Hydrothermal conversion of chrysotile to amorphous silica or brucite

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Chrysotile (Mg₃Si₂O₅(OH)₄) was treated hydrothermally in acid or alkaline hydroxide solution. By hydrothermal treatment in 1 M HCl, HNO₃ or H₂SO₄ solution at 180°C for 48 h chrysotile changed to amorphous silica by complete extraction of magnesium component and its fibrous morphology was held in spite of changing chemical composition. The maximum specific surface area (S BET) of the fiberous amorphous silica was 127 m²/g. It was converted to Mg(OH)₂ by complete dissolution removal of silica component in 20 M NaOH or KOH solution at 180°C for 48 h and the fiberous morphology of chrysotile disappeared.

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Key-words : Chrysotile, Asbestos, Hydrothermal reaction

[Received August 11, 2009; Accepted September 11, 2009]

1. Introduction

Asbestos is a generic name of fibrous silicates which belong to amphiboles and serpentine minerals and is well known as a harmful material for human body. Chrysotile (Mg₃Si₂O₅(OH)₄) which is one of asbestos had been used widely as building materials since it had advantage such as low cost, chemical stability and good thermal isolation property etc. In decade wide spread of chrysotile in human life has been serious social problem and detoxification technique of chrysotile in building materials has been paid attention. A variety of detoxification techniques of building materials containing asbestos such as chrysotile have been proposed, for example, low temperature decomposition with calcium salts, detoxification system by microwave heating, and detoxification by low temperature heating and grinding.

There has been no report for hydrothermal treatment of chrysotile, though hydrothermal synthesis of chrysotile was reported. Herein we will describe hydrothermal treatment of chrysotile and some properties of the products by hydrothermal reaction of chrysotile.

2. Experimental

Test samples of chrysotile (Mg₃Si₂O₅(OH)₄) were handled in a closed chamber. Chrysotile (0.5 g) was put into a Teflon-lined stainless steel autoclave (70 mL) and 1 M H₂SO₄, HNO₃ and HCl solution (50 mL) or 10–20 M NaOH and KOH solution (50 mL) were added. The reaction temperature was 180°C and the reaction duration was 14–48 h. The products were separated by filtration and washed with distilled water, and dried at 50°C. X-ray powder diffraction patterns (XRD) of the products were performed by a Rigaku X-ray diffractometer (RINT2000) with monochromated Cu Kα radiation. The specific surface area (S BET) of the products was measured by a BELSORP-mini II adsorption measurement instrument with N₂ gas after evacuating the samples at 110°C for 8 h. The pore size distribution curve was obtained by BJH method. The morphology of the products was observed by SEM (JEM–6500F field emission scanning electron microscope) and TEM (JEM–2000FXII transmission electron microscope), and the chemical composition was checked by EDX attached with SEM.

3. Results and discussion

Figure 1 shows the X-ray powder diffraction patterns of chrysotile and the samples produced by hydrothermal treatment. In acid solution chrysotile changes to an amorphous phase. When alkaline hydroxide solution is used, severe condition of more than 20 M concentration and 48 h reaction duration is needed to change from chrysotile to Mg(OH)₂. Dilute concentration and short reaction time do not complete the change and chrysotile remains in the product.

The amorphous phase produced by acid solution has fibrous morphology similar to chrysotile as shown in Fig. 2 and EDX
Fig. 2. SEM images of chrysotile (left) and the sample (right) produced by hydrothermal treatment in 1 M HCl solution for 48 h. Superimposed figure indicates the result of EDX analysis.

