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Properties of Layer Silicates Formed from $MgO–SiO_2–H_2O$ Mixtures at 25 °C

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Magnesium oxide is gaining an interest as an agent for stabilizing fluoride and some heavy metals in contaminated soils. When it is mixed with contaminated soils, it hydrates to form brucite into which fluoride and heavy metals are incorporated substituting hydroxyl and octahedral magnesium ions, respectively. There is a report that magnesium oxide reacts also with SiO_2 to form sepiolite, which may induce when inhaled by human. We aged mixtures of magnesium oxide–silica–water for up to 50 days and characterized the reaction product by X–ray diffraction, Fourier transform infrared spectroscopy and electron microscopy. The magnesium oxide and silica in the starting mixture disappeared rapidly in 5 days but a significant amount of brucite did not form. Instead, poorly crystalline layer silicate formed. The crystallinity did not improve to a noticeable extent in 50 days. The infrared spectra and morphology under electron microscope suggested that the formed silicate is poorly ordered smectite but not sepiolite.

INTRODUCTION

Magnesium oxide (MgO) reacts with water fairly rapidly at normal temperatures to form crystalline magnesium hydroxide, brucite. If fluoride ions (F^-) are present in a reaction milieu, they are incorporated in brucite lattices replacing hydroxyl ions (OH^-). In addition, divalent metal cations having relatively small ionic radius are also incorporated in place of Mg^{2+}. For these reasons, MgO is gaining increasing interest as a stabilizing agent for fluoride and toxic heavy metals in contaminated soil, particularly in Japan. Garcia *et al.* (2004) used low grade MgO to stabilize heavy metal cations in soils contaminated mainly with flue–dust of pyrite roasting and found that it is highly effective to reduce the solubility of Zn and Cu. They interpreted their experimental results in terms of low soluble hydroxide formation due to the alkalinity of MgO. It is highly probable that a part of Zn and Cu ions were incorporated in octahedral sites in brucite. Fukazawa *et al.* (2006) examined several commercial MgO–based stabilizing agents and reported that the incorporation of F^- into crystal lattice of brucite is the most important mechanism for stabilization of F^-. Shimomura and Higuchi (2006) injected a slurry of an MgO–based F^- adsorption agent and monitored the F^- concentration in a water taken from downstream wells for 400 days. They found that the F^- concentration significantly decreased after the injection practice.

Meanwhile, MgO is very reactive with silica and silicic acid. Trioctahedral layer silicates crystallize fairly rapidly from co–precipitated hydrated silica–magnesia gels at low temperatures (Henin, 1956). And, Temuujin *et al.* (1998) examined the $MgO–SiO_2$ reaction without adding water, which formed layer silicates at normal temperatures. Moreover, Hast (1956) found that sepiolite crystallized from mixtures of MgO, noncrystalline SiO_2 and water at 37 °C. Sepiolite is a fibrous trioctahedral 2:1 layer silicate. According to these findings, it is possible to yield sepiolite if large amounts of MgO are mixed with soils containing silica or silicious minerals. Mesothelioma–inducing activity of sepiolite has considered being much lower than that of asbestos (Hast, 1956). If sepiolite surely forms when MgO comes to contact with SiO_2, it would be better to refrain from using MgO in stabilization practices in view of increasing concern about methoselioma induced by fibrous minerals. However, it is not certain whether these reactions surely advance in normal temperatures in soils.

In the present study MgO was mixed with noncrystalline SiO_2 and water and aged at 25 °C for up to 50 days and analyzed for newly formed minerals during aging with combination of methods. The results showed that the reaction between MgO and SiO_2 was very rapid. The results of the mineralogical analyses suggested that the major reaction product was trioctahedral smectite but not sepiolite.

MATERIALS AND METHODS

Reagent grade MgO (Kanto Chemical Co.) and SiO_2 (Mallinckrodt Co., 100 mesh powder) were mixed at an MgO/SiO_2 molar ratio of 0.750 to prepare a stock $MgO–SiO_2$ mixture. The molar ratio of 0.750 came from that in sepiolite that has a structural formula of $Mg_3(Si_4O_{11})\cdot nH_2O$. From the stock mixture, 15.00 g portions were taken and mixed with 45.00 g of water in bags made of polyethylene–nylon laminated sheet. The bags were heat–sealed to prevent evaporation of water and aged in a room kept at 25 °C. After 0, 1, 5, 10, 30 and 50 days of aging, the aged samples were freeze–dried. The 0 day of aging means that the sample was freeze–dried

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just after mixing with water. It took about 1 hour to freeze samples in a freezer and 0 day does not literally mean that no reaction took place. MgO and SiO_2 were treated in the same manner as the references. The reaction temperature of 25 °C was chosen instead of that employed in the experiments of Hast (1956) because the soil temperature seldom rises above 30 °C.

