Preparation and properties of tristrontium aluminate as an alternative component of mineral trioxide aggregate (MTA) cement

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This study evaluated tristrontium aluminate (S_3A) and its viability as a component for tricalcium silicate (C_3S) cements. The properties of S_3A , C_3S , and S_3A/C_3S mixtures were evaluated in terms of setting time, compressive strength, flowability, and radiopacity. X-ray diffraction (XRD) pattern verified the powder synthesized in the laboratory as S_3A , consequently, confirming the preparation method. S_3A exhibited the lowest setting time, followed by C_3S and S_3A/C_3S mixtures. Compressive strength of C_3S was significantly higher than S_3A . The S_3A/C_3S mixture showed comparable compressive strength to C_3S for 1-day post initial mixing. There was no significant difference in flowability between S_3A/C_3S and mineral trioxide aggregate (MTA). S_3A showed comparable radiopacity to MTA, whereas that of the S_3A/C_3S mixture was significantly lower comparatively; however, it achieved sufficient radiopacity (3 mm aluminum thickness equivalent). Further studies are needed to improve the manufacturing process of S_3A and evaluate the bioactive effect of strontium.

Keywords: Strontium aluminate, Mineral trioxide aggregate, Compressive strength, Flowability, Radiopacity

INTRODUCTION

Mineral trioxide aggregate (MTA) was introduced in the early nineties as a retrograde filling material, which could also be employed for fixing perforation^{1,2}. MTA is composed primarily of Portland cement, which is the main ingredient of mortar and concrete; further, it contains tricalcium silicate, dicalcium silicate, tricalcium aluminate, and a small amount of tetracalcium aluminoferrite^{3,4}. Moreover, bismuth oxide forms approximately 20% of the composition of MTA and acts as a radiopacifier⁴. MTA rapidly gained popularity as it established itself for its sealing ability⁵, biocompatibility^{6,7}, and antibacterial activity^{8,9}. MTA showed a remarkable capacity to induce hard tissue formation in an exposed pulp¹⁰⁻¹². Thus, the scope of application of MTA gradually expanded to include apexification, pulpotomy, and pulp capping¹³. Grey MTA was the first to be introduced as having the aforementioned composition, whereas white MTA was later introduced for esthetic applications; this was due to its purified composition that comprised a reduced iron oxide content, which was deemed as the cause of MTA's

grey color³. Several drawbacks of MTA were observed, including poor handling properties¹⁴ and long setting time¹⁵; these were of concern due to the ease with which the cement was washed out during placement. One of the reasons for the long setting time was the presence of bismuth oxide, which was shown to increase porosity and decrease compressive strength of the cement¹⁵. Bismuth oxide was also responsible for tooth discoloration in the use of both grey and white MTA^{16,17}.

Tricalcium silicate ($3CaO \cdot SiO_2$; C_3S) was found to be the main active ingredient in Portland cement, as it composes roughly 52% of MTA¹⁸. Novel C_3S -based dental repair cements may prove to be more favorable than Portland cement-based materials as C_3S exhibits a higher purity and does not contain trace elements¹⁹. Pure C_3S was shown to have sufficient biocompatibility and hard tissue promoting ability^{19,20}; further, it exhibits a shorter setting time than MTA²¹. However, C_3S cement did not have sufficient radiopacity²¹.

Strontium (Sr) is an alkaline earth element similar to calcium (Ca) and is naturally found in bone and teeth at a concentration of one hundred to several hundred parts per million (ppm). The effects of improving acid

resistance and remineralization by incorporating Sr in teeth has been reported²²⁻²⁵. Uo and Wada suggested that the above effects of Sr were related to the rapid incorporation into teeth from the surrounding fluid; this newly added Sr was found to exist in the Ca site of hydroxyapatite^{26,27}. Furthermore, strontium ranelate is available commercially as an osteoporosis treatment and its effectiveness as a pulp capping material to induce remineralization in an exposed rat dental pulp was also reported²⁸. In addition, Sr was shown to effectively enhance the radiopacity of glass ionomer cements²⁹.

