Studies of milling technology's approaches for establishing the chemical recycles on some wasted glasses.

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1. The Objects and Targets of This study.

**Objects of this study**
- To explore the possibilities of **chemical recycle** technology
- Material science approaches for environmental cleanup

**Targets of development**
- With **wasted glass materials**
- Silicate devices for environment cleanup
- In-line measurement system development
2. Some directions for wasted glass chemical recycle applications

① **Silicate resources for minerals and ceramics synthesis**

- IREP the first Meeting in Imabari, 2013
- M. Kamitani, A. Nakahira, T. Wakihara et al. ISAC-5, Wuhan, China 2014


② **Ion exchanging devices for environmental cleanup**

- 2nd meeting on Environmental radioactive decontamination technology, Tokyo 2013
- M. Kamitani, A. Nakahira, T. Wakihara et al. ISAC-5, Wuhan, China 2014

③ **The dehydration condensation for like cement**


Synthesized LTA in Bamboo inside pore

Condensed mass from LCDG
3. Fundamental procedure of chemically activation for wasted glass by Ball milling

Energy consumption of milling with ball media

Fracture mode of glass grain by impact

ref. Rumpf, HStruktur der Zerkleinerungswissenschaft Aufbereitungs-Technik No. 8/1966 421-435

Fig. 1 model of generating forces in ball mill

Fig. 2 fracture model from reference
Optimization of ball milling condition by DEM simulation

![Diagram of ball milling process](image)

- **Normal force**
- **Shear force**

Fig. 3 DEM simulation based on Voigt model

### Energy Equation

\[ E_w = \sum_{j=1}^{n} \frac{1}{2W} m v_j^2 \]

- **m**: Ball weight
- **v**: Impact speed
- **W**: Specimen weight
- **n**: Number of impact
Energy consumption

Ball: $\varnothing = 10\text{-}30\text{mm}$ steal
Mill dimension

$L = 725\text{mm}$

$d = 725\text{mm}$

Ball: $\varnothing = 10\text{-}30\text{mm}$ steal

$d_B = 10\text{ mm}$

$d_B = 15\text{ mm}$

$d_B = 30\text{ mm}$

Fig. 4 Impact energy estimation by DEM simulation.

This point
4. Experiment and Results

① Milling test plan

<table>
<thead>
<tr>
<th>No.</th>
<th>Glass species</th>
<th>Glass weight (kg)</th>
<th>Ball milling condition</th>
<th>sampling (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>①</td>
<td>LCDG 1)</td>
<td>32</td>
<td>0.95 15 50</td>
<td>○ ○ ○ ○ ○ ○ ♦</td>
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<tr>
<td>②</td>
<td>LCDG</td>
<td>24</td>
<td>0.95 15 50</td>
<td>— — ○ ○ ○ — —</td>
</tr>
<tr>
<td>③</td>
<td>LCDG</td>
<td>32</td>
<td>0.85 15 50</td>
<td>— — ○ ○ ○ — —</td>
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<tr>
<td>⑥</td>
<td>SLG 2)</td>
<td>12</td>
<td>0.75 15 Al₂O₃ 50</td>
<td>— ○ ○ ○ ○ ○ ○</td>
</tr>
<tr>
<td>④</td>
<td>SLG</td>
<td>30</td>
<td>0.95 20 50</td>
<td>○ ○ ○ ○ ○ ○ ○</td>
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<tr>
<td>⑤</td>
<td>SLG</td>
<td>30</td>
<td>0.95 15 50</td>
<td>○ ○ ○ ○ ○ ○ ○</td>
</tr>
</tbody>
</table>

Table.1 Test plan

① milling test plan:
- Ball: φ = 15mm steal
- Mill dimension: L=725mm, diameter=725mm
- Ball filling ratio=0.5
- Raw material: 24-32 Kg

② Glass weight (kg)

③ Test ⑥ is another experiment for in-line measuring system development.

1) ①②③: LCDG alumino-silicate glass: \( \text{SiO}_2 / \text{Al}_2\text{O}_3 / \text{CaO} / \text{Na}_2\text{O} = 58.8 / 17.1 / 9.5 / 0.3 \) (wt% ratio)

2) ④⑤: Soda-Lime Glass: \( \text{SiO}_2 / \text{CaO} / \text{Na}_2\text{O} = 73 / 5 / 17 \) (wt% ratio)

3) Milling by small 50L mill on another glass: \( \text{SiO}_2 / \text{Al}_2\text{O}_3 / \text{MgO} / \text{Na}_2\text{O} = 60.2 / 15.2 / 7.2 / 16.8 \) (wt%)
Grain size distribution change

Fig. 5  Grain size distribution of test2 and test5 by Laser diffraction MT-3000 II
③ Morphology on SEM’s images

Fig. 8  SEM’s images of T-2 and T-5 samples that 6 hr milled.
Fig. 9  BET specific surface area of T-2 and T-5 measured by Bellsorp mini II.
XAFS analysis  Si-K

Fig. 10  XAFS profiles of T-2 and T-5

The monochromator serves soft X-rays in the energy region from 585 to 4000 eV.
KTP (KTiOPO4)

Thanks UVSOR
Titration for surface analysis

Fig. 11  Titration curves of T-2 and T-5 samples.

