Hydrogen Production and Morphological Change of Chrysotile Asbestos in the Radiolysis of Aqueous Solutions

Noboru Aoyagi,* Ryuji Nagaishi, Fumitaka Esaka, and Reiji Yamada

Division of Environment and Radiation Sciences, Nuclear Science and Engineering Directorate, Japan Atomic Energy Agency (JAEA), Tokai-mura, Naka-gun, Ibaraki 319-1195

(Received February 22, 2007; CL-070198; E-mail: aoyagi.noboru@jaea.go.jp)

A high yield of H_2 gas was unprecedentedly produced by the radiolysis of water-containing asbestos while the morphology of them turned fibrous bundles into nonfibrous particles in 0.40 M H_2SO_4 solution over 2.0 MGy dose of irradiation.

Aerodynamic behavior of fibrous serpentine and amphibole asbestos penetrates into the deep lung influentially when inhaled, causing lung cancer and mesothelioma.[1] Although an attempt to convert asbestos into nonfibrous form is difficult because of its chemical stability and fire-proofing potential, the decomposition or removal of toxicologically hazardous chrysotile asbestos, $Mg_3Si_2O_5(OH)_4$, has mainly been challenged by chemical treatment with fluorosulfonic acid, melting down under high temperature with added salt such as $CaCl_2$ or vitrification with molten salt.[2] Most of them, however, have technical or economical difficulties which require at least about 873 K or produce a large amount of unnecessary by-products. Radiation-assisted digestion of asbestos using γ-ray or electron beam has not been reported, and comparison with recently developing microwave-assisted method[2c] would open the future recycle or disposal system of asbestos-containing materials.

In the meantime, interfacial reaction between solid and water under photon or high-energy radiation is of significant interest in both radiation chemistry and surface chemistry. Since the system of mixture has high complexity, many chemical reactions originated from radiation are far from elucidation though the radiolysis of aqueous solutions studied well. Production of H_2 gas, in particular, is one of central topics, the production yield of hydrogen gas under γ-radiolysis can be higher in the presence of solid surface such as silica, alumina, zeolite, and other metal oxides than in bulk water. Henglein,[3] Nakashima and Tachikawa,[4] and lately LaVerne and Tonnies[5] reported that production of H_2 gas is enhanced by γ-radiolysis of water molecules adsorbed onto oxide particles such as silica, titania, alumina, and so on. No works have been performed to tubular oxide-assisted H_2 gas production.

In the present communication, we report the usefulness of asbestos providing high yield of H_2 gas under the radiolysis of aqueous solutions and also report the morphological change during the radiolysis for the sake of nontoxic treatment.

Chrysotile was mainly used as received. The other amphibole asbestos (anthophylite, amosite, crocidolite, and tremolite) were also used. γ-Ray or electron beam irradiation was performed for aqueous solutions containing these asbestos. Quantitative analyses of produced gases were performed via gas chromatography. Surface analysis with SEM was used for morphological observation.[6] The absorbed dose of aqueous system and heterogeneous system involving solid and liquid phase was evaluated by a cellulose triacetate (CTA) film dosimeter.

Ultrapure water and 0.40 M H_2SO_4 were irradiated in the absence and presence of asbestos (Figure 1). The relationship between H_2 gas generation and irradiation within total doses of 15–140 kGy for 6 h revealed linearity. Other amphibole asbestos also exhibited higher production yields than any sort of oxide particles such as silica and alumina investigated in this study and another one.[5]

Incidentally, can the production yield be changed under longer lixiviation period or higher dose of irradiation? Two series were performed to see it. In the first series, chrysotile fiber which had been leached in 0.40 M H_2SO_4 without irradiation for a day was used. The systems having these asbestos resulted in the highest yield: double value of solid square (■) in Figure 1 (not shown). The morphological structure by SEM did not show any difference from original chrysotile within these ranges of dose irradiated by γ-ray. In the second series, chrysotile after irradiation in 0.40 M H_2SO_4 at much higher dose of 1.0 MGy was used, resulting in only a half yield of square (■) in Figure 1.

