Synthesis of recycled cements using hydrothermally treated waste soda lime glass

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Waste soda lime glass powder was hydrothermally treated twice at 150°C, and the resulting powder was mixed with CaCO₃ powder in the weight ratio of 1:3 and heat-treated at 1450°C. The resulting powder was identified as Ca₃SiO₅ as the main phase with small amounts of Ca₃Al₂O₆, which are both common Portland cement sources. The elemental composition of the resulting cements was evaluated and all minor components (Cl, Na, SO₃, etc.) were found to be less than the JIS standard value for eco-cement.

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Only a small fraction of glass products such as glass bottles and building windows are recycled, and most glass products are discarded, totaling over 600 million tons per year in Japan.¹⁾ The chemical composition of waste glass products is close to clay or sand; therefore, many investigations have been reported on the use of waste glass powder as a partial cement replacement.^{2)–4)} However, there are no reports of trying to apply the waste glass to recycled cement directly.

It has been reported that municipal waste incineration ashes can be converted into recycled cements, and such recycled cement is known as “eco-cement”.^{5),6)} These eco-cements have been practically applied to buildings.⁷⁾ The chemical composition of an eco-cement is defined by a JIS standard.⁸⁾ In particular, the minor components of the eco-cement are severely restricted because they inhibit the hardening of raw cements during practical concrete formation. The minor components specified in the standard are MgO, SO₃, and total alkali metals and chlorides. The JIS standard is noted later in **Table 1**.

In our previous study, we converted soda-lime glass powders in the form of general waste glass to silicon dioxide raw materials using a hydrothermal process, and fabricated silicon oxynitride powders using the hydrothermally treated soda lime glass.⁹⁾ The Na in soda-lime glass can be removed by a hydrothermal process,⁹⁾ and hydrothermally treated soda-lime glass is thus expected to be used for the synthesis of recycled cements as a raw silicate material. In the present investigation, we report the synthesis of recycled cements using waste soda lime glasses. We then evaluate the chemical composition of the resulting cement and compare it with the eco-cement in the JIS standard.

CaCO₃ (calcite, Wako, particle size 2–7 μm) and SiO₂ (quartz, Kojundo, particle size 3–5 μm) powder were used as standard materials, and waste soda lime glass powder was used as the raw material for the synthesis of recycled cements. Soda lime glass was milled to a particle size of less than 10 μm. The ground particles were added to ion-exchanged water at a concentration of 5 g/L and 100 mL of the suspension was hydrothermally treated twice at 150°C for 24 h. A scanning electron microscopy (SEM)

image of the resulting powder is shown in **Fig. 1**, from which the particle size of the hydrothermally treated powder can be seen to be 2–3 μm. Hereafter, we refer to this resulting powder as the post-treated glass powder. The SiO₂ powder or post-treated glass powder was mixed with CaCO₃ and milled (the mixing ratio is described in the results section), and the mixture was heat-treated at 1450°C for 20 h.

The crystallographic structures of the powders were characterized using an X-ray diffractometer (XRD, Rigaku Miniflex) with Cu Kα radiation (30 kV, 15 mA). The microstructure of the powder was observed using SEM (JEOL JSM-6510). The elementary composition of the sample was evaluated using an X-ray fluorescence spectrometer (XRF, Rigaku ZSX PRIMUS).

Commercial CaCO₃ and SiO₂ powders were mixed in a molar ratio of 3:1 and the mixture was heat-treated at 1450°C for 20 h. **Figure 2** depicts the XRD pattern of the resulting powder, from which the powder can be assigned as Ca₃SiO₅ (C3S; JCPDS: 3-0301). The C3S production reaction did not proceed at heat-treatment temperatures of less than 1450°C and heat-treatment times of 20 h, so we employed C3S production reaction conditions of 1450°C for 20 h.

CaCO₃ powder and post-treated glass powder were mixed and milled in the weight ratio of 3:1, and the mixture was heat-treated at 1450°C for 20 h. **Figure 3** illustrates the XRD pattern of the resulting powder. The sample exhibits a main phase comprising C3S with small amounts of Ca₃Al₂O₆ (C3A; JCPDS: 33-0251), where C3A is also one of the Portland cement compositions. The silicate source of soda lime glass includes silicon and aluminum; thus, the C3S and C3A phases appeared in the resulting powder. Other phases were not observed.

