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Water cleaning ability and local structure of iron-containing soda-lime silicate glass

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Abstract A relationship between waste-water cleaning ability and local structure of iron-containing soda-lime silicate glass, $15Na_2O{\cdot}15CaO{\cdot}xFe_2O_3{\cdot}(70\text{-}x)SiO_2$ (x = 10–50 in mass%), abbreviated as NCFSx glass, was investigated by means of ^{57}Fe-Mössbauer spectroscopy, redox titration with $KMnO_4$ for the determination of chemical oxygen demand (COD) and inductively coupled plasma optical emission spectroscopy (ICP-OES). Mössbauer spectra of NCFSx glass with "x" of 10 and 30 were composed of two doublets: one due to $Fe^{III}O_4$ tetrahedra (T_d) with isomer shift (δ) of 0.23–0.26 mm s^{-1} and quadrupole splitting (Δ) 1.01–1.04 mm s^{-1}, and the other due to $Fe^{II}O_6$ octahedra (O_h) with δ of 1.00–1.03 mm s^{-1} and Δ of 2.03–2.05 mm s^{-1}. Absorption area for $Fe^{II}(T_d)$ was decreased from 9.7 to 6.5 and 0.0 % when "x" was increased from 10 to 30 and 50. A leaching test performed with 500 mL of artificial waste water and 2.0 g of NCFS50 revealed waste-water cleaning ability of soda-lime glass, e.g., COD was reduced from 280 to 55.2 mg L^{-1} after 10 day-leaching. After 10 day-leaching, it proved that iron was dissolved into waste water to a level of $5.3_7 \times 10^{-1}$ mg L^{-1}. These results prove that organic matter could be effectively decomposed with iron-containing soda-lime silicate glass.

Keywords Iron containing soda-lime silicate glass · ^{57}Fe-Mössbauer spectroscopy · Chemical oxygen demand (COD) · Inductively coupled plasma optical emission spectroscopy (ICP-OES)

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1 Introduction

A huge amount of garbage is being discharged in the environment in both developing and industrial countries. OECD reported that the annual total amount of municipal waste discarded from the OECD affiliated countries was calculated to be 622Mt, corresponding to 580 kg/person [1]. Recycling or reusing waste materials is strongly required. Kubuki et al. reported that iron silicate glass prepared by recycling the ash discharged from municipal garbage combustion plant was effective to reduce the chemical oxygen demand (COD) of artificial waste water [2, 3]. Recently, it proved that organic matter was effectively decomposed with $0.5x(Na_2O{\cdot}CaO){\cdot}5Fe_2O_3{\cdot}(95\text{-}x)SiO_2$ glass with "x" of 20–40 [4]. In order to elucidate the relationship between waste-water cleaning ability and iron content, iron-containing soda-lime silicate glass, $15Na_2O{\cdot}15CaO{\cdot}xFe_2O_3{\cdot}(70\text{-}x)SiO_2 (x = 10–50)$ was investigated by means of COD measurement, inductively coupled plasma optical emission spectroscopy (ICP-OES) and ^{57}Fe-Mössbauer spectroscopy.

2 Experimental

Soda-lime silicate glass, $15Na_2O{\cdot}15CaO{\cdot}xFe_2O_3{\cdot}(70\text{-}x)SiO_2 (x = 10–50$ in mass%), abbreviated as NCFSx, was prepared by a conventional melt-quenching method. A mixture of reagent grade Na_2CO_3, $CaCO_3$, Fe_2O_3 and SiO_2 placed in a platinum crucible was melted at 1400 °C for 1 h. A dark brown glass sample was obtained by dipping the bottom of the crucible into ice-cold water. Two grams of well pulverized samples with a particle size less than 75 μm were soaked for 10 days in 500 mL of artificial waste water of which the original COD value was about 300 mg L^{-1}. COD was determined with $KMnO_4$ according to 'JIS-K010217'. Dissolved cations, Na^+, Ca^{2+}, Fe^{II} plus Fe^{III} and Si^{IV}, were measured by ICP-OES. Mössbauer spectra were recorded by a constant acceleration method with a source of ^{57}Co(Rh) at room temperature. Isomer shift (δ) values were obtained with respect to α-Fe.

