- *Technical Paper* -

BEHAVIOR OF HIGH CALCIUM RECYCLED GLASS WITH DIFFERENT PARTICLE SIZE ON ASR

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ABSTRACT

Aiming to increase the use of recycled material in the construction industry meting the sustainable development goals, many efforts have been made to evaluate the performance of concrete structures with waste materials. There is no too much available information about high calcium content glass with different particle sizes influence on ASR so this study aims to investigate it. The ASR results shows that the samples under 0.600mm decrease the expansion and the consumption of CH confirmed the pozzolanic activity of the material for small particle sizes.

Keywords: Alkali-silica reaction, recycled glass, glass particle size, calcium content.

1. INTRODUCTION

The united Nation set 17 goals to promote a sustainable development, ensuring balance between social, economic and environmental sustainability. These goals have as a target to be fulfilled by 2030. As the deadline is approaching, the initiatives to promote the goals are also in focus by all industries. The concrete industry is one of the biggest contributors for harmful effects on the environment. The high exploitation of natural resources and carbon dioxide emissions makes this sector crave for sustainable alternatives. The use of recycled materials to make concrete can help to decrease harmful effects, giving destination for waste material and decreasing the emission of greenhouse gases, as a result these actions can be related to goals 12 and 13 from UN [1] (Figure 1).

Fig. 1 – 12 and 13 SDG's

2. ALKALI-SILICA REACTION

Recycled glass, used as cement or aggregate substitute, can present a promissory option due to the high content of Silicon dioxide. However, this material can react strongly and result in a phenomenon of the formation of a hydrophilic gel that expands and can result in cracks on cement structures called alkali-silica reaction (ASR). The most accepted fundamental model for the mechanism of reaction is described by Rajabipour [2] and can be seen at Figure 2.

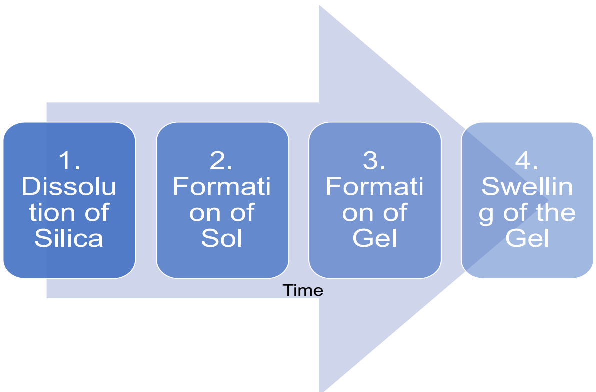

Fig. 2 – Alkali-silica reaction mechanism over the time– Adapted from [2]

Until now, many expansion mechanisms have been proposed however the comprehension, perdition and description of the development of the ASR still limited and incomplete [3]. To better achieve the goal of fully understand this concrete pathology, the conditioning factor for the reaction to happen have to be considered. The initial understanding of the reaction from previous studies [4] stated that reactive silica, sufficient alkali and moisture have to be together for the reaction to happen.

If one of these components is excluded, the reaction would stop, and the structures would be protected. Pozzolanic materials can also be used because they reduce the alkalinity of the pore solution by consuming CH to form cementitious products.

Based on that, the current design methods to protect the structure from ASR requires that the water, high alkali cement and reactive aggregate should be avoided to be together and the also use of pozzolanic materials is recommended. However, more factors can show influence on the occurrence and intensity of the reaction. According to Figueira [3], currently four factors are understood by the scientific society as to have to occur simultaneously to develop ASR. (1) reactive aggregate in an amount within a critical range; (2) high OH^-

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(alkali) concentration for silica attack; (3) a source of soluble calcium to react with silica and form deleterious gel; and (4) high moisture content. As conditioning factors for ASR to occur, if any of this factor is removed the reaction will not happen. This inclusion of soluble calcium source is due to the importance of this ion on the development of the reaction. It is undeniable that calcium participates actively in the reaction, however its precise role stills unknown. The common source of calcium on cement structures is mostly in the cement paste hydration and according to Rajabipour [2], two major roles are played by this material: (1) alkali recycling by exchange with alkali (K and Na) in the gel; and (2) it influences the properties and composition of the gel so its consequent expansion capacity.

