Journal of Hazardous Materials 265 (2014) 151–157

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Thermochemical destruction of asbestos-containing roofing slate and the feasibility of using recycled waste sulfuric acid

Seong-Nam Nam [a,*], Seongkyeong Jeong [b], Hojoo Lim [c]

[a] *Engineering Research Institute, Seoul National University, Daehak-dong, Gwanak-gu 151-744, South Korea*
[b] *Environmental Resource Recirculation Division, National Institute of Environmental Research, Environmental Research Complex, Kyeongseo-dong, Seo-gu, Incheon 404-708, South Korea*
[c] *Indoor Environment and Noise Division, National Institute of Environmental Research, Environmental Research Complex, Kyeongseo-dong, Seo-gu, Incheon 404-708, South Korea*

HIGHLIGHTS

- Asbestos-containing roofing slates (ACS) were thermochemically treated.
- 5 N H_2SO_4 with 100 °C heating for 10–24 h showed complete disappearance.
- Asbestiform of ACS was changed to non-asbestiform after treatment.
- Favorable destruction was occurred at the $Mg(OH)_2$ layer rather than SiO_2 sheet.
- Equivalent treatability of waste acid brightened the feasibility of this approach.

ARTICLE INFO

Article history:
Received 30 May 2013
Received in revised form 22 October 2013
Accepted 5 November 2013
Available online 13 November 2013

Keywords:
Asbestos containing slate
Chrysotile
Thermochemical destruction
X-ray diffraction
Polarized light microscopy
Scanning electron microscopy

ABSTRACT

In this study, we have investigated the feasibility of using a thermochemical technique on ~17% chrysotile-containing roofing sheet or slate (ACS), in which 5 N sulfuric acid-digestive destruction was incorporated with 10–24-h heating at 100 °C. The X-ray diffraction (XRD) and the polarized light microscopy (PLM) results have clearly shown that raw chrysotile asbestos was converted to non-asbestiform material with no crystallinity by the low temperature thermochemical treatment. As an alternative to the use of pricey sulfuric acid, waste sulfuric acid discharged from a semiconductor manufacturing process was reused for the asbestos-fracturing purpose, and it was found that similar removals could be obtained under the same experimental conditions, promising the practical applicability of thermochemical treatment of ACWs. A thermodynamic understanding based on the extraction rates of magnesium and silica from a chrysotile structure has revealed that the destruction of chrysotile by acid-digestion is greatly influenced by the reaction temperatures, showing a 80.3-fold increase in the reaction rate by raising the temperature by 30–100 °C. The overall destruction is dependent upon the breaking-up of the silicon-oxide layer – a rate-limiting step. This study is meaningful in showing that the low temperature thermochemical treatment is feasible as an ACW-treatment method.

1. Introduction

Asbestos and asbestos-containing materials have been widely used in many applications, such as insulators, asbestos cement and fireproof construction materials, because of their low thermal conductivity and high mechanical strength. However, asbestos is known to be extremely carcinogenic, especially in causing a severe asbestosis, lung cancer and pleural mesothelioma when the respiratory system is exposed to it. As a result, nowadays, in most countries the mining, refinement and use of asbestos have been banned, apart from some exceptional applications.

From a toxicological point of view on asbestos, although there have been many studies by toxicologists and clinical research scientists to elucidate the clear mechanisms that cause severe toxicities, little is known about the crucial processes at the cellular/molecular levels, and still such studies leave unanswered which chemical or physical properties of asbestos are key factors in disease causation. Chemical reasons are explained with mineralogical compositions of asbestos. For instance, magnesium from chrysotile or iron from iron-containing asbestos (e.g., amosite or crocidolite) may be leached intracellularly, thereby inducing toxicity of the fibers [1,2], or causing cytotoxicity through generating a highly reactive species (e.g., a hydroxyl radical or reactive oxygen) [3].

* Corresponding author. Tel