3 Results and discussion

Mössbauer spectra of NCFSx glass with "x" of 10, 30 and 50 measured before leaching test are shown in Fig. 1. Mössbauer spectra are analyzed into one intense paramagnetic doublet due to tetrahedral Fe^{III} and a weak doublet due to octahedral Fe^{II} with δ values of 0.23–0.26 and 1.00–1.03 mm s^{-1}, respectively. These values indicate that most iron atoms are present as tetrahedral Fe^{III} playing a role of network former (NWF), with a small amount of octahedral Fe^{II} as network modifier (NWM) [5, 6]. Quadrupole splitting (Δ) values for tetrahedral Fe^{III} and octahedral Fe^{II} were estimated to be 1.01–1.04 and 2.03–2.05 mm s^{-1}, respectively. It is noted that relative absorption area for octahedral Fe^{II} was decreased from 9.7 to, 6.5 and 0.0 % with an increasing value of "x". This can be explained by the increasing role of tetrahedral Fe^{III} as NWF, since substitution of Fe_2O_3 for SiO_2 results in a decreased fraction of NWF; SiO_2 is a typical NWF oxide, while Fe_2O_3 is an 'intermediate' oxide which can change its structural role, depending on the glass composition [5, 6]. Identical Mössbauer parameters were obtained for tetrahedral

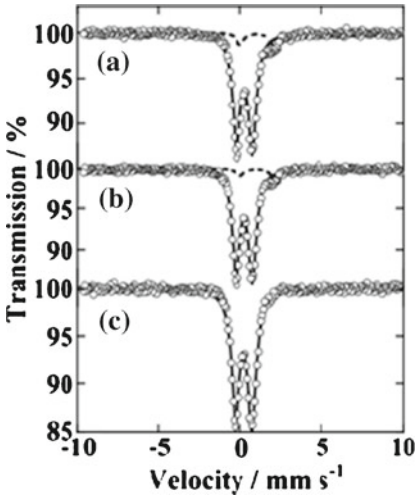

Fig. 1 Mössbauer spectra of NCFS*x* glass with "*x*" of **a** 10, **b** 30 and **c** 50

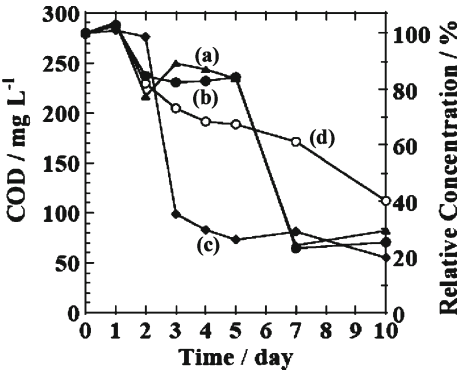

Fig. 2 Decrease in chemical oxygen demand (COD) after leaching test performed with artificial waste water and NCFS*x* glass with "*x*" of **a** 10, **b** 30, **c** 50, and **d** without the glass sample

Fe^{III} after leaching test with artificial waste water, suggesting that 3D-glass network structure was scarcely affected by the leaching.

In Fig. 2, COD values are plotted against the time of leaching conducted with 500 mL of artificial waste water and 2.0 g of NCFS*x* glasses. COD was reduced from 280 to 55.2 mg L^{-1} when the artificial waste water was mixed with NCFS*x* glass ($x = 50$) for 10 days, as shown in Fig. 2c. First-order rate constant (k) for COD decomposition can be estimated by

$$C_t = C_0 \exp(-kt), \tag{1}$$

where C_0 and C_t are COD values before and after t-day leaching. Figure 2c yielded k of $4.7_0 \times 10^{-1}$ day^{-1} for NCFS50 glass. Smaller k values of $6.7_3 \times 10^{-2}$ and $3.8_6 \times 10^{-2}$ day^{-1} were obtained for NCFS*x* glass with "*x*" of 10 and 30, respectively. Experimental results given in Fig. 2 suggest that water-cleaning ability or COD reducing ability is correlated with Fe_2O_3 content.