On the other hand, tristrontium aluminate ($3\text{SrO} \cdot \text{Al}_2\text{O}_3$; S_3A) is well-known as one of the components of industrial cement and shows similar hydration and setting behaviors as those of C_3S and other major components of MTA cement³⁰. Therefore, S_3A is a potential material that can be utilized as a component of the MTA cement in order to improve the remineralization and enhance the radiopacity without adding bismuth oxide.

The aim of this study was to synthesize S_3A as a cement component to provide sufficient radiopacity; further, an investigation was carried out to elucidate the properties of the S_3A and its mixture with C_3S , which is the major ingredient of MTA. This investigation was performed in terms of setting time, compressive strength, relative flowability, and radiopacity. We hypothesized that adding the S_3A component to C_3S cement will improve its radiopacity without negatively affecting the setting time, compressive strength, and relative flowability.

MATERIALS AND METHODS

Preparation of S_3A and experimental cements

S_3A cement was prepared from strontium hydroxide octahydrate ($\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$; Kanto Chemical, Tokyo, Japan) and aluminum hydroxide ($\text{Al}(\text{OH})_3$; Kanto Chemical), which were mixed at a molar ratio of 3:2. The mixture was heated at 180°C for 2 h to evaporate the water of hydration, then ground in the agate mortar. Obtained powder was calcined at $1,200^\circ\text{C}$ for 4 h. Then, the calcined powder was ground again in the agate mortar. The crystal phase of obtained powder was identified using an X-ray diffractometer (XRD, Miniflex, Rigaku, Tokyo, Japan) with a scanning speed of $2^\circ/\text{min}$. Synthetic C_3S powder was provided by Nippon Shika Yakuhin (Shimonoseki, Japan) and used for the following experiments as is. The mixture of S_3A and C_3S ($\text{S}_3\text{A}/\text{C}_3\text{S}$) was prepared by mixing aforementioned S_3A and C_3S powders at a 1:1 weight ratio. ProRoot MTA (Dentsply, Johnson City, TN, USA) was used as a commercial MTA product for comparison with the experimental cements. In this study, S_3A , C_3S , and $\text{S}_3\text{A}/3\text{C}_3\text{S}$ mixture cements were mixed with distilled water (DW) at water/powder (W/P) ratios of 0.6, 0.5, and 0.6, respectively. Those W/P ratios are the minimum values for each experimental cement to produce sufficient workability. MTA was mixed with DW at a W/P ratio of 0.33 as recommended by the manufacturer.

Scanning electron microscopy (SEM) observation

SEM observation was carried out for S_3A , C_3S , and MTA powders. In addition, the cured cements were observed after 1 day (d) and 28 d post initial mixing.

Setting time evaluation

Setting time was estimated according to ISO 9917-1; 2007³¹. The mixed cement specimen was filled into a stainless-steel mold with inner dimensions of 8×10 mm and 5 mm height. Each specimen was given the indentation test using a Vicat needle (1 mm in diameter) and with 400 g of weight in a plastic container kept at $37 \pm 1^\circ\text{C}$ and $>90\%$ humidity. Indentations were repeated every 60 s until the needle failed to make a complete circular indentation in the cement. The setting time was calculated as the time taken from the mixing of cement to the time where the needle failed to create an indentation. Three replicates of each material were tested.

Compressive strength evaluation

The compressive strength was determined according to ISO 9917-1; 2007³¹ specifications. The cement was mixed with DW with the corresponding W/P ratio and filled into a separable cylindrical stainless steel mold of 4 mm in diameter and 6 mm in height. After filling the mixture, both sides of the mold were covered by glass plates, then kept at 37°C and 100% humidity. The specimens were divided into two groups. One half was kept for 1 d and another was kept for 28 d. Each specimen was carefully removed from the mold and its new dimensions (diameter and height) were measured using a screw micrometer (QuantuMike series 293, Mitutoyo, Kanagawa, Japan). The compressive strength of these specimens was evaluated using the universal testing machine (EZ-LX, Shimadzu, Kyoto, Japan) with a test speed of 0.75 mm/min. Five replicates of each material were tested.