Structural information can account for the relation between dose and specific surface area as shown in Figure 1b, in which the specific surface area of original chrysotile was determined

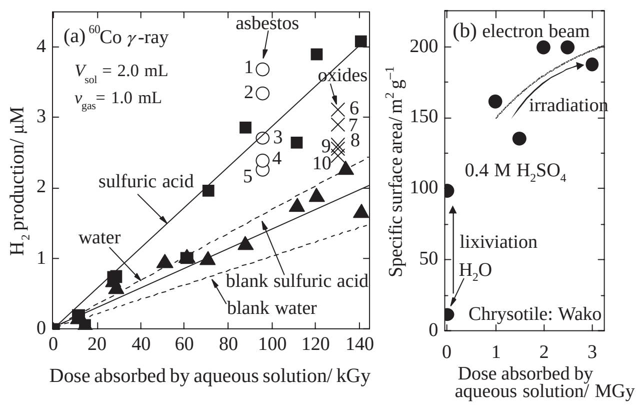

Figure 1. Influence of irradiation into heterogeneous asbestos–water system; (a) Production of H_2 gas as a function of ^{60}Co γ-ray dose in water (▲) and 0.4 mol/L H_2SO_4 (■). All asbestos were weighed at 0.100 g (5 wt %). A variety of 5 wt % using JAWEs' (Japan Assosiation for Working Environment Measurement) asbestos (1: crocidolite, 2: amosite, 3: chrysotile, 4: tremolite, 5: anthophylite) and oxides (6: quartz wool, 7: silica gel, 8: γ-alumina, 9: silica, 10: α-alumina) contained system are compared. (b) Increase of specific surface area in chrysotile (5 wt %) by irradiation and lixiviation. 800 keV electron beam was used. Chrysotile in water and H_2SO_4 was set in a petri dish covered with kapton® seal. Specific surface area was estimated by BET method using N_2 gas.

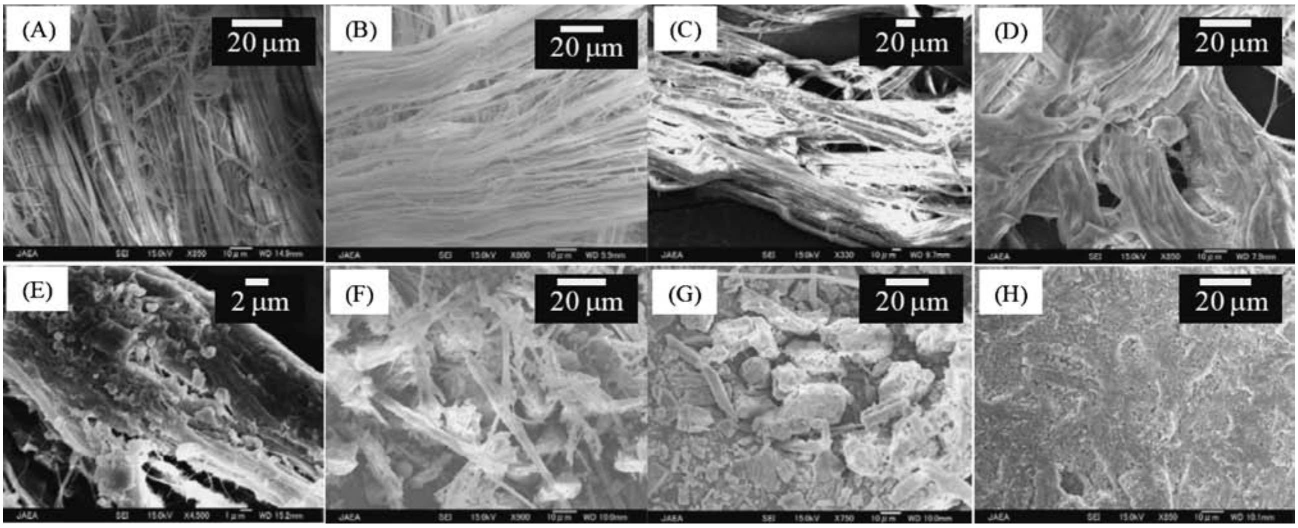

Figure 2. SEM images of a fragment in chrysotile fibers irradiated by 800 keV electron beam. (A): original, (B): after 10.0 MGy irradiation in water, (C): nonirradiated in 0.40 M H_2SO_4, (D): after 2.0 MGy irradiation in 0.40 M H_2SO_4, (E): the deposition of $MgSO_4$ onto silica surface. (E) is an expanded view of (D), (F): 10.0 MGy irradiation in 0.40 M H_2SO_4, (G): 10.0 MGy irradiation in 0.80 M H_2SO_4, and (H): 10.0 MGy irradiation in 17.8 M H_2SO_4.

as 11.25 m^2/g. Chrysotile is comprised of sheets of tetrahedral silica in a pseudo-hexagonal network joined to sheets of octahedral magnesium hydroxide. Acidic leaching is considered to lead layered silica disordered. Outer layer forming "brucite," $Mg(OH)_2$, is partly leached in H_2SO_4 without irradiation, resulting ten times higher value of specific surface area ($\approx$100 m^2/g). This unveiled sample in the first series was the most efficient material for gas production. Up to 3.0 MGy irradiation, specific surface area was increased doubly and saturated at around the 200 m^2/g; however, gas production yield was smaller for the irradiated samples. Therefore, it seems that dislayered structure of asbestos contributed surface spreading with nanofibrils peeled, resulting in low production yield of gas.

