Eco-Design of CaO-Al2O3 (Fe2O3)-SiO2 System

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Abstract: The main chemical components of various industrial wastes are consisted of CaO, Al2O3, Fe2O3 and SiO2, and they have different chemical characters, i.e. acidic and cation exchange properties in SiO2, basic and anion exchange properties in CaO and amphoteric properties in Al2O3 and Fe2O3. It is, therefore, interesting to develop some functionalities utilizing and combining these different chemical characters and adjusting the chemical compositions and controlling of the structural and textural states of those wastes by mixing and/or some special treatments. We therefore synthesized some materials from those wastes with respective to the whole framework of eco-design of CaO-Al2O3(Fe2O3)-SiO2 systems; (1) glass ceramics prepared from mixtures of Kira, silica-rich byproducts from beneficiation processes of silica sand and plastic clay, and paper sludge ash (PSA), byproducts generated from paper making industry, (2) simultaneous sorbent materials of amorphous CaO-Al2O3-SiO2 (CAS) and CaO-Fe2O3-SiO2 (CFS) compounds from PSA, coal fly ash and/or steel making slag.

Keywords: Eco-Design, CaO-Al2O3(Fe2O3)-SiO2 System, Glass-Ceramics, Simultaneous Sorbents

1. INTRODUCTION

Many trials have been performed to process reduce, re-use and recycle of various wastes such as municipal waste incinerated ash, sewage sludge ash, coal fly ash (CFA), blast furnace slag, steel making slag (SMS), agricultural waste ashes, paper sludge ash, etc. generated from our industrial and social activities. Although some useful materials of zeolites [1], glass-ceramics [2,3], activated carbon [4,5], Ni steam reforming catalyst [6] have been prepared using these wastes, most of the actual re-usages are limited to raw materials for cement production and building materials. We, therefore, still need to develop another effective ways to further progress such activities to sustain our human life style.

Considering various industrial wastes, their main chemical components are consisted of CaO, Al2O3, Fe2O3 and SiO2. These components have different chemical characters, i.e. acidic and cation exchange properties in SiO2, basic and anion exchange properties in CaO and amphoteric properties in Al2O3 and Fe2O3. It is, therefore, interesting to develop some functionalities utilizing and combining these different chemical characters and adjusting the chemical compositions and controlling of the structural and textural states of those wastes by mixing and/or some special treatments.

On this background, we think that it is important to design total framework of eco-cycle and eco-system for these industrial wastes. Our considering whole framework of eco-system is schematically shown in Fig. 1. In this paper, we will report two examples of our synthesized materials from those wastes of CaO-Al2O3(Fe2O3)-SiO2 systems. They are; (1) glass ceramics prepared from mixtures of Kira, silica-rich byproducts from beneficiation processes of silica sand and plastic clay, and paper sludge ash (PSA), byproducts generated from paper making industry and (2) simultaneous sorbent materials of amorphous CaO-Al2O3-SiO2 (CAS) and CaO-Fe2O3-SiO2 (CFS) compounds from PSA, coal fly ash and/or steel making slag (SMS).

2. EXPERIMENTAL

2.1. Glass-ceramics

The starting materials were wastes of Kira (Maruishi Materials), PS and PSA (Fuji Paper Making Union), sludge generated during the purification of drinking water (WPS; Asaka Plant, Tokyo) and glass cullet (WG; Toyo Glass), and additives of CaCO3 (Wako Chemical) and dolomite (CaMg(CO3)2; Kasuga, Gifu). Their chemical compositions are shown in Fig. 2. Their dried powder mixtures were melted at 1300-1500°C for 2 h and water-quenched to obtain granular glass. The resulting granular glasses were ball milled and sieved to <100 mesh. Pellets and testpieces were formed by uniaxial press and fired at 700-1300°C for 1 h to obtain glass-ceramics.

The chemical compositions of the samples were determined by X-ray fluorescence (XRF; RIX2000, Rigaku). XRD measurements were performed using monochromated Cu Kα radiation (XRD-6100, Shimadzu) to identify the crystalline phases. The glass transition tempera-
ture and crystallization temperatures were determined by DTA (Thermoplus, Rigaku). The linear thermal expansion coefficients of the samples were measured using a dilatometer (TMA8310, Rigaku) at 25-600°C. The apparent densities were measured by the Archimedes method using water.