The first phenomena, called alkali recycling, happens in the 1st stage of ASR mechanism presented at Figure 2, silica dissolution. As silica is being attacked by the OH^-, the pH of the solution trend to decrease, however some alkalis incorporated in the silica gel are replaced by Ca ions and it recycle the alkalis back to the concrete pore solution, consequently there is a decrease of calcium in the pore solution and it promotes dissolution of solid portlandite and increase in pH. In the absence of Ca ions, the dissolved specimens would remain in solution [2]. So, the consumption of portlandite can be related to the ASR reaction.

The second importance is related to the calcium ions on the properties and composition of ASR gel. The Figure 3 summarizes the changes in chemical composition, physical and mechanical properties and structural changes in the ASR gel from the increase of calcium in the pore solution. The high concentration of calcium results in a more viscous gel, with less expansive properties and better strength. The increase in viscosity of the gel reaches a point of crystallization and posterior precipitation of the C-S-H products. Shi & Lothenbach [5] also studied the role of the calcium on the formation of ASR products and concluded that the ASR products are reduced at high Ca/Si ratio and it results in the formation of C-S-H or, non-expansive cementitious products.

Between the other main factors about the ASR, the reactive silica source role is also interesting. As said by Rajabipour [2], it is expected that if the aggregate gets smaller, the reaction will happen more intensely due to the increase in surface area so ASR products and expansion would increase. However, the experiments showed that effect of expansion is related to a pessimum aggregate size effect. The most common explanation is related to the smaller particle size and pozzolanic reaction, but the explanation for big particle sizes still unclear. The author investigated the SEM analysis of aggregates with different particle sizes and verify that in the surface of aggregate, pozzolanic reaction was occurring more intensely and C-S-H could be observed, however inside the aggregate cracks more ASR gel was formed. The study attributed the behavior to the big particles have more cracks, so more gel is formed, and more expansion observed [6].

Taylor [7] considered ASR as a pozzolanic reaction on

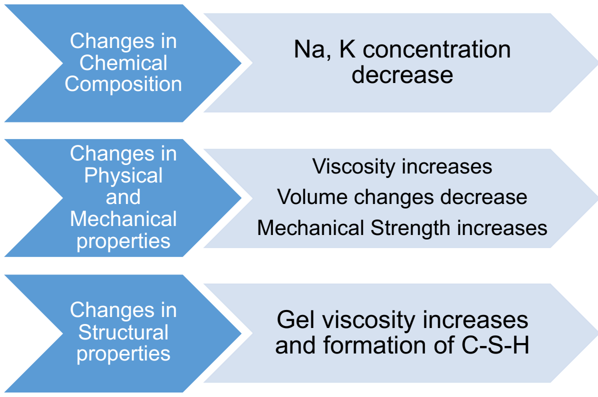

Fig. 3 – Consequences of increase in Calcium concentration in the ASR products– Adapted from [2] and [12].

chemical terms, with the different effects in concrete related to the particle size and siliceous material. In his book, he explains that in pozzolanic reaction the gel is formed in an environment rich on Ca^{2+}, so it is quickly converted in C-S-H. On the other hand, ASR is formed in a poor environment of calcium because the cement paste cannot supply it fast enough and a huge amount of gel overflow is formed.

Following many considerations about the occurrence and behavior of ASR in structures, many studies used not only natural reactive aggregates but also recycled material in cement structures in order to evaluate the durability issue related to ASR. The studies with recycled components aim to give destination to the waste materials promoting a more sustainable development of the society. It can be observed that, for recycled glass used in cement structures, the bibliographic reviews ([8] and [9]) states that ASR become weaker as de particle size decrease. However, there is no agreement about which particle size provide the particle size pessimum effects for ASR ([10] and [11]). When it is used in an appropriated dosage and size, the recycled glass can mitigate the reaction in concretes susceptible to ASR due to the chemical composition and amorphous high reactive properties. The complexity of the recycled material also gives more variants to be considered in the process of the reaction to happen. The color, type, proportion and use as binder or aggregate can also play a role in the reaction. The glass chemical composition is directly correlated with the color and type (such as soda-lime glass), so it also is an important consideration factor to describe the reaction possibilities. The glass used in this study is a rich calcium material, with low amount of sodium and mixed colors (however the predominant color is green). The calcium content was considered as high because among the bibliographical review ([8] and [10]), the overall amount of CaO in the chemical composition is around 10%, but this study material is 2 times higher (Table 1).

