



Development of a testing method for asbestos fibers in treated materials of asbestos containing wastes by transmission electron microscopy



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ABSTRACT

Appropriate treatment of asbestos-containing wastes is a significant problem. In Japan, the inertization of asbestos-containing wastes based on new treatment processes approved by the Minister of the Environment is promoted. A highly sensitive method for testing asbestos fibers in inertized materials is required so that these processes can be approved. We developed a method in which fibers from milled treated materials are extracted in water by shaking, and are counted and identified by transmission electron microscopy. Evaluation of this method by using asbestos standards and simulated slag samples confirmed that the quantitation limits are a few million fibers per gram and a few $\mu\text{g/g}$ in a sample of 50 mg per filter. We used this method to assay asbestos fibers in slag samples produced by high-temperature melting of asbestos-containing wastes. Fiber concentrations were below the quantitation limit in all samples, and total fiber concentrations were determined as $47\text{--}170 \times 10^{-6}$ f/g. Because the evaluation of treated materials by TEM is difficult owing to the limited amount of sample observable, this testing method should be used in conjunction with bulk analytical methods for sure evaluation of treated materials.

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1. Introduction

Asbestos is any of a group of naturally occurring fibrous silicate minerals. It has been used for many purposes, including building materials, lagging, seals, and brake pads, because of its tensile strength, chemical inertness, thermal stability, heat retention, and anti-wear properties (Morinaga, 2008). In Japan, about 10 million t of asbestos was imported and used from the 1930s to the 2000s. Despite its usefulness, the inhalation of asbestos fibers causes respiratory diseases such as asbestosis, mesothelioma, and bronchial cancer (World Health Organization, 1986; Dodson and Hammer, 2006), so the production and use of asbestos-containing products were globally regulated. In Japan, the production, importation, and use of asbestos products which contain more than 1% of crocidolite and amosite by weight were prohibited in 1995, and products which contain more than 1% of chrysotile were prohibited in 2004 except for essential uses. In 2006, the regulation of asbestos-containing products was strengthened (the limit was reduced to 0.1%), and so exposure to asbestos in production and use was likely to have diminished. Concern about exposure to asbestos is now focused on the renovation or demolition of buildings

containing asbestos, and the disposal of asbestos-containing wastes. The stock of asbestos-containing building materials in Japan is estimated to be about 40 million tons, and the annual emission of more than 1 million tons of asbestos wastes will continue until the 2030s (Japan Asbestos Association, 2003). In fact, the emission quantity might prove larger than this estimate, because the estimation was performed in 2003, when the limit was 1%. In the treatment of asbestos-containing wastes in Japan, friable wastes are classified as “hazardous wastes” and are treated by high-temperature melting, or by solidification with cement or double-bagging followed by landfilling. Non-friable asbestos-containing wastes are also landfilled separately from other wastes. However, the capacity of landfills is limited, and careless excavation or development of landfill sites may cause exposure to asbestos, which does not degrade. Therefore, to reduce the amount of asbestos containing wastes sent to landfill, the Japanese government is promoting the treatment of asbestos wastes based on new inertization processes approved by the Minister of the Environment (Yoshida and Hata, 2006).

There are a lot of studies about asbestos inertization technologies such as high temperature treatment including firing (Gualtieri and Tartaglia, 2000; Fujishige et al., 2007; Gualtieri et al., 2008; Zaremba and Peszko, 2008; Viani and Gualtieri, 2013), melting and vitrification (Sakai et al., 1995; Dellisanti et al., 2009; Kasai

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et al., 2011; Osada et al., 2013), microwave heating (Di Vesto et al., 2003; Leonelli et al., 2006), and hydrothermal conversion (Anastasiadou et al., 2010; Kozawa et al., 2010). Non-thermal treatment technologies are also developed such as mechanochemical reaction (Plescia et al., 2003; Hashimoto et al., 2005; Colangelo et al., 2011), and reaction with strong acid (Sugama et al., 1998; Yanagisawa et al., 2009). In these studies, inertized materials are often evaluated by X-ray diffraction (XRD) for confirming mineralogical conversion of asbestos and scanning electron microscopy (SEM) for confirming disappearance of fibrous structures.

Before an inertization process can be approved by the Minister of the Environment of Japan, the applicant must demonstrate that the treatment products do not contain any accessible asbestos. In the approval process, testing method consists of qualitative analysis by dispersion staining (DS) and quantitative analysis XRD (Japan Industrial Standard, 2008) is adopted. However, XRD is not sensitive enough because its quantitation limit is around 0.1% by weight. DS is also inadequate because it cannot resolve thin and small fibers, particularly fibers thinner than 0.25 μm , which are strongly carcinogenic (Stanton et al., 1981; Pott, 1978). Transmission electron microscopy (TEM) is often used for the analysis of asbestos in air (Rickards, 1974; Burdett and Rood, 1983; ISO, 1995; NIOSH, 1994), water (Speil, 1974; Beaman and File, 1976; EPA, 1983), soil and sediment samples (Pitt, 1988; Webber et al., 2004). It might be suitable for testing of treated asbestos wastes, because it can resolve thin and small fibers, and it can correctly identify fibers from their morphological and crystallographic properties and by their elemental composition obtained by energy-dispersive X-ray spectrometric (EDS) analysis. For example, Gualtieri et al. observed changes in thermally treated chrysotile bundles in asbestos slate by TEM and confirmed recrystallization of newly formed silicate on the bundles (Gualtieri et al., 2008). Sakai et al. determined asbestos fiber concentrations in melting-treated materials by TEM and assessed treatment efficiency by comparison with fiber concentrations in samples of soils and sediments (Sakai et al., 1995). In this study, we developed a TEM method for testing asbestos fibers in treated asbestos wastes and it evaluated it with slag samples obtained by melting treatment of asbestos wastes.