The four-point bending strengths were measured on unpolished testpieces using a universal testing machine (DCS-R-10TS, Shimadzu) at a cross-head speed of 0.5 mm/min. The microhardness was measured using a Vickers tester (MHT2, Matsuzawa) on polished samples with an indentation of 9.8 N for 15 s. The chemical resistance was examined in 1 mass% HCl solutions at 90°C for 24 h. The chemical durability was determined as the weight difference before and after the chemical leaching.

2.2. Simultaneous sorbent materials

The starting materials were PS, SMS (Oita, Nippon Steel), Ca(NO₃)₂·4H₂O, Al(NO₃)₃·9H₂O, Fe(NO₃)₃·9H₂O, Si(OCH₃)₄ (Wako Chemicals) and SiO₂ gel (Toso). The synthetic samples were prepared by coprecipitation method [7] and ball milling method [8] were fired at 500-1000°C in air and N₂ flow conditions. The chemical compositions of the samples were shown in Fig. 2.

The chemical compositions of the samples were determined by XRF (RIX2000, Rigaku). XRD measurements were performed using monochromated Cu Kα radiation (XRD-6100, Shimadzu) to identify the crystalline phases.

![Fig. 2 Chemical compositions of wastes and resulting materials prepared from the wastes.](image)

The N₂ adsorption-desorption isotherms of the samples were measured using an automatic gas adsorption instrument (Autosorb-1, Quanta Chrome) and the specific surface area was calculated by the BET method. The magnetic properties of selected samples were measured using a vibration sample magnetometer (BHV-50H, Riken Electronics).

The simultaneous uptake of Ni²⁺ and NH₄⁺ was monitored using a batch method with sample/solution ratio of 0.1 g/50 ml reacted at room temperature for 24 h. The concentrations of Ni²⁺ and phosphate were analyzed by ICP-OES (Prodigy, Leeman Labs.) while those of NH₄⁺ were by an ion chromatography (IA-200, TOA-DKK). The uptake ability was calculated from the difference of the concentrations before and after the experiments. For selected samples, saturated sorption capacity (Qₒ) was calculated based on the sorption isotherms using Langmuir equation.

3. RESULTS AND DISCUSSION

3.1. Glass-ceramics

The chemical compositions of wastes and glass-ceramics are plotted in three components diagram (Fig. 2). Glass-ceramics of CC, CM and PS samples were prepared from Kiras mixing with CaCO₃, dolomite and PSA, respectively, while that of WP was prepared by mixtures of WPS, WG and CaCO₃. By adjusting the compositions of those glass-ceramics, they can melt at 1300-1500°C. The raw materials, synthesized glass cullet, glass-ceramics heated at 1000°C and deformed glass-ceramics heated at ≥1200°C are shown in Fig. 3. The glass-ceramics of CC, CM1 and CM2 are shiny and white color but the color becomes darker in PS and further in WP due to increase of coloring components such as Fe₂O₃, TiO₂ and MnO.

Various properties of the glass-ceramics [7-11] are listed in Table 1 with comparison of commercial glass-ceramics (NEOPAIRES). The crystalline phases in those glass-ceramics depend on the compositions of glass, and wollastonite (CaSiO₃) and quartz solid solution in additives of CaO component in the CC, PS and WP samples while diopside (CaMgSi₂O₆) and anorthite (CaAl₂Si₂O₈) in those of CaO and MgO in the CM samples. All these glass-ceramics showed surface crystallization mechanism and not volume crystallization. The bending strengths range from 63 to 130 MPa and are higher than that of commercial glass-ceramics (50 MPa). They show a tendency to increase with increase of SiO₂ content. Addition of MgO component is especially effective to enhance the strength by crystallization of diopside instead of wollastonite. The Vickers microhardness values range from 5.2 to 7.6 GPa. These values are higher than that of commercial glass-ceramics and addition of MgO component is also very effective. The thermal expansion coefficients of the glass-ceramics range from 4.7×10⁻⁶ to 7.2×10⁻⁶/K and are similar level with the commercial glass-ceramics. Those of PS samples show a
Table 1. Various properties of glass-ceramics prepared from wastes