With that said, this research has as an overall objective to promote and contribute for the use of recycled materials in the construction industry. If the behavior of the recycled glass can be evaluated when used in cement structures, it can also provide a destination to this recycled material.

Also, due to the importance of calcium for the reaction and the lack of explanation about the ASR mechanism on particle size, this work has as objective to investigate the high calcium content recycled glass with different particle sizes when used in cement mortar for ASR expansion.

3. TEST PROGRAMS

3.1 Materials and Mix Proportions

The recycled crystal sand glass is from Osaka region in Japan and it is considered as mixed colors with predominant green color (Figure 4). The recycled glass chemical composition can be seen at Table 1. To try to isolate the particle size effect in the mix design, the samples were cast using the same amount of reactive aggregate and cement with addition of 6 different graded recycled glass particle sizes from 0 to 2.36 mm. The addition of material was referent to 15% of the aggregate amount. The gradation of the material was made using standard sieves with the mesh from 0.150mm to 2.36 mm. In total, 5 sieves were used (0.150;0.300;0.600;1.18 and 2.36), and the glass powder (0.075 mm) was provided already sieved from the partner company. The reference mix (1 - REF) was made by using the reactive aggregate, water, and cement in the same proportion of the other samples (from 2 to 7) however a non-reactive material was used instead of glass with different particle sizes (addition of 15%) so the proportion of aggregate cement was kept for all mixes. From this, the experiment aimed to keep the expansion of the reference mix only related to the reactive aggregate, so the influence of the different particle sizes can be observed in the other mixes to compare the results.

The mix design proportion for accelerated mortar bar test was based on the ASTM C 1567, with some adaptation on the cement aggregate ratio (m) value from 2.25 to 2.58. As the solid material increase water binder ratio was also changed, increasing from 0.47 to 0.50. The reactive aggregate used as glass crystal sand. Ordinary Portland cement was used as binder. The mixes were named accordingly to the biggest particle size in the retained sieve. The mix design can be seen on Table 2.

The TG-DTA samples was prepared by casting 7 proportion: 6 mixes with 75% of ordinary Portland cement (OPC) and 25% of recycled glass with different particle sizes (in volume) and the reference mix with only OPC. The water cement ratio as fixed as 0.50.

3.2 Testing Methods

The shape of each particle size was closely observed by using a light microscopic model Keyence VHX-200 digital microscope with zoom of 50, 100 and 175 times. The reactivity of the recycled glass for ASR, the expansion was measured by performing the accelerated mortar bar test (AMBT) from ASTM C1567. For this, the standard established that readings were made on 1, 2, 5, 7, 10 and 16 days of age in a curing condition inside a NaOH solution at 80 degrees Celsius. The current experiment was adapted, and the readings were extended

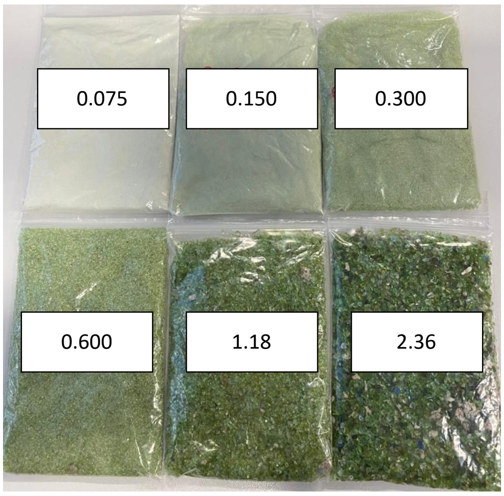

Fig.4 - Recycled glass

Table 1 Recycled glass chemical composition.