The X–ray diffractograms (XRD) of the samples were recorded with Rigaku RINT 2000 V X–ray diffractometer operated at an accelerating voltage of 40 kV and a tube current of 20 mA. The freeze–dried samples were homogenized by soft grinding and packed in glass holders. The infrared (FTIR) spectra were recorded by diffuse reflectance method with Jasco FT/IR 4600–PLUS Fourier transform infrared spectrophotometer. The samples for IR spectroscopy were made by mixing 5 mg portions of the freeze–dried samples with 500 mg of KBr. For electron microscopy, a small portion of a sample before drying was suspended in deionized water and homogenized by ultrasonication. A drop of diluted suspension was placed on a plastic microgrid, air–dried and examined in a JEOL 100 CX electron microscope. The pH of the samples was determined by glass electrode on suspensions shaken for 6 hours at a sample : water ratio of 1 g : 10 mL.

RESULTS AND DISCUSSION

Fig. 1 shows the pH of the suspension of the $MgO–SiO_2$ mixtures reacted for 0 to 30 days in the air–tight plastic bags. The pH value just after mixing was 9.2. The pH rose to about 9.5 after 1 day of aging and gradually dropped to 8.3 after 30 days of aging. Since the bags are gas–tight (Wada and Ono, 2003), the observed decrease in pH is probably due to the advancement of $MgO–SiO_2$ reaction but not due to the absorption of atmospheric CO_2.

Fig. 2 shows the XRD patterns of SiO_2, MgO, their mixtures and the aged samples. The sample name is indicated on the right of each pattern. The pattern designated by 0 is the diffraction pattern formed by the sample just after mixing with water. Since it took approximately 1 hour to freeze completely in a freezer, hydration some $MgO–H_2O$ and $MgO–SiO_2–H_2O$ reactions might have been taken place as indicated by the faint peaks at 0.477 and 0.237 nm. The numbers indicated at the vertical lines are d–spacings of the corresponding diffraction peaks. The SiO_2 used showed a single broad peak centered at about 0.392 nm, which is characteristic to noncrystalline silica. The MgO showed two characteristic peaks at 0.243 and 0.211 nm and the admixture of SiO_2 and MgO exhibited the characters of the both. Just after mixing the admixture of SiO_2 and MgO with water, the peaks from MgO greatly reduced and, instead, two new peaks at 0.477 and 0.237 nm appeared. These are characteristic peaks of brucite. The intensities of the peaks arising from brucite were strongest after 1 day of aging and decreased. After 10 days of aging and on, they were no longer detectable. This trend was contrasting to that observed for MgO–water system where the peaks from brucite rapidly increased during 10 days of aging and the intensity of the strongest peak at 0.237 nm was comparable to the peak at 0.211 nm of the starting MgO. The broad peak characteristic to noncrystalline silica also gradually diminished and finally merged into new very broad peak extending from 18° to 30°. The sample aged for 50 days exhibited new broad peaks in ranges from 18° to 30° and 33° to 40°, of which the latter is characteristic to poorly crystalline layer silicate minerals.

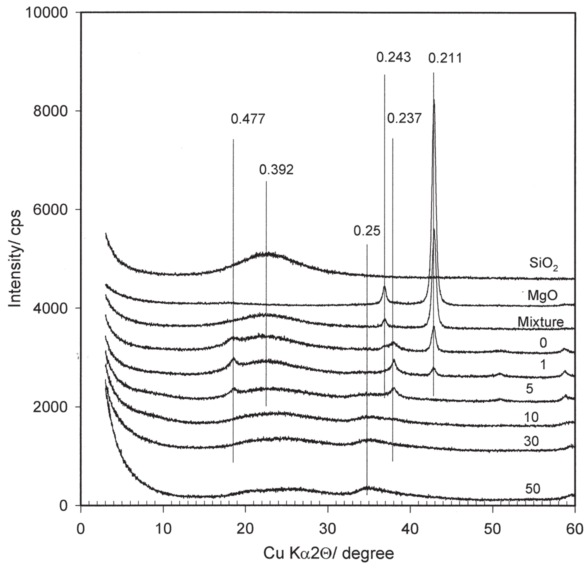

Fig. 2. X–diffraction patterns of SiO_2, MgO, and their mixtures aged for 0, 1, 5, 10, 30 and 50 days.

