h and vacuum degassing for 10 min. The slurry was subsequently centrifuged at 3290 G for 160 min. The concentration of metal ions in the obtained supernatant was then measured with the ICP emission spectrometer.

Calibration curves were prepared for the Mg²⁺ and Al³⁺ ions using standard samples of the ions (Magnesium Standard Solution 1000 ppm and Aluminum Standard Solution 1000 ppm, Fujifilm Wako Pure Chemical Corporation, Japan). The respective standard samples were diluted to 1, 2, 4, 5, and 10 ppm, and the calibration curves were plotted using six points for each concentration including only water.

2.2. Slurry and green body characterization using AES-12

2.2.1. Slurry preparation for characterization

AES-12 was used as the alumina powder (i.e., without a sintering aid), deionized water as the dispersion medium, and PCA as the dispersant. MgCl₂ (Fujifilm Wako Pure Chemical Corporation, Japan) or AlCl₃ (Tokyo Chemical Industry, Japan) was used as an additive. PCA (0.1, 0.5, 1.0, 2.0, 2.3, 3.0, 3.6 mg·g⁻¹ Al₂O₃, respectively) was added to the deionized water and stirred with a stirrer for 15 min, followed by ultrasonic bathing for 15 min. MgCl₂ or AlCl₃ was then added to achieve a Mg²⁺ or Al³⁺ concentration of 0.37 mM. This was followed by the addition of alumina to achieve a particle concentration of 40 vol%, with subsequent ball milling for 1 h and vacuum degassing for 10 min. Three types of test slurry were prepared by the above procedures, namely, slurry without metal ions, slurry with 0.37 mM of Mg²⁺, and slurry with 0.37 mM of Al³⁺. Additional slurry samples were prepared using larger amounts of MgCl₂ or AlCl₃ to achieve a Mg²⁺ or Al³⁺ concentrations of 10 mM. The reason for this will be discussed in Section 4.1.
2.2.2. Evaluation of flow characteristics
A rheometer (MCR302, Anton Paar, Japan) was used to evaluate the flow characteristics of the test slurry samples. During measurement, the shearing rate was increased from 0 to 200 s$^{-1}$ over 180 s at a temperature of 25°C and then decreased back to 0 s$^{-1}$ over the same time period. The shear stress was measured over the entire duration.

2.2.3. Measurement of the amount of PCA adsorbed
The test slurry was centrifuged at 3290 G for 160 min and the supernatant was collected. The amount of unadsorbed PCA in the obtained supernatant was measured using a total organic carbon meter (TOC-V CSN, Shimadzu Corporation, Japan), and this was subtracted from the original amount of PCA added to obtain the amount of PCA adsorbed. It was confirmed in advance that the PCA did not settle, even after centrifuging at 3290 G.

2.2.4. Measurement of the zeta potential of alumina powder
The zeta potential of the alumina powder particles in the test slurry was determined based on the electrophoretic mobility measured by an electrophoretic zeta potential analyzer (Model 502, Nihon Rufuto, Japan). One drop of the test slurry was mixed with 400 ml of deionized water, and aqueous NaOH was added to adjust the pH. The electrophoretic mobility of the particles was measured 16 times, and the average value was adopted. The zeta potential was subsequently determined using Henry’s equation [27], as follows:

\[
u_E = \frac{2\varepsilon_0 k T \Psi_c}{3\mu} f\left(\frac{kx}{2}\right)\]

(1)

\[
f\left(\frac{kx}{2}\right) = \frac{3}{2} - \frac{1}{2 + 0.144(kx/2)^4}\]

(2)

\[
k^{-1} = \left(\frac{\varepsilon_0^2 N_A \sum X_i Z_i^2}{\varepsilon_0 k T}\right)^{\frac{3}{2}}\]

(3)

2.2.5. Measurement of green body packing fractions
Slip casting of the test slurry was conducted by pouring the slurry into a 3 × 3 cm square-section vinyl chloride cylinder placed on a plaster board such that the charging height was 1 cm. This setup was used to produce four green bodies for each type of test slurry. The produced green bodies were dried at room temperature and then calcined. The packing fraction of each green body was subsequently calculated by the Archimedes method, with the average result for the four samples for each type of slurry adopted for that slurry type.