	Recycled Glass Crystal Sand	
	Content	wt%
1	SiO_2	69.2740
2	CaO	20.9849
3	Na_2O	4.6117
4	K_2O	1.8740
5	Al_2O_3	1.8376
6	Others	1.4178

Table 2 Mix Proportion.

<table>
<tr><th colspan="2">Mix</th><th>Water (g)</th><th>Cement (g)</th><th>Reactive Agg (g)</th><th>Non-reactive Agg (g)</th><th>Diff. glass particle size (g)</th></tr>
<tr><td>1</td><td>REF</td><td rowspan="7">220</td><td rowspan="7">440</td><td rowspan="7">990</td><td>148.5</td><td>-</td></tr>
<tr><td>2</td><td>0.075</td><td rowspan="6">-</td><td rowspan="6">148.5</td></tr>
<tr><td>3</td><td>0.15</td></tr>
<tr><td>4</td><td>0.30</td></tr>
<tr><td>5</td><td>0.60</td></tr>
<tr><td>6</td><td>1.18</td></tr>
<tr><td>7</td><td>2.36</td></tr>
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Fig.5 TG-DTA – Sample preparation and test

until 28 days. The residual calcium hydroxide amount was measured by casting cement paste of a mix of OPC and glass with different particle sizes. The curing was performed inside a chamber of controlled temperature and humidity (20ºC and 60% RH). The samples were test on 7, 21, 28 and 91 days of age. At the specific day, the samples were immersed in acetone and put on vacuum condition for 3 hours. So, the samples were crushed and sieved in 0.150mm. After, the material was tested using a TG-DTA – MTC 21000SA Bruker on Nitrogen atmosphere. The process can be seen at Figure 5. As the samples were sieved in the 0.150 mm, the material of 0.300, 0.600, 1.18 and 2.36 mm was retained in the sieve. The 0.075mm and 0.150 mm recycled glass particles were incorporated in the material analyzed in the TG-DTA because it passed in the sieve mesh.

4. RESULTS AND DISCUSSION

4.1 Light Microscopic Analysis

The particle sizes were observed individually in the microscope to verify the shape and surface of the samples. As can be seen in Figure 6, the particles are mostly round in one dimension with a very rough surface. The samples also present a crushed flat pattern in the other dimension, characteristic of the crushing process of the recycled material. The irregular surface is considered an important factor to consider about the formation of the ASR gel in the interface cement paste aggregate. It can be seen that as the size increase, it is more evident that the surface of the aggregate become irregular and with cracks. It can have huge influence on the gel formation and ASR expansion as explained by Rajabipour [6]. In his work, he stated that bigger particles have wider and accessible cracks than fine glass. In the surface, they could observe that only C-S-H was formed, however, inside the cracks the amount of expansive ASR gel was higher. The possible explanation is that the small cracks in fine particles makes difficult for the diffusion of hydroxyls ions and absorption of moisture by the gel. The bigger particles have wide cracks and allow the penetration and diffusion of hydroxyls inside the glass particles. At Figure 7, it can be seen large cracks in the glass particle (2.36mm) and this characteristic can be related to the high expansion observed in the ASR mortar bar test in the next section.

4.2 ASR - Accelerated Mortar Bar Test

The results show (Figure 8) that recycled glass with particle size smaller than 0.300mm did not present a deleterious expansion in 28 days of ASR experiment. The particle size of 2.36mm presented the most expansive result, followed by 1.18mm at 28 days of age. The reference (REF) mix, composed by reactive aggregate and addition of 15% of non-reactive material, was the 3rd larger expansion showing that the particles sizes of 2.36mm and 1.18mm had more overflow of expansive gel. Particle size smaller than 0.600 reduced ASR expansion when compared to the reference mix. The particle size has been related to ASR by various authors and for a high calcium content glass the expectations was to reduce the expansion due to the higher availability of calcium to react and form C-S-H [6]. This investigation observed that under 0.600 mm the glass particle has the property of decrease the expansion when compared to the reference mix. This investigation needs a better look in the interface between the aggregate and cement paste to confirm the Ca/Si ratio and morphology of the gel around and inside the cracks of