Solid concentration is 10%  1N-NaOH used
Measured by DT-1200
5. For **Silica resource**

**Fig.12** SEM’s images of autoclaved grains

Test2-6hr-milling reacted in S-solution for 3-12hr at 95°C
Fig. 13  XRD profiles of autoclaved sample
6. For Ion exchange device

① aqueous washing treatment

![Figure 14: BJH profiles of T-5-6hr milling samples that washed by pure water.]

Fig. 14  BJH profiles of T-5-6hr milling samples that washed by pure water.

- Washed by water
  - BET = 9.6 m²/g
- T-2 6hr milled
  - BET = 2.8 m²/g
② Decommissioning of radioactive materials; $^{137}\text{Cs}$

Testing solution

Wash out solution from sewage ashes in Fukushima pref.

$^{134}\text{Cs}: 213\pm7.5$ (Bq/kg)
$^{137}\text{Cs}: 383\pm14$ (Bq/kg)

Ge detector model GC-3020, Canberra

Concentrate to around $^{137}\text{Cs}: 1200$ Bq/kg

Fig.15 photos and schematic view of radioactive Cs removing test.
<table>
<thead>
<tr>
<th>material</th>
<th>w/s</th>
<th>shaking time (min)</th>
<th>$^{137}\text{Cs}$ initial (Bq/kg)</th>
<th>$^{137}\text{Cs}$ remain (Bq/Kg)</th>
<th>removing (%)</th>
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<tbody>
<tr>
<td>washed milling Glass powder T-2-6hr&amp;washed</td>
<td>10</td>
<td>10</td>
<td>1262</td>
<td>902</td>
<td>18.9</td>
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<tr>
<td>fine Mordenite</td>
<td>10</td>
<td>10</td>
<td></td>
<td>382.9</td>
<td>69.6</td>
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<tr>
<td>coarse Mordenite</td>
<td>10</td>
<td>10</td>
<td></td>
<td>786</td>
<td>37.7</td>
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<tr>
<td>A-type Zeolite</td>
<td>10</td>
<td></td>
<td></td>
<td>1219</td>
<td>3.3</td>
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</table>

Table 3 Test result of removing $^{137}\text{Cs}$
7. For Dehydration Condensation

① Hardening procedure

6hr milled LCD glass (30g)

Mixing

Casting

RT one night

Hardened sample
Fig.16  SEM’s images of hardens samples
④ Chemical bonding

Fig. 18 FT-IR spectrums of samples
8. Inline measuring for ball milling

① The model of glass milling from T-⑥
Specific surface area measurement by NMR

- A short RF Pulse B1
  Rotates H atoms

- When B1 disappears, H atoms realign with Bo producing a signal

\[
R_{av} = \psi_p SL \rho_p (R_s - R_b) + R_b
\]

\[
R_{av} = K_A S \psi_p + R_b
\]

\[
R_{av} \text{: reciprocal of sample relaxation time}
\]

\[
\psi_p \text{: volume fraction of particles}
\]

\[
S \text{: surface area}
\]

\[
R_s \text{: reciprocal of adsorption relax.time}
\]

\[
R_b \text{: reciprocal of solvent}
\]

\[
K_A \text{: coefficient of wettability}
\]

\[
R_{sp} = \frac{R_{av} - R_b}{R_b}
\]

Pulse NMR

**T2 mode:** Spin-Spin relaxation
③ Comparison with BET and $R_{2sp}$

Fig. 20: The relaxation time curves on T-6

Fig. 21: Comparison with calculated surface area and BET
9. Summary of this presentation

1) We’ve confirmed structural changes of wasted glass materials by ball milling.

2) By ball milling, the higher impact energy makes disorder on grain surface or inner structure. We consider they play as dissolving points, and/or to be meso scale cavities on grain surface. It is very important knowledge for the chemical recycling technology.

3) We’ve recognized these phenomenon induced by “Mechanochemical effect”

4) We would develop the operating methods for environmental cleanup with these devices

5) We’ve already developed the optimized milling systems on inline surface area measuring that mainly consists with P-NMR.