3. Results

3.1. Metal ion concentration
Table 2 gives the metal ion concentrations measured by the desktop ICP emission spectrophotometer for the two types of alumina powder without PCA added. In the case of the AES-12 alumina powder, particle concentrations of 5 and 10 vol% produced slight Al$^{3+}$ elutions of 0.11 and 0.19 mM, respectively. In the case of the AES-11E alumina powder, a particle concentration of 5 vol% produced slight Mg$^{2+}$ and Al$^{3+}$ elutions of 0.35 and 0.32 mM, respectively, while the corresponding values for a particle concentration of 10 vol% were both 0.29 mM. This indicated an insignificant effect of the particle concentration on the amount of metal ions eluted.

Figure 1 shows the corresponding results for the addition of PCA to the alumina powder. Figure 1(a) shows the concentration of metal ions eluted from AES-12 associated with the PCA dosage, while Figure 1(b) shows the results for AES-11E. As can be observed, about 5 mM of Al$^{3+}$ was eluted from AES-12 with little variation in the exact amount with additions to the PCA dosage. In the case of AES-11E, the amounts of Mg$^{2+}$ and Al$^{3+}$ eluted increased with increase in the PCA dosage up to 8.0 mg·g$^{-1}$ Al$_2$O$_3$.

3.2. Slurry and green body characterization using AES-12

3.2.1. PH change
Table 3 shows the results of pH measurements of all the test slurry samples prepared using AES-12. When no metal ions were added, the pH of the test slurry samples varied from 9.05 to 9.59, 9.05 to 9.62, and 8.92 to 9.15, and 8.50 to 8.63, respectively. In all the test slurry samples, the pH was observed to decrease slightly with increases in the PCA dosage.

3.2.2. Flow characteristics
Figure 2 shows the results of the apparent viscosity measurements of test slurry samples using AES-12 described in Section 2.2.1 for a shear rate of 10.2 s$^{-1}$. Figure 2(a) shows the results for slurry samples without and with 0.37 mM of metal ions with respect to the

| Table 2. Concentrations of metal ions eluted from the alumina slurry particles without PCA. |
|-----------------------------------------------|
| Particle concentration (vol%) | Mg$^{2+}$ (ppm) | Al$^{3+}$ (mM) |
|-----------------------------|----------------|--------------|
| AES-12                      | 5              | -            | 3.03 0.11 |
|                             | 10             | -            | 5.19 0.19 |
| AES-11E                     | 5              | 8.44 0.35    | 7.69 0.29 |
|                             | 10             | 7.11 0.29    | 6.60 0.32 |
PCA dosage, while Figure 2(b) shows the corresponding results for slurry samples containing 10 mM of metal ions. As can be observed in Figure 2(a), the presence of 0.37 mM of metal ions did not change the apparent viscosity relative to that with no metal ions. In addition, the apparent viscosity was lowest at a PCA dosage of 1.0 mg·g\(^{-1}\)Al\(_2\)O\(_3\), which was also considered to produce the best particle dispersion in the slurry. Figure 2(b) shows that, in the presence of 10 mM of metal ions, the apparent viscosity increased in the range of small PCA dosages. In the system with 10 mM of Mg\(^{2+}\), the apparent viscosity was lowest when the PCA dosage was 2.0 mg·g\(^{-1}\)Al\(_2\)O\(_3\), while it was lowest in the system with 10 mM of Al\(^{3+}\) when the dosage was 3.0 mg·g\(^{-1}\)Al\(_2\)O\(_3\). These results indicate that the presence of about 10 mM of metal ions increased the apparent viscosity of the slurry.