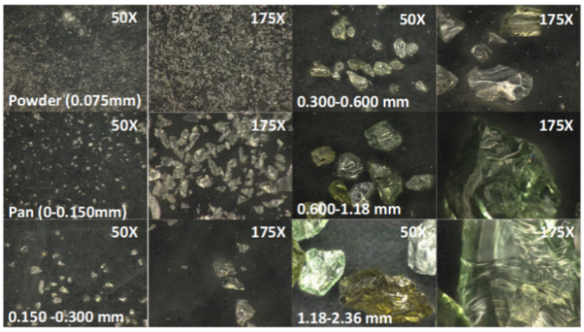

Fig.6 Light microscopic vision of the different particle size of glass

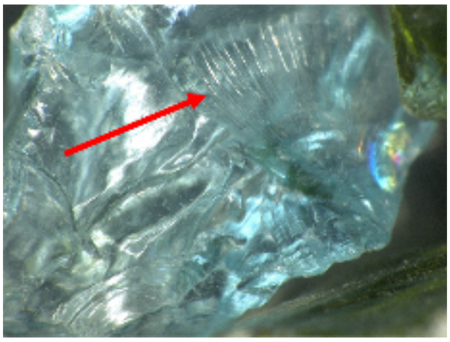

Fig.7 Light microscopic – cracks in the glass particles 100X.

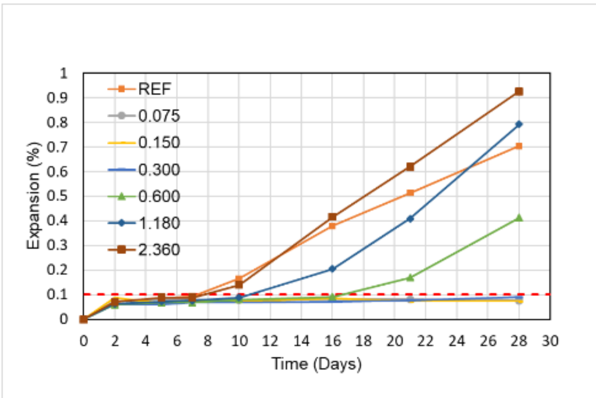

Fig.8 ASR expansion of different particle sizes

the aggregate. However, with a micro reading of the calcium content throw-out the TG-DTA readings, it was possible to have an overview of the availability of calcium and hydration degree of the material.

4.3 TG-DTA

The TG-DTA was used in order to investigate the amount of residual CH in the samples over the time. It also helped to visualize the amount of hydrated products by the investigation of ignition loss (IL). The value of IL was read after 100 degrees due to the free water evaporation process. The results of calcium hydroxide residual amount and percentage of ignition loss can be seen at Figures 9 and 10.

The Figure 9 shows that as the particle size decrease, less calcium hydroxide can be observed in the samples. This effect is widely discussed as a pozzolanic reaction from the active amorphous silica from the recycled glass and the calcium hydroxide from the hydration of cement.

This phenomenon of use of small particles and decrease in ASR expansion can also be related to the packing property of the small particles to fill the small spaces working like a filler that decrease porosity and increase the concrete durability. However, in this case, the consumption of calcium hydroxide indicates that the pozzolanic reaction is happening in the samples.

Over the time, the increase amount of CH increases slightly for the reference mix (100% OPC), this behavior is not followed by the 0.075 mm sample. It indicates that the pozzolanic reaction is occurring strongly and the calcium hydroxide is also being strongly consumed. The other particle sizes showed a tendency to increase the CH amount over the time, even when the samples did not have harmful behavior for ASR expansion. It indicates that the aggregate source of calcium is also working on providing calcium ion to the pore solution by the dissolution of the aggregate. This calcium can make the gel more viscous and with a high Ca/Si ration, culminating in the precipitation of C-S-H instead of expansive gel (as said by [2] and [5]).