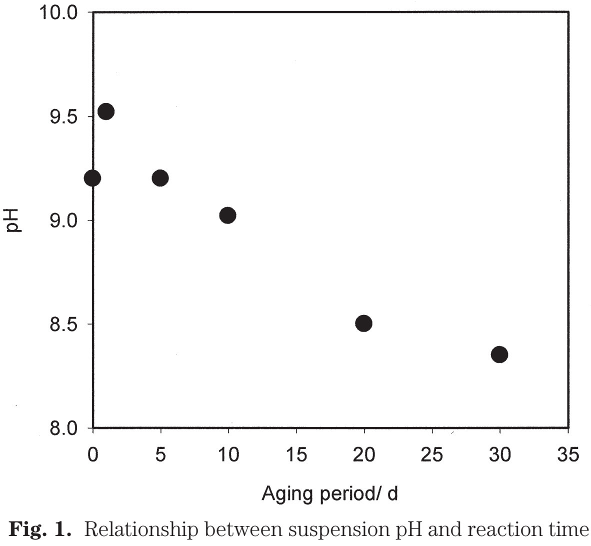

Fig. 1. Relationship between suspension pH and reaction time.

The observed change in the XRD patterns suggests that the SiO_2 and MgO reacted in the aqueous medium and some Mg silicate minerals formed. In detail, the weak peaks from brucite appeared only at early stage of the aging, which indicates that the kinetics of the reaction between SiO_2 and MgO was comparable to the hydration of MgO. This experiment clearly shows that brucite would not form when MgO is mixed with soils containing unstable silica or silicious minerals. In view of the solubility, quarts in soils is unlikely to react with the added MgO, but biogenic silicas, opaline silica in young volcanic ash soils (Shoji and Masui, 1971) and allophane having high Si content may react.

The diffuse asymmetrical peak with maximum at about 0.25 nm suggests that the major reaction product is layer silicate. However, it is difficult to identify the mineral species since no distinct 001 reflection was observed. To assist drawing an inference, the ratio of diffraction intensity of every aged sample to that of the sample just after mixing was calculated and plotted in Fig. 3. The plot designated by 50, for example, is the intensity ratio of the XRD pattern of the sample aged for 50 days to that of the sample just after mixing. The plot range was restricted to a range from 3° to 10°. Fig. 3 shows that the relative diffraction intensity in this range increased with aging time. The increase was particularly large at about 4°, which correspond to d–spacing of around 2 nm. The increase in relative intensity in a range from 7° to 10°, where the strongest 011 reflection of sepiolite is found, was not marked. These facts suggest that the possible layer silicate formed in the present experiment was smectite but not sepiolite.

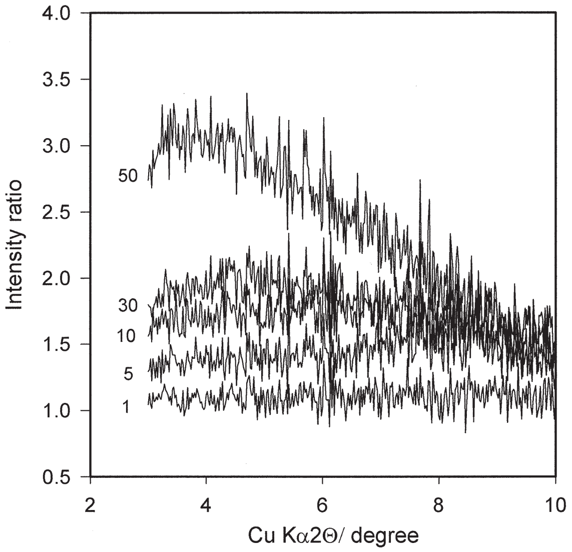

Fig. 3. Relative diffraction intensities of the samples aged for 1, 5, 10, 30 and 50 days to that of the sample just after mixing. For detailed explanation, see text.

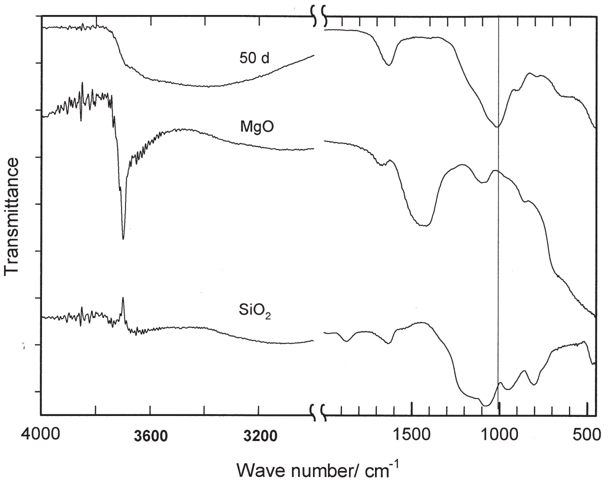

Fig. 4. FTIR spectra of SiO_2, MgO, and reaction product aged for 50 days.