<table>
<thead>
<tr>
<th>Properties</th>
<th>CC</th>
<th>CM1</th>
<th>CM2</th>
<th>PS</th>
<th>WP</th>
<th>NEOPAIRES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting temp. [°C]</td>
<td>1400</td>
<td>1350</td>
<td>1350</td>
<td>1400</td>
<td>1300</td>
<td>–</td>
</tr>
<tr>
<td>Crystalline phase</td>
<td>wollastonite</td>
<td>diopside</td>
<td>anorthite</td>
<td>quartz(SS)</td>
<td>wollastonite</td>
<td>wollastonite</td>
</tr>
<tr>
<td>Density [g/cm³]</td>
<td>2.56</td>
<td>–</td>
<td>–</td>
<td>2.46-2.50</td>
<td>2.81</td>
<td>2.7</td>
</tr>
<tr>
<td>Bending strength [MPa]</td>
<td>81(8)*</td>
<td>130(14)</td>
<td>73(14)</td>
<td>63(5)-66(3)</td>
<td>99(13)</td>
<td>50</td>
</tr>
<tr>
<td>Vickers hardness [GPa]</td>
<td>6.6(3)</td>
<td>7.4(8)</td>
<td>7.6(5)</td>
<td>6.0(1)-6.4(3)</td>
<td>5.2(7)</td>
<td>5.2</td>
</tr>
<tr>
<td>Thermal expansion coefficient [×10⁻⁶/K]</td>
<td>5.2</td>
<td>6.7</td>
<td>4.7</td>
<td>6.3-8.1</td>
<td>7.2</td>
<td>6.1</td>
</tr>
<tr>
<td>Acid weight loss [mg/cm²]</td>
<td>0.31(2)</td>
<td>0.4</td>
<td>1.3</td>
<td>4.7(4)-8.4(2)</td>
<td>17.7(13)</td>
<td>3.4</td>
</tr>
<tr>
<td>Alkali weight loss [mg/cm²]</td>
<td>1.60(3)</td>
<td>2.3</td>
<td>1.4</td>
<td>0.71(2)-0.85(4)</td>
<td>0.23(5)</td>
<td>1.3</td>
</tr>
</tbody>
</table>

*: The numbers in parentheses represent the standard deviation in the last decimal place.

non-linearity owing to the phase transition of quartz and cristobalite. The weight loss values of the glass-ceramics after leaching in acid and alkali solutions are 0.31-17.7 and 0.23-1.60 mg/cm², respectively. The leaching rates calculated from these data are 0.35-20.2×10⁻⁸ and 0.26-1.82×10⁻⁸ g/cm² s⁻¹, respectively. The chemical durability of the glass-ceramics to acid and alkali is found to be a trade-off relationship and higher durability for acid solution with increasing glass former components of SiO₂ and Al₂O₃ while higher durability for alkali solution with increasing glass modifier components of CaO, MgO and Na₂O.

The WP glass-ceramics was also prepared by heating under an atmosphere flowing N₂. The resulting samples heated at 1000°C showed a light body and thinner color compared with those heated in air. This is due to the partial reducing of Fe ion from Fe³⁺ to Fe²⁺ and generation of O₂ gas by the reaction: 2Fe₂O₃→4FeO+O₂. Such a different taste of glass-ceramics are interesting to expand the application field to artistic field.

In conclusion, glass-ceramics with preferable properties and variety of appearances are able to be prepared from various wastes as the main starting materials and are considered to be one of the useful ways for re-usage of various wastes.

3.2. Simultaneous sorbent materials of CAS and CFS

The chemical compositions of synthesized CAS [12] and CFS [13] samples and SMS [14] are plotted in Fig. 1. The samples with these composition ranges are X-ray amorphous but the samples with higher contents of (CaO+MgO+Na₂O+K₂O) than the above composition ranges include crystalline phases in the as-prepared state. The CAS samples keep high specific surface area (S_BET) >100 m²/g and X-ray amorphous state even heated up to 800°C while the CFS samples show much lower S_BET values and crystallized from lower temperatures. Since the SMS contains higher content of Fe₂O₃ than Al₂O₃, this shows closer characteristics of CFS than CAS. It devitri-fies only by grinding treatment, thus, the glassy phase is very unstable.