The Figure 10 shows the timeline of particle dissolution, pozzolanic reaction and ASR as discussed by [6] and [8]. As it was explained in the second chapter of this work, the pozzolanic reaction can happens faster in smaller particles and produce C-S-H instead of expansive components. The bigger particles are not fully dissolute and the difference in calcium concentration in the pore solution and ASR products can result in different expansion ratios. Figures 11 and 12 show the difference between the normal reactive aggregate and high calcium glass reactive aggregate. The normal aggregate has more reactive silica inside, so the reaction rim is more likely to become richer in Silica. Only an external region of the reaction rim will be rich in calcium that comes from the hydration of cement (Figure 11). However, the high calcium glass has more calcium ions because of the dissolution process and can provide then to the rim, so it makes more likely to the high calcium part of the rim to be bigger than in a normal reactive aggregate situation (Figure 12). The increase in concentration of calcium in the reaction rim, makes the ASR products more viscous and because of this it is more difficult to the hydroxyls to penetrate deeper and react the glassy SiO_2 of the aggregate to keep up with the reaction, so the speed of the reaction decrease.

In this study, the amount of calcium hydroxide increased for the large particle sizes when compared to the reference mix (cement paste). The only probable source of calcium in the mixes are from the glass. So, with this, it is acceptable to suppose that the reference mix has a limited amount of calcium from the hydration, however, as the glass is dissolved in the high pH of the cement environment in the mixes, more calcium is added to the pore solution, resulting in calcium hydroxide ($Ca\text{-}(OH)_2$). The medium particles have more surface area so the jump of CH amount was higher than the bigger particles over the time as can be seen at Figure 9. For all big particle size samples, at 91 days the CH amounts got more stable. It can mean that the surface of the aggregate reached the reaction rim more reach in calcium and, as water was not provided in the curing condition (sealed at

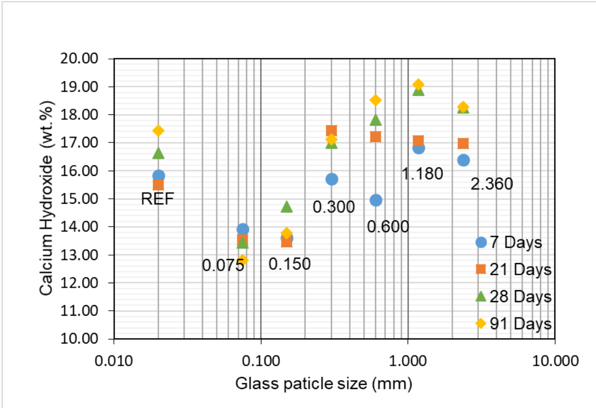

Fig.9 TG-DTA - Calcium hydroxide of different particle size

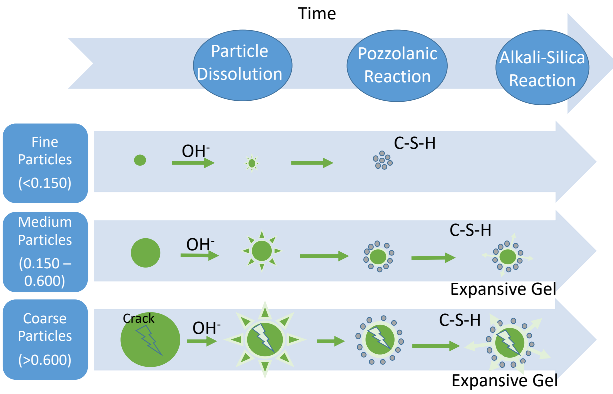

Fig.10 Particle size and reactions over the time – adapted from [6] and [8]