Analysis indicates that magnesium component is completely extracted by this hydrothermal treatment. Leaching of magnesium component in chrysotile destroyed the layer-type structure, though the fibrous morphology of chrysotile was held. It is well-known that the components of the clay minerals except SiO₂ can be leached out by acid solution to yield porous SiO₂. A variety of clay minerals such as metakaolinite,17) antigorite,18) chrysotile19–21) montmorillonite,22,23) chlorite,14) phlogopite,15) vermiculite,16) talc17) and sepiolite18) have been attempted to make porous silica by selective acid leaching. Souquet reported that complete leaching of chrysotile was accomplished by treating it for 2 h. at 90°C with 6 M HCl and the product was non-crystalline porous fibers.29) But she did not measure the specific surface area of the product. Yasue et al. reported that chrysotile converted to porous amorphous silica with high specific surface area (SBET = 500 m²/g) under the condition of in 0.5–6 M HCl and H₃PO₄ solution at 20°C.10) Also Mao et al prepared precursors of zeolites by leaching chrysotile with 0.5–6 M HCl and H₂SO₄ solution at 80°C.11) The precursors were amorphous material with high specific surface area (SBET = 460 m²/g). Their results are very similar to each other and the specific surface area of the leaching products increased with the amount of removal magnesium component. Our result is consistent with these previous works in respect with that the magnesium component of chrysotile can be removed completely by acid leaching. A new finding is that fibrous morphology of chrysotile can not destroy even under severe hydrothermal condition in acid solution.

Nitrogen adsorption-desorption isotherms and pore size distribution curves of chrysotile and the products by hydrothermal reaction are shown in Fig. 3. The SBET values of amorphous silica are 86, 94 and 127 m²/g for HCl, HNO₃ and H₂SO₄ solutions, respectively in spite of complete removal of magnesium component for every sample and these values are larger than that (21 m²/g) of chrysotile. Although the specific surface area is dependent on acid solution, the pore size distribution curves are very similar to each other. The maximum SBET value (127 m²/g) is smaller than that (~500 m²/g) of the porous products prepared by milder leaching condition as mentioned above.10,11) By taking into account of nitrogen adsorption-desorption isotherms and pore size distribution curves the amorphous silicas prepared under hydrothermal condition have no porous structure. As shown in Fig. 4, TEM image supports that it has no micropore. The 2:1 layered clay minerals such as montmorillonite22,23) and vermiculite6) can yield porous amorphous silica with high specific surface area by acid leaching. In these cases the selective leaching of the octahedral layers may produce micro pores to bear high specific surface area. Although chrysotile does not belong to the 2:1 layered clay minerals, it is expected that a porous product can be obtained by similar mechanism during acid leaching. The specific surface area of the products depended on the amount of removed magnesium component and chrysotile could produce porous materials with high specific surface area (SBET = 500 m²/g) under mild conditions.10,11) The reason why the specific surface area of the products obtained by hydrothermal conditions is small is that SiO₂ layers in chrysotile may polymerize to yield nonporous materials. Similar behavior could be found in acid leaching of talc (Mg₃Si₂O₅(OH)₂), the product of which was nonporous silica with low specific surface area (SBET < 40 m²/g) formed by removal of magnesium component and polymerization of SiO₂ layers.17) On the other hand crystalline Mg(OH)₂ produced by high concentrated alkaline hydroxide solution does not have fibrous morphology as shown in Fig. 5. The low SBET value (10 m²/g) and the pore size distribution curve of Mg(OH)₂ indicate that this product is not a porous material. Complete extraction of silica component of chrysotile occurs under hydrothermal condition in high concentrated alkaline hydroxide solution and simultaneously brucite Mg(OH)₂ is crystallized. Formation of non-fibrous Mg(OH)₂ suggests that chrysotile is dissolved and only magnesium component is precipitated under these conditions. Silica component plays an important role of holding fibrous morphology and this result may suggest the hint of detoxification of fibrous chrysotile.
4. Conclusion

Chrysotile was converted to non-porous amorphous silica with fibrous morphology by acid leaching under hydrothermal condition. The $S_{\text{BET}}$ value of the product was 127 m$^2$/g and was smaller than that (~500 m$^2$/g) of the porous product prepared by milder acid leaching condition. A non-fibrous brucite, Mg(OH)$_2$ was precipitated by reacting chrysotile in high concentrated alkaline hydroxide solution under hydrothermal condition.

References


Fig. 5. SEM image of the sample produced by hydrothermal treatment in 20 M NaOH solution for 48 h. Superimposed figure indicates the result of EDX analysis.