### 3.2.3. Amount of PCA adsorbed

Table 3 shows the measured amounts of PCA adsorbed for the test slurry samples using AES-12 described in Section 2.2.1. Figure 3(a) shows the results for the test slurry samples without and with 0.37 mM of metal ions.
metal ions with respect to the PCA dosage, while Figure 3(b) shows the corresponding results for the slurry samples containing 10 mM of metal ions. It can be seen from Figure 3(a) that the presence of 0.37 mM of metal ions in the slurry did not change the amount of PCA adsorbed compared with the amount in slurry with no metal ions. However, Figure 3(b) shows that the presence of 10 mM of metal ions increased the amount of PCA adsorbed. This is considered to be due to adsorption of PCA onto the surface of the slurry particles in a state of aggregation through cross-linking of the added metal ions with the PCA molecules. Further, a comparison of the results for Mg$^{2+}$ and Al$^{3+}$ reveals that the amount of PCA adsorbed was greater for 10 mM of Al$^{3+}$. It is considered that ions with a higher valence were cross-linked with more PCA molecules and aggregate. Chen et al. [28] added various types of metal ions to a water-soluble anionic conjugated polymer solution and measured the particle size of the polymer through dynamic light scattering (DLS). They reported that the addition of metal ions caused interchain aggregation and increased the polymer particle size, with the increase more significant when trivalent metal ions were added as compared with monovalent or divalent metal ions. Karahan et al. [29] also reported that the addition of Cu$^{2+}$ to a polymer solution resulted in the formation of an intermolecular complex. Hence, it is considered in the present study that Mg$^{2+}$ and Al$^{3+}$ in the water cross-linked with PCA molecules to form aggregates.

### 3.2.4. Zeta potentials of alumina powders

Figure 4 shows the measured zeta potentials of the alumina powders used to prepare the test slurry samples with AES-12 in Section 2.2.1. Figure 4(a) shows the zeta potentials of the test slurry samples without and with 0.37 mM of metal ions with respect to the PCA dosage, while Figure 4(b) shows the corresponding results for the slurry samples containing 10 mM of metal ions. As can be seen, the metal ions produced no change in the zeta potential, even at a high concentration. For all the slurry samples, the absolute value of the zeta potential increased, however, with increases in the PCA dosage between 0.1 and 2.0 mg·g$^{-1}$ Al$_2$O$_3$, while higher dosages produced no further change.

![Figure 3](image-url) Adsorbed amounts of PCA in slurry samples using AES-12 (a) without and with 0.37 mM of metal ions and (b) without and with 10 mM of metal ions.

![Figure 4](image-url) Effects of the PCA dosage on the zeta potentials of the slurry samples using AES-12 (a) without and with 0.37 mM of metal ions and (b) without and with 10 mM of metal ions.
3.2.5. Green body packing fractions
Figure 5 shows the determined packing fractions of green bodies obtained by slip casting of the test slurry samples made with AES-12 described in Section 2.2.1. Figure 5(a) shows the packing fractions with respect to the PCA dosage for the green bodies obtained from the test slurry samples without and with 0.37 mM of metal ions, while Figure 5(b) shows the corresponding results for slurry samples containing 10 mM of metal ions. The error bars in the figure indicate the maximum and minimum values for the four green bodies. It can be seen from Figure 5(a) that the presence of 0.37 mM of metal ions in the slurry did not change the green body packing fraction compared with slurry containing no metal ions in the slurry. In addition, the packing fraction increased with increases in the PCA dosage until reaching a maximum at a dosage of 1.0 mg·g⁻¹ Al₂O₃, after which the packing fraction began to decrease gradually. Figure 5(b) shows that the overall packing fraction of green bodies made with slurry containing 10 mM of metal ions might be lower than that when no metal ions were present. When 10 mM of Mg²⁺ was added, the packing fraction reached a maximum at a PCA dosage of 2.3 mg·g⁻¹ Al₂O₃, while the maximum was reached at a PCA dosage of 3.0 mg·g⁻¹ Al₂O₃ in the case of 10 mM of Al³⁺. The maximum values show that the addition of 10 mM of metal ions decreased the green body packing fraction. Further, the maximum packing fraction produced with 10 mM of Mg²⁺ added was greater than that produced with 10 mM of Al³⁺ added.

4. Discussion
4.1. Metal ion concentration
As indicated in Table 2, the slurry system consisting of only AES-11E alumina and deionized water eluted about 0.32 mM of Mg²⁺ (about 7.8 ppm), which indicates a Mg(OH)₂ solubility of 9 ppm (at 20°C). Based on this observation, MgCl₂ and AlCl₃ were added to the alumina slurry to achieve Mg²⁺ and Al³⁺ concentrations of 0.37 mM.