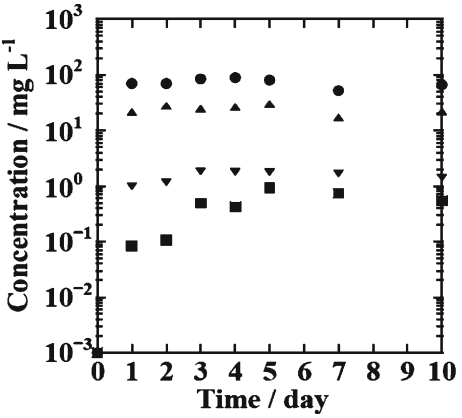

Fig. 3 Dissolved amount of (•) Na^{+}, (▲) Ca^{2+}, (▼) Si^{IV} and (■) total iron ($Fe^{II} + Fe^{III}$) after waste-water leaching test with NCFS*x* glass with "*x*" of 50

In Fig. 3 is plotted dissolved amounts of cations obtained during the leaching experiment with NCFS*x* glass ($x = 50$). A gradual increase in the concentration of iron was observed from $8.2_4 \times 10^{-2}$ to $1.0_6 \times 10^{-1}$, $4.9_3 \times 10^{-1}$, $4.2_1 \times 10^{-1}$, $9.3_7 \times 10^{-1}$, $7.4_3 \times 10^{-1}$ and $5.3_7 \times 10^{-1}$ mg L^{-1} after leaching of 1, 2, 3, 4, 5, 7 and 10 days. In case the of NCFS*x* glass with "*x*" of 10 and 30, lower iron concentration of $4.3_4 \times 10^{-1}$ and $4.4_6 \times 10^{-1}$ mg L^{-1} was obtained after 10-day leaching test, indicating that dissolution of iron is related to Fe_2O_3 content. It is noteworthy that water cleaning ability evaluated with COD reduction rate, as illustrated in Fig. 2, is increased with Fe_2O_3 content of NCFS*x* glass. In a previous leaching test with $15Na_2O{\cdot}15CaO{\cdot}5Fe_2O_3{\cdot}65SiO_2$ glass [4], a smaller *k* value of $2.7_3 \times 10^{-1}$ day^{-1} was obtained together with a total iron ($Fe^{II} + Fe^{III}$) dissolution amounting to $5.4_6 \times 10^{-2}$ mg L^{-1} after 10 day-leaching. These experimental results indicate that dissolved iron atoms are closely related to the waste-water cleaning effect or COD reducing effect observed after leaching test with NCFS*x* glass.

4 Summary

Mössbauer spectra of $15Na_2O{\cdot}15CaO{\cdot}xFe_2O_3(70\text{-}x)SiO_2$ glass ($x = 10$–50), abbreviated as NCFS*x* glass, are composed of an intense quadrupole doublet due to tetrahedral Fe^{III} with δ value of 0.23–0.26 and Δ of 1.01–1.04 mm s^{-1}, in addition to weak octahedral Fe^{II} with δ of 1.00–1.03 and Δ of 2.03–2.05 mm s^{-1}. The absorption area (A) for octahedral Fe^{II} was decreased from 9.7 to 0.0 % with an increasing amount of "*x*" which was changed from 10 to 50. NCFS*x* glass with "*x*" of 50 showed a largest amount of total iron ($5.3_7 \times 10^{-1}$ mg L^{-1}) after 10 day-leaching, which was consistent with high waste-water cleaning effect evaluated from the decrease in COD from 280 to 55.2 mg L^{-1}. A first-order rate constant (k) of $4.7_0 \times 10^{-1}$ day^{-1} was obtained from the decreasing rate of COD. These results suggest that the decrease in COD is directly related to the dissolved amount of iron. It is expected that large amount of glass wastes should be recycled to iron-containing silicate glass so that they could be utilized for water cleaning.

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