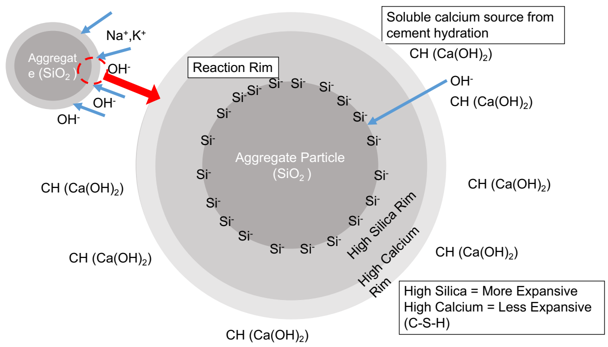

Fig.11 Normal reactive aggregate – Reaction Rim

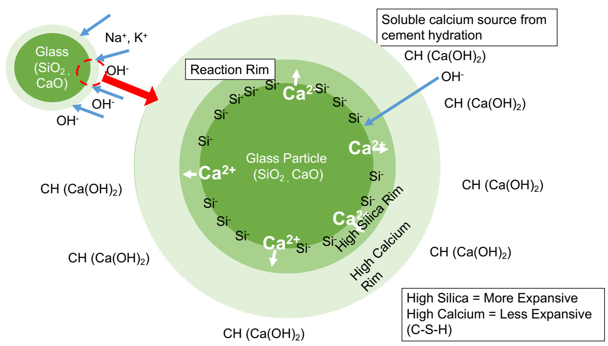

Fig.12 High calcium reactive aggregate – Reaction Rim

20˚C), the reaction speed went down. So, if water is not provided (because water increases the mobility of the ions), the reaction can reach a limit. In this experiment, the short time of reading from the ASTM C1567 did not permit to achieve this period for the expansion readings. The Figure 13 shows the CH reading from TG-DTA of the samples from the accelerated mortar bar test (ASTM C 1567) at 28 days of experiment. The values increase with the particle size and the large particle got a very close value of expansion such as the reference. As the expansion increased, the amount of CH also increased. The Figure 14 shows the relation between the ASR expansion and calcium hydroxide residual amount from TG-DTA analysis. The clear relationship can be seen that when the CH increase, the expansion also increases for big particle sizes (over 0.600mm). For small particle sizes (under 0.300), the increase in calcium hydroxide amount is not harmful and give more evidence to the pozzolanic reaction mechanism related to the particle size of the material.

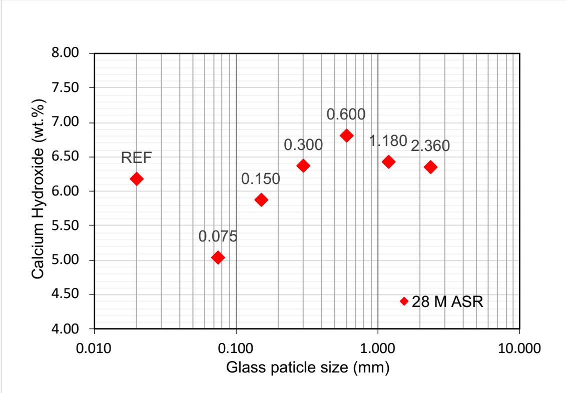

Fig.13 TG-DTA - Calcium hydroxide of ASR ASTM test mortar at 28 days

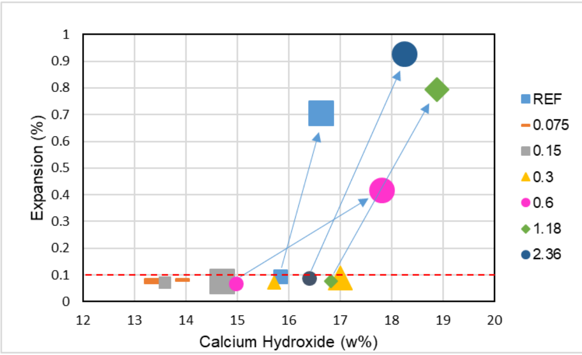

Fig.14 Calcium hydroxide and ASR expansion 7 and 28 days

5. CONCLUSIONS

As the main conclusion, this study presents the result that the pozzolanic activity is happening in the small particle sizes of the recycled glass aggregate and this material has potential to be used as ASR suppressing agent in cement structures, promoting the use of this recycled material. Also, it can be seen that the particle size of the glass is directly correlated to the expansion of the cement structures on ASR. As the particle gets smaller, the pozzolanic reaction takes more place instead of ASR and the expansion decreases. These findings hope to promote the use and increasing research knowledge of recycled materials on construction industry in Japan and all over the world contributing for the sustainable development goals.

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