As apparent from Figure 1, the addition of PCA to the slurry system dramatically increased the elution of Mg²⁺ and Al³⁺. This is attributed to cross-linking of the metal ions and PCA molecules, as illustrated in Figure 6. It is considered that an increase in the PCA dosage
increased the number of carboxy groups that cross-linked with metal ions, resulting in an increase in the amount of eluted metal ions. Although the corresponding details for AES-12 alumina are unknown, the amount of eluted Al$^{3+}$ is considered to be almost constant, at about 5 mM, possibly due to different manufacturing methods. As seen in Figure 1(b), depicting the case of AES-11E alumina, because it was suggested that about 10 mM of metal ions could be eluted at most, MgCl$_2$ and AlCl$_3$ were added to the alumina slurry prepared in Section 2.2.1 such that the added concentrations of Mg$^{2+}$ and Al$^{3+}$ were 10 mM.

4.2. Slurry and green body characterization using AES-12

4.2.1. PH change

Table 3 shows that the pH values of all the test slurry samples prepared using AES-12 showed only small variations, ranging from 8.50 to 9.65. In addition, the fraction of dissociated acid groups (a) of PCA in this pH range can be considered to be approximately 1 [30,31]. Based on the above information, the changes in pH are considered to have had no effect on the slurry or green bodies.

4.2.2. Slurry samples without and with 0.37 mM of metal ions

The addition of 0.37 mM of metal ions to the slurry system produced no changes in the apparent viscosity, amount of PCA adsorbed, or zeta potential. In addition, no change was observed in the packing fraction of the green bodies obtained by slip casting. This indicates that a metal ion concentration of 0.37 mM does not affect the state of dispersion of the alumina particles in slurry, regardless of the ion species. The apparent viscosity of the slurry samples gradually increased with increases in the PCA dosage beyond 2.0 mg·g$^{-1}$ Al$_2$O$_3$, however, accompanied by a decrease in the green body packing fraction. The increased apparent viscosity and decreased packing fraction are attributed to compression of the electric double layer and adsorbed layer [32] due to increases in the ion concentration in the solvent with increases in the amount of unadsorbed PCA. Because the thickness of the electric double layer is approximately the reciprocal of $\kappa$ [m$^{-1}$], it is clear from Equation (3) that the electric double layer is compressed with increases in the ion concentration. As is also clear from Figure 3(a), the ratio of the amount of unadsorbed PCA increased with increases in the PCA dosage above 2.0 mg·g$^{-1}$ Al$_2$O$_3$. It is considered that this higher ratio weakened the repulsive force between the alumina particles in the slurry, resulting in greater aggregation, increased apparent viscosity, and a lower green body packing fraction.

4.2.3. Slurry samples without and with 10 mM of metal ions

The addition of 10 mM of metal ions changed the slurry and green body characteristics, including the apparent viscosity and amount of PCA adsorbed, as well as the green body packing fraction. The ion species also impacted the changes. These observations are attributed to the adsorption behavior of PCA. There was still almost no change in the zeta potential, however, which could be explained as follows: Although Figure 3(a) indicates that the amount of PCA adsorbed increased with increases in the metal ion concentration, resulting in a higher charge on the particle surface, it can be seen from Figure 7(b,c) that cross-linking between the carboxy groups and metal ions reduced the charge. There was thus almost no net change in the particle surface charge with the addition of metal ions.

As concerns the addition of 10 mM of Mg$^{2+}$, it can be seen from Figures 2(b), 3(b) and 5(b) that, within the range where the adsorbed amount of PCA is 100% (PCA dosage 0.1–1.0 mg·g$^{-1}$ Al$_2$O$_3$, the level with no unadsorbed PCA), the apparent viscosity increased while the green body packing fraction decreased significantly compared to slurry without metal ions. In fact, no slurry can even be prepared when the PCA dosage is 0.5 mg·g$^{-1}$ Al$_2$O$_3$ or less. Beyond the 100% PCA adsorption line (dosages of 2.0–3.6 mg·g$^{-1}$ Al$_2$O$_3$, where unadsorbed PCA in present), the apparent viscosity and green body packing fraction remained unchanged. These results indicate, as shown in Figure 7(b), that within the range where the amount of adsorbed PCA was 100%, metal ions and PCA molecules were cross-linking and the conformation was changed, resulting in

![Figure 7](image-url)