Fig. 4 shows FTIR spectra of the starting SiO_2, MgO and the reaction mixture aged for 50 days. The reaction product is characterized by broad absorption band in a range from 3600 to 3200 cm^{-1} arising from structural OH, strong band arising from Si–O stretching vibration centered at 1050 cm^{-1} and weak but distinct peak at 900 cm^{-1} probably arising from Mg–OH. The strong bands at 1200 and 800 cm^{-1} that are characteristic to noncrystalline silica were almost missing in the spectrum of the reaction product. The strong absorption band characteristic to MgO at 1450 cm^{-1} was also absent in the spectrum of the reaction product. These spectra together with the XRD patterns (Fig. 2) clearly show that neither SiO_2 nor MgO remained in the sample that was aged for 50 days. An absorption band at 1200 cm^{-1} that is characteristic to sepiolite (Marel and Beutelspacher, 1976) was missing in any of the spectra of the aged samples. Although the FTIR spectrum of the reaction product did not offer information that is sufficient for the identification of the mineral species, comparison with standard IR spectra of specimen minerals (Marel and Beutelspacher, 1976) suggest the main product was poorly crystalline smectite.

The electron microscopy showed that the SiO_2 and MgO used in the present experiment consisted of coarse irregular shaped and rectangular particles having diameters ranging from several to several tens mm, respectively. Just after mixing with water, the rectangular MgO particles broke down into much finer particles. After 10 days of aging, large silica particles also broke down to much smaller particles and very fine filamentous particles appeared. The morphology of the product was similar to that observed by Hast (1956). These filamentous particles did not show apparent sign of crystal growth during the 50 days of aging. Fig. 5 shows a

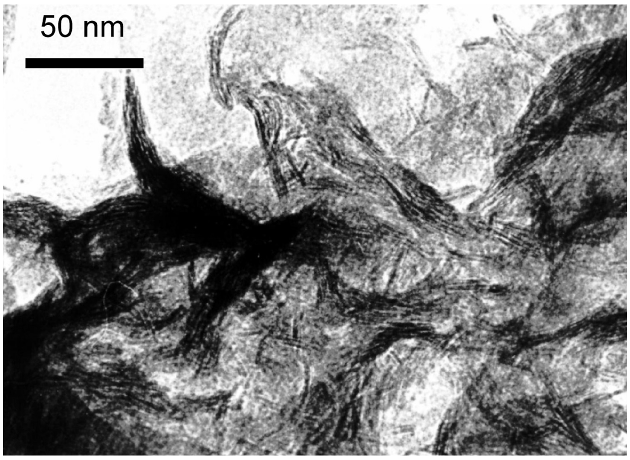

Fig. 5. Transmission electron micrograph of the reaction product found in a sample aged for 10 days.

high resolution electron micrograph of some such particles found in a sample aged for 10 days. The lattice images found on particles in Fig 5 indicate that the product is layer silicate. The lattices have many imperfections and the stacking is not regular. The average distance between the lattices measured on several photographs was about 0.9 to 1.3 nm, indicating that the product is 2:1 layer silicate. Staggered stacking of ribbons, which is characteristics to sepiolite, was not noticed. All these results suggest that the major reaction product in the present synthetic experiments is poorly ordered smectite but not sepiolite. Incomplete lattice images in Fig. 5 indicate the presence of many vacancies in both octahedral and tetrahedral sites.

The structural formula of a trioctahedral 2:1 layer Mg silicate mineral is $Mg_6Si_8O_{20}(OH)_4$. The OH/Mg molar ratio is about 0.67 or a little bit higher if there are some vacancies in the octahedral sites. This value is only one third of the value of OH/Mg ratio in brucite. One of the major mechanisms of F^- fixation in the MgO–water interaction is the uptake of F^- in the lattice of brucite (Fukazawa *et al*., 2006; Shimomura and Higuchi, 2006). Therefore, the presence of silica or silicious minerals and the formation of smectite–like minerals are unfavorable for stabilization of F^- because the reaction of MgO with silica leads to the formation of minerals with less OH content.

On the contrary, presence and formation of smectite–like minerals would not be disadvantageous to the stabilization of heavy metals like Cu, Ni and Zn. The formation of silicate minerals incorporating contaminants would be beneficial for the stabilization of heavy metals because silicate minerals are more stable than brucite under acidic environment. The effects of silicic acid on the stabilization of F^- and some heavy metals are being examined. The results will be reported elsewhere.

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