2. Materials and methods

2.1. Materials and apparatus

For TEM calibration we used three kinds of asbestos standards: chrysotile (Japan Association for Working Environment Measurement JAWE 131), crocidolite (Union for International Cancer Control (UICC)), and amosite (UICC). Nitric acid and chloroform were of reagent grade. Polycarbonate filters (Whatman Nuclepore filter, pore size 0.22 μm , diameter 47 mm) were used with filtration apparatus (Sartorius Stedim Biotech, Aubagne, France). Nickel TEM meshes with an 80- μm grid (200 mesh) were purchased from Ouken Shoji. Fiber-free water was obtained by filtration of purified water (Millipore, Milli-Q gradient) through a membrane filter (Advantec, pore size 0.45 μm , diameter 47 mm). All glassware was washed with dilute nitric acid before use. Samples were carbon-coated with an auto carbon coater JEC-530 (JEOL Ltd., Tokyo, Japan). Laboratory A (our institute) used a JEM-2010 transmission electron microscope equipped with JED-2300T energy-dispersive X-ray detector (JEOL, Tokyo, Japan) for fiber counting and identification. For TEM observations, the acceleration voltage was 80 kV and the magnification was $\times 10,000$. Laboratory B (Kaneka Techno Research Corporation) used a H-7650 TEM (Hitachi High-Technologies Co., Tokyo, Japan) for electron diffraction analysis and an H-8100 TEM for energy-dispersive X-ray spectroscopic analysis.

The acceleration voltage was 100 kV (H-7650) or 200 kV (H-8100) and the magnification was $\times 10,000$.

2.2. Slag samples

To evaluate the newly developed testing method, eight kinds of slag samples were obtained from three types of furnaces (Table 1). Asbestos packing (67% chrysotile by weight) or asbestos slate (12% chrysotile) was added to some wastes.

We also prepared simulated slag samples by spiking a suspension of asbestos standards into slag extracts. The amount of slag on each filter was set at 50 mg, and amounts of asbestos were the same as in the standard samples. The slag held 33.0 $\mu\text{g/g}$ of chrysotile, 56.6 $\mu\text{g/g}$ of amosite, and 37.2 $\mu\text{g/g}$ of crocidolite. TEM grids were prepared and observed as for asbestos standards.

2.3. Analytical procedure

Slag samples are too hard to be ground and smashed. Because severe milling might pulverize fibrous materials to be determined into power and weathering of slag in the environment might be very slow to release fibers, it is considered to be enough that samples are reduced to below 0.5 mm. Slag samples were milled in an agate mortar with an agate pestle until the grain size was reduced to below 0.5 mm. Five grams of milled sample was transferred to a plastic bottle and 50 mL of fiber-free water was added. The bottle was shaken for 6 h at 200 rpm to extract fibers. The slurry was filtered through a stainless steel sieve (grid size 0.075 mm) to remove coarse particles. The bottle and sieve were washed out with fiber-free water, and the eluate was added to the filtrate. The volume of filtrate was topped up to 100 mL with fiber-free water. An aliquot of filtrate (usually 1 mL) was mixed in fiber-free water and filtered through a polycarbonate filter. The filter was dried and coated with 15–20 nm carbon using with a carbon coater. We prepared three filters and made three grids from each; pieces were cut from the center, midpoint, and margin and put on Ni TEM meshes. The meshes were placed on a bundle of slide glasses wrapped with a filter paper, which was then placed in a Petri dish filled with chloroform; the polycarbonate filter body was dissolved overnight by chloroform vapor. The TEM grids were initially observed at low magnification (about $\times 1000$). If the carbon layer was seriously damaged or more than 50% of the grid openings were covered with slag particles, the grid was discarded and another one was prepared from a more dilute sample. In counting fibers, several grid openings were randomly chosen from two grids, and fibers longer than 0.5 μm and thicker than 0.05 μm with an aspect ratio of more than 3 were counted. Fibers were also identified by shape, comparison of their electron diffraction (ED) pattern with those of asbestos standards, and comparison of their elemental composition obtained by EDS analysis with those of asbestos standards.

The asbestos fiber concentration (C , f/g) was calculated as:

$$C = (n \times A_f) / (k \times A_g \times w)$$

where n = asbestos fiber count (f); A_f : valid filter area (mm^2); k = number of observed grid openings; A_g = area of grid opening (mm^2); and w = sample weight (g).

The detection limit was calculated by the same equation with $n = 1$, and the quantitation limit of 2.99 times the detection limit was derived from the 95% upper limit of the Poisson distribution. The asbestos weight concentration was calculated from the sum of weights of individual minerals, which were calculated by multiplying fiber volume by density (2.55 g/cm^3 for chrysotile, 3.43 g/cm^3 for amosite, and 3.37 g/cm^3 for crocidolite). Fiber volume was calculated from the length and width, when fibers identified

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