*Figure 7. Formation mechanisms of the adsorbed PCA layer in slurry samples (a) without metal ions, (b) in the 100% PCA adsorption range with metal ions, and (c) beyond the 100% PCA adsorption range with metal ions.*
a decrease in the surface area of the particles covered by PCA, accompanied by a reduction in the repulsive force between particles. This resulted in significant aggregation of the alumina particles in the slurry. The apparent viscosity was therefore considered to increase, while the green body packing fraction decreased. On the other hand, Figure 7(a) shows the formation mechanisms of the adsorbed PCA layer in slurry samples when no metal ions were added. Because metal ions were nearly absent, PCA was adsorbed on the alumina particle surfaces in an extended state. It was, therefore, that considered possible the alumina particle surfaces were completely covered by a small amount of PCA (dosages of 1.0 mg·g⁻¹ Al₂O₃), causing the particles to be dispersed, and that green bodies with a high packing fraction (0.619 [-]) were obtained as a result. Beyond the 100% PCA adsorption range, as shown in Figure 7 (c), some of the unadsorbed PCA present when no metal ions were added was adsorbed, resulting in further coverage of the particle surface. It is, therefore, considered that the apparent viscosity and green body packing fraction are unaffected by the addition of metal ions. Further, the maximum green body packing fraction when 10 mM of Mg⁺² was added corresponded to a PCA dosage of 2.3 mg·g⁻¹ Al₂O₃, suggesting that more PCA was needed compared with when no metal ions were added (1.0 mg·g⁻¹ Al₂O₃). This trend is due to the increase in the amount of PCA required to cover the particle surface sufficiently when PCA molecules are cross-linked with metal ions.

In the case of the addition of 10 mM of Al³⁺, it can be seen from Figures 2(b), 3(b), and 5(b) that, within the range where the amount of adsorbed PCA was 100% (PCA dosage 2.0–2.3 mg·g⁻¹ Al₂O₃), the apparent viscosity increased while the green body packing fraction significantly decreased. No slurry could even be prepared when the PCA dosage was 1.0 mg·g⁻¹ Al₂O₃ or less. Beyond the range of 100% PCA adsorption (3.0–3.6 mg·g⁻¹ Al₂O₃), neither the apparent viscosity nor the green body packing fraction changed. These observations are similar to the case of the addition of Mg⁺². In addition, the maximum green body packing fraction for the addition of 10 mM of Al³⁺ corresponded to a PCA dosage of 3.0 mg·g⁻¹ Al₂O₃, indicating a need for more PCA than with the addition of 10 mM of Mg⁺² (2.3 mg·g⁻¹ Al₂O₃ maximum). These results indicate that the addition of metal ions with a higher valence increases the PCA dosage required to maximize the green body packing fraction.

5. Conclusion

In this study, we prepared alumina slurry samples using two different types of alumina powder. ICP emission spectrometer measurements showed that the amount of metal ions eluted from the alumina particles and the sintering aid increased with the addition of a dispersant. In the case of aqueous alumina slurry prepared using AES-12 alumina, the presence of a small amount of metal ions of about 0.37 mM was found to have no effect on the rate of dispersion of the alumina particles or the characteristics of green bodies produced from the slurry, regardless of the ion species. However, the presence of about 10 mM of metal ions significantly affected these properties. The maximum amount of PCA adsorbed increased while the maximum green body packing fraction decreased. These effects were more pronounced when the amount of PCA added was such that it was entirely adsorbed by the alumina particles in the slurry.

Although the present study utilized common alumina slurries and focused on Mg⁺² and Al³⁺, its considerations can be applied to slurries containing other metallic materials. The resultant amount of eluted metal ions is considered to be one of the most important determinants of the optimal amount of dispersant to be added to a slurry.

Nomenclature

| Symbol | Description |
|--------|-------------|
| μ | Medium viscosity |
| ε₀ | Permittivity of free space |
| ε_r | Relative permittivity |
| Ψ | Zeta potential |
| k⁻¹ | Debye length |
| x | Particle diameter |
| k | Boltzmann constant |
| T | Absolute temperature |
| e | Elementary electric charge |
| N_A | Avogadro’s number |
| C_i | Concentration of ion i |
| Z_i | Valence of ion i |

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Disclosure statement

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