All the sorption isotherms of the CAS and CFS samples for Ni²⁺, NH₄⁺ and PO₄³⁻ were better fitted by the Langmuir equation than the Freundlich equation. Therefore, the saturated sorption capacity (Q₀, mmol/g) was calculated based on the Langmuir equation. The Q₀ values of the CAS and CFS samples heated at 600°C for each adsorbate are shown in Fig. 4. It is clear that both CAS and CFS samples have an ability to sorb cations and anion simultaneously. As a general tendency, the resulting Q₀ values are higher for Ni²⁺ and PO₄³⁻ but lower for NH₄⁺. They are also higher in the CFS samples than the CAS samples. As a result of examination of the tendency between Q₀ values and chemical compositions, A certain tendency was observed for (CaO+Al₂O₃) content in the CAS while CaO content in the CFS samples as shown in Fig. 5. From the previous results [12-14], the uptake mechanisms for these ions are considered to be as fol-
lows; (1) ion substitution (ligand change) by selective dissolution of CaO from the samples and uptake of cations for the charge balance, (2) precipitation of Ca-phosphate phases from dissolved CaO and PO₄³⁻ in the solution due to its low solubility, (3) sorption of PO₄³⁻ to Al-OH or Fe-OH groups and that of NH₄⁺ to Si-OH groups on the surfaces of the samples. In the case of CAS, Al₂O₃ are thought to have a high sorption ability and/or dissolution precipitation reaction to uptake the adsorbates of Ni²⁺ and PO₄³⁻. On the other hand, the uptake of those ions shows a good correlation with CaO content in the CFS samples, thus, the other components are relatively inert to the uptake reaction. The low Q₀ values for NH₄⁺ in the CAS and CFS samples are attributed to the low solubility products of NH₄OH than Ni(OH)₂ and H₂O. Considering the balance of uptake ability of the CAS and CFS samples for three ions, the composition ranges of Ca=20-40, Al=40-70 and Si=10-30 atm% in the CAS and Ca=25-40, Fe=15-30 and Si=30-60 atm% in the CFS are preferable composition as simultaneous sorbent materials. Such composition ranges can be arranged by mixing of wastes such as SMS, CFA, PSA, Kira and Al dust.

The following differences are considered for the CFS compared with the CAS samples; (1) higher uptake ability for arsenate and arsenite ions, (2) higher durability for acid solution, (3) utilization of magnetization power for the separation of adsorbents from the solution by magnet, and so on. We have an interest to the magnetization power. The CFS sample with composition of Ca:Fe:Si=34:9:32:6:32.5 (ca. 1:1:1) was heated at 600-900°C in an atmosphere with flowing N₂ (N₂-sample). Although little differences are observed in the XRD patterns of these N₂-samples compared with those heated in air (Air-samples), the color became darker in the N₂-samples. This may indicate formation of maghemite (γ-Fe₂O₃), magnetite (Fe₃O₄) and/or their intermediate phase as well as hematite (α-Fe₂O₃) in the N₂-samples while only hematite in the Air-samples. Since maghemite and magnetite have ferri-magnetic property to show magnetization power but hematite has antiferromagnetic property, these magnetic phases can be confirmed from VSM measurement. The VSM curves of the N₂-samples show hysteresis loop similar to maghemite and magnetite but those of the Air-samples show no hysteresis similar to hematite. This is also confirmed by a magnet. The Q₀ values of the N₂- and Air-samples heated at 600°C and 900°C for Ni²⁺, PO₄³⁻ and NH₄⁺ are listed in Table 2. In the 600°C, the Q₀ values of the N₂-sample are clearly higher than the Air-sample. This tendency becomes more evident in the 900°C samples and more than doubly higher than the Air-sample. Since the S_{BET} values of these samples are similar at same heating temperatures, such clear differences in Q₀ values are interesting but the reason is uncertain in the present. The N₂-samples are, therefore, very effective as simultaneous sorbent materials because of their higher Q₀ values and also easy separation of sorbent from the solution using a magnet.

### 4. SUMMARY

Eco-systems for reuse of various wastes consisted of CaO-Al₂O₃-Fe₂O₃-SiO₂ components such as paper sludge, steel making slag, coal fly ash, Kira, etc are proposed to effectively prepare some functional materials using these wastes as the major starting materials. In this paper, two examples of glass-ceramics and simultaneous sorbent materials prepared from wastes are introduced. The results are summarized as follows:

1. Glass-ceramics with variety of colors are able to prepare from wastes as the major starting materials and they show very good mechanical, thermal and chemical properties important to the application as building materials.
2. Simultaneous sorbent materials of amorphous CaO-Al₂O₃-SiO₂ (CAS) and CaO-Fe₂O₃-SiO₂ (CFS) are synthesized by coprecipitation and ball milling methods. The both samples show excellent sorption capacity for Ni²⁺ and PO₄³⁻ but fair capacity for NH₄⁺. The capacities show increase with increasing of (CaO+Al₂O₃) content in the CAS while CaO content in the CFS. The CFS samples heated in flowing N₂ shows enhancement of sorption capacities compared with those in air. These samples have also an advantage in separation of sorbent from the solution using a magnet.

### ACKNOWLEDGMENTS

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### REFERENCES

5. K. Okada, N. Yamamoto, Y. Kameshima and A. Yasumori, J.