The SEM pictures in Figure 2 illustrate the alteration of chrysotile by lixiviation with irradiation. When chrysotile was leached in H_2SO_4, the slight change of bundle size was found (C). Bundle network spread more and more with increasing dose of electron beam, making interlocking structure of fibrils (D). Formation of particles assigned to $MgSO_4$ (E) was promoted so that nonfibrous parts prevailed over original fiber (F), (G). In 17.8 M H_2SO_4, no more fibril was observed (H). Although chrysotile was decomposed, other amphibole asbestos, anthophylite, amosite, crocidolite and tremolite, did not change morphologically in spite of 10 MGy dose, leached in 17.8 M H_2SO_4.

The EDX data indicated that Mg^{2+} was trapped inside the Si–O network (Table 1) even in the sample (H). The concentration of Mg^{2+} in supernatant was measured by inductively coupled plasma mass spectrometry (ICP-MS). Total concentration C_{Mg} was almost constant in either H_2O or H_2SO_4 within 50–500 kGy. The results of H_2SO_4 indicate that almost all the Mg-containing sheet was leached from original chrysotile, and morphology of residual silica-containing solid was changed while keeping constitution.

The treatment with 2.0 M NaOH after irradiation revealed complete dissolution of fibrous products. Furthermore, reduction of Cr^{VI} in aqueous neutral or basic solution was promoted by

Table 1. Elemental composition (%), Mg/Si and Mg/S ratio obtained by EDX[a]

SEM image	Mg	Si	S	Mg/Si	Mg/S
A	54.20	45.80	—	1.18	—
B	30.52	23.18	—	1.32	—
C	22.79	27.65	—	0.82	—
E	21.14	3.66	19.57	5.78	1.08
F	18.71	26.58	15.32	0.70	1.22
G	10.60	24.69	7.91	0.43	1.34
H	5.31	23.76	33.39	0.22	0.16
$MgSO_4$	21.76	—	23.62	—	0.92

[a]Values on E were obtained from particles.

γ-ray irradiation in solid-coexisting heterogeneous system.[7] In conclusion, irradiation against asbestos in solutions can promote the hydrogen gas production and cause the morphological change of chrysotile without providing heat or chemicals. Further investigation using spent fuel[8] from nuclear industries will be a great help to deal asbesto decomposition in the "chemically green" way.

References

1 G. Falini, E. Foresti, G. Lesci, N. Roveri, *Chem. Commun.* **2002**, 1512; B. Fubini, C. Otero Areán, *Chem. Soc. Rev.* **1999**, *28*, 373.
2 a) T. Sugama, R. Sabatini, L. Petrakis, *Ind. Eng. Chem. Res.* **1998**, *37*, 79. b) M. Fujishige, R. Sato, A. Kurihara, I. Karasawa, A. Kojima, *J. Ceram. Soc. Jpn.* **2006**, *114*, 844. c) M. Sato, *Ceramics* **2006**, *41*, 855. (in Japanese).
3 A. Henglein, *J. Phys. Chem.* **1979**, *83*, 2209.
4 M. Nakashima, E. Tachikawa, *Appl. Radiat. Isot.* **1986**, *37*, 527.
5 J. A. LaVerne, S. E. Tonnies, *J. Phys. Chem. B* **2003**, *107*, 7277.
6 F. Esaka, K. T. Esaka, C. G. Lee, M. Magara, S. Sakurai, S. Usuda, K. Watanabe, *Talanta* **2007**, *71*, 1011.
7 R. Nagaishi, Z. Yoshida, R. Yamada, Y. Hatano, *Radiat. Phys. Chem.* **2006**, *75*, 1051.
8 K. Makuuchi, F. Yoshii, K. Hyakutake, *Radiat. Phys. Chem.* **1995**, *46*, 523.

Published on the web (Advance View) June 16, 2007; doi:10.1246/cl.2007.890