In order to confirm the microstructure of the resulting powder, SEM observation was carried out. **Figure 4** presents the SEM image of the resulting powder. Most of the particles had a plate-like shape, and the particles are assumed to be C3S.¹⁰⁾ Bulk-like particles as a secondary phase were observed, and the particles are assumed to be C3A.¹¹⁾ These results agree well with the XRD results.

Elemental analysis was carried out for the resulting powder using the post-treated glass powder as a raw material, and the composition in terms of weight percent is shown in **Table 1**. The

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Table 1. Mass % of the composition of the JIS R5214-2009, the resulting powder and the representative commercial eco-cement (by Taiheiyo-cement)¹²⁾

	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	Cl ⁻	MgO	P ₂ O ₃	Na ₂ O (Alkali)	ig.loss
JIS	—	—	—	—	≤4.5	≤0.1	≤5.0	—	≤0.75	≤5.0
Powder	73.52	22.36	3.32	0.17	0.01	—	0.54	0.01	0.03	0.04
Commercial	—	—	—	—	3.56	0.032	1.82	—	0.50	1.66

Fig. 1. SEM image of hydrothermally treated soda lime glass powder.

Fig. 2. XRD pattern of the powder resulting from heat treatment of CaCO₃ and SiO₂ in a molar ratio of 3:1 at 1450°C.

Fig. 3. XRD pattern of the powder resulting from heat treatment of CaCO₃ and post-treated glass powder in a weight ratio of 3:1 at 1450°C.

composition of eco-cement in the JIS standard⁸⁾ is also described in Table 1. The Na content of the resulting powder was 0.03 wt % because Na in the post-treated glass was removed from the soda lime glass (source) by the hydrothermal treatment.⁹⁾ The TiO₂ content of the powder in the present study was less than 0.04%, and this result is assumed to be attributable to the fact that TiO₂ was barely present in the raw soda lime glass. From Table 1, all

Fig. 4. SEM image of the powder resulting from heat treatment of CaCO₃ and post-treated glass powder in a weight ratio of 3:1 at 1450°C.

of the minor components were less than the JIS standard values for eco-cement;⁸⁾ thus, the recycled cement was confirmed to be successfully synthesized using a soda lime glass source. Hardening tests of the resulting cement have not yet been performed and need to be carried out in the future.

In summary, we have successfully synthesized recycled cements C3S and C3A with few minor components using hydrothermally treated waste soda lime glass powder; thus, the hydrothermally treated soda lime glass is assumed to be suitable for synthesis of recycled cements.

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References

- 1) Recycle data book, Japan Environmental Management Association for Industry (2013) 16.
- 2) M. Terro, *Build. Environ.*, **41**, 633–639 (2006).
- 3) N. Schwarz, H. Cam and N. Neithalath, *Cement Concr. Compos.*, **30**, 486–496 (2008).
- 4) R. Idir, M. Cyr and A. T-Hamou, *Cement Concr. Compos.*, **33**, 19–29 (2011).
- 5) S. Sano, M. Ichikawa, T. Tamashige, T. Matsuto and N. Tanaka, *J. Jpn. Soc. Mater. Cycles Waste Manage.*, **13**, 131–140 (2002).
- 6) K. Sudo, H. Harada and T. Takahashi, *Ceramics*, **34**, 349–353 (1999).
- 7) Y. Masuda, T. Tochigi and Y. Nagashio, *Concr. J.*, **46**, 3–9 (2008).
- 8) JIS R5214:2009.
- 9) S. Yoshida, H. Miyazaki, S. Sugahara, Y. Seike, H. Suzuki and T. Ota, *J. Jpn. Soc. Mater. Cycles Waste Manage.*, **25**, 84–88 (2015).
- 10) K. Sekino, *Inorg. Mater.*, **4**, 483–490 (1997).
- 11) E. Sakai, K. Raina, K. Asaga, S. Goto and R. Kondo, *Cem. Concr. Res.*, **10**, 311–319 (1980).
- 12) http://www.taiheiyo-cement.co.jp/service_product/cement/pdf/ecocement_v3.pdf, Taiheiyo-cement pamphlet (2011).