Relative flowability

The relative flowability was estimated by using the specimen weight normalized spread area under compression using a previously reported method³². A total of 0.06 g of powder for each cement was mixed with DW at the corresponding water/powder ratio. The hydrated cement was placed on a glass slab using a plastic ring of 6 mm in diameter and 1 mm thickness. The weight of the cement was measured using a precision balance (AG245, Mettler Toledo, Greifensee, Switzerland). After removing the ring, a second glass slab was placed on top of the cement and a weight of 1 kg was applied for 60 s at room temperature (24°C). After removal of the weight, the surface of the cement was scanned with a flatbed scanner at a resolution of 600 dots-per-inch (dpi) (ApeosPort-IV C3375, Fuji Xerox, Tokyo, Japan). Afterwards, the surface area of the spread cement was calculated using image analysis software (ImageJ, Ver.1.52K, National Institute of Health, Bethesda, MD, USA). The relative flowability was calculated according to the following equation:

$$\text{Relative Flowability} = \frac{\text{area (mm}^2\text{)}}{\text{weight of paste (g)}}$$

Five replicates of each material were tested.

Radiopacity

Radiopacity was estimated according to ISO 6876: 2012³³⁾ specifications. The specimens were prepared by mixing each cement powder with the corresponding W/P ratio, and then formed into a disk shape (10 mm in diameter and 1 mm thickness) using a plastic mold. The specimens were placed on an X-ray imaging plate with an aluminum step wedge of varying thickness (1–10 mm), and the X-ray was irradiated using dental X-ray equipment (MaxiX, Morita Corp., Kyoto, Japan) with the following conditions; a voltage of 70 kV, a current of 7 mA, an exposure time of 0.63 s, and 15 cm distance between the imaging plate and cone end. The radiographs were obtained with an imaging plate reader (Carestream CS 7600, Carestream Health Japan, Tokyo, Japan). The mean grey value (MGV) of the specimen was estimated using ImageJ and the aluminum (Al) thickness equivalent was estimated using the aluminum step wedge. Three replicates of each material were tested.

Statistical analysis

A two-way ANOVA test was used for compressive strength evaluation followed by multiple comparisons with Bonferroni correction. A one-way ANOVA was used to compare between tested groups for setting time, flowability, and radiopacity followed by a pairwise comparison with Tukey's HSD ($\alpha=0.05$) (IBM SPSS Statistics for Windows, Version 23.0. IBM, Armonk, NY, USA).

RESULTS

XRD analysis of the synthesized S_3A powder

The XRD pattern of the synthesized S_3A powder is shown

in Fig. 1. All observed peaks could be ascribed to those of the tristrontium aluminate ($Sr_3Al_2O_6$; powder diffraction database (PDF) #5529) for the powders that calcined at temperatures higher than 1,200°C. Conversely, the powder that calcined at 1,100°C showed small peaks assigned to strontium oxide (SrO ; PDF #9238) and also a small halo, which might be derived from the amorphous phase that remained around 28°C. Thus, it was considered that calcination at a temperature higher than 1,200°C is necessary for the synthesis of S_3A .

Scanning electron microscopy (SEM) observation

SEM images of S_3A , C_3S , and MTA powders (Fig. 2) show that S_3A primarily comprised crude particles larger than several tens of micrometers (μm), which exhibited irregular shapes with rough surfaces. Additionally, small amounts of micro particles of a few micrometers were observed. C_3S comprised elongated spherical primary particles with a homogenous particle size of about 1 μm . A part of the particles formed aggregates from secondary particles of several to 20 μm size. MTA particle size

Fig. 1 XRD pattern of the strontium aluminate powders calcined at various temperatures.

Fig. 2 SEM images of S_3A , C_3S , and MTA powders.

was distributed from a few to 20 μm . The particle size distribution was homogenous in C_3S , while S_3A showed the highest inhomogeneity with the widest range of particle sizes, followed by MTA, which showed moderate inhomogeneity. Furthermore, the radiopacifier of MTA appeared as white particles in the image (arrowed).

Figure 3 shows the SEM images of the cements at 1 d and 28 d after setting. The S_3A cement shows the needle-like precipitations at 1 d after setting. After 28 d, the precipitate was increased but the shape was unaltered. In contrast, C_3S cement shows spherical aggregates after 1 d and the shape remained unchanged even after 28 d. The shape of original MTA powder could be identified on 1 d after setting. After 28 d, the gaps among the MTA resource powders were filled with small precipitations.

Setting time

Setting time results (Fig. 4) for the 3 groups were evaluated. S_3A (90.67 min (SD 3.79)) showed the lowest

significant setting time followed by C_3S (152.67 min (SD 5.03)) and $\text{S}_3\text{A}/\text{C}_3\text{S}$ (299 min (SD 1)) ($p < 0.001$). Adding S_3A to C_3S at a 1:1 ratio increased setting time significantly.

Compressive strength

The compressive strength results were evaluated for the 3 groups (S_3A , C_3S and $\text{S}_3\text{A}/\text{C}_3\text{S}$) for 1 d and 28 d after mixing, which can be seen in Fig. 5. C_3S showed a significantly higher compressive strength compared to S_3A at both times. Adding S_3A to C_3S at a 1:1 ratio did not lower the compressive strength significantly as compared to C_3S on 1 d; however, a significant decrease in compressive strength was observed after 28 d. There was no significant increase in compressive strength between 1 d and after 28 d within each group except for C_3S .

Fig. 3 SEM images of S_3A , C_3S , and MTA cements at 1 d and 28 d after kneading.

Fig. 4 Setting time analysis. Different letters between each column indicate significant differences ($p < 0.05$).

Fig. 5 Compressive strength of S_3A , C_3S , and $\text{S}_3\text{A}/\text{C}_3\text{S}$ cements after 1 d and 28 d from cement kneading. Different letters between each column indicate significant differences ($p < 0.05$).

Fig. 6 Relative flowability of cement paste. Different letters between each column indicate significant differences ($p < 0.05$).

Relative flowability

The relative flowability (Fig. 6) that was evaluated for the 4 groups (S₃A, C₃S, S₃A/C₃S and MTA) showed no significant difference between S₃A and C₃S, as well as between S₃A/C₃S and MTA. However, both S₃A/C₃S and MTA had significantly lower flowability than both S₃A and C₃S ($p < 0.001$).

Radiopacity

S₃A and S₃A/C₃S mixture achieved the requirement of the Al thickness of 3 mm, as shown in Fig. 7. There was no significant difference between the radiopacity of S₃A and MTA. S₃A/C₃S mixture showed significantly lower radiopacity than MTA ($p < 0.001$); however, it still attained a 3 mm Al thickness.

DISCUSSION

MTA cement is based on calcium silicate, which has low radiopacity. Therefore, heavy element oxides (e.g. bismuth oxide) were added as radiopacifiers. Past investigations showed that bismuth oxide is not an inert component, but actively reacts in the hydration mechanism of MTA. This reaction generates a weaker microstructure as compared to hydrated Portland cement, which leads to an increased porosity and a decrease in compressive strength^{34,35}. Considering the tooth discoloration caused by bismuth oxide^{16,17}, an alternative cement component that has enough radiopacity is desirable. In this study, we focused on S₃A as the self-setting and radiopaque component for MTA cement.

In this study, S₃A could be synthesized under calcination at 1,200°C from the hydroxide of strontium and aluminum as a resource. Portland cement clinker is usually calcined at 1,400–1,500°C. Therefore, S₃A would be a good fit in an energy saving process. As shown in Fig. 2, the particle sizes of S₃A were still larger than other cements and their shape was irregular. This caused the

Fig. 7 (a) Radiopacity values of cements presented as Al thickness equivalent (mm). The dotted line shows the 3 mm Al thickness from which the cement radiopacity is considered sufficient. Different letters between each column indicate significant differences ($p < 0.05$). (b) Digital radiograph of cements samples and Al step-wedge.

S₃A and S₃A/C₃S mixture to require a larger W/P ratio (0.6) than that of C₃S (0.5) and MTA (0.33).

The long setting time is a drawback of C₃S-based cements. In this study, S₃A showed shorter setting time (90.7 min) than C₃S (153 min). Generally, it has been well-established that aluminate shows faster hydration than silicate³⁶. Therefore, the shorter setting time of S₃A is reasonable. S₃A/C₃S mixture showed longer setting time (299 min) than that of the other components and also comprised a reported value for ProRoot MTA (261 min)³⁷. Because of this reason, the mismatch of particle size in S₃A and C₃S could be suggested. If S₃A powders had a larger particle size than C₃S, then the packing efficiency of particles in their mixture would be decreased and the setting reaction would be slower.

Concerning the compressive strength, S₃A exhibited a strength that was one-third to that of C₃S for one day as well as after 28 d of maturation. For the S₃A/C₃S

mixture, compressive strength after 1 d was comparable to that of C₃S. Further, C₃S showed significant increase in the compressive strength from 1 to 28 d, whereas both S₃A and the S₃A/C₃S mixture did not show a significant increase. This was a result of the fast hydration reaction of aluminate as described above. The compressive strength of commercial MTA (ProRoot MTA) has been reported as 27.41 and 86.02 MPa after 1 d⁽³⁸⁾ and 28 d⁽³⁹⁾ of maturation, respectively. Based on the low compressive strength of S₃A-based cements, a high W/P ratio and a low packing density of the cement was suggested, which were caused by its large particle size and irregular shape. Thus, considering the extension of the setting time of the S₃A/C₃S mixture, the improvement in the filling in terms of the shape and size of the particle should be studied in the future.

Relative flowability was chosen as a representative for observing the properties of the cements. In this study, S₃A was mixed with higher W/P ratio, which was the reason of its apparently high flowability. Because MTA could be kneaded at almost half the W/P ratio than S₃A, it contributes toward its high compressive strength.

S₃A showed similar radiopacity to the commercial MTA without the addition of a radiopacifier, such as bismuth oxide. Even in the S₃A/C₃S mixture, if enough radiopacity was achieved, S₃A would contribute as the fast hydrated, and radiopaque component of the MTA cement.

Another type of strontium aluminate (SrAl₂O₄) is popularly used in phosphors. SrAl₂O₄ nano-particles have been reported as non-cytotoxic⁽⁴⁰⁾. Therefore, S₃A could be expected to have low cytotoxicity. However, further estimation of cytotoxicity and the biological effects of S₃A should be carried out in future studies.

CONCLUSION

In this study, S₃A was synthesized from strontium and aluminum hydroxides by calcination at 1,200°C. S₃A displayed a faster setting time than C₃S and MTA cements. Further, S₃A showed a similar radiopacity as that of MTA without the addition of a radiopacifier. The radiopacity was high enough for the mixture of S₃A to C₃S, which is a major component of MTA. Therefore, S₃A can be suggested as a possible cement component that facilitates a fast setting time and a sufficient radiopacity. Current S₃A powders have large particles with irregular shapes. This resulted in lower compressive strength; therefore, these require a high W/P ratio for kneading. Further improvement in the particle shape, size, and distribution of S₃A is required. In addition, the bioactive effect for the hard tissue regeneration of strontium derived from S₃A should be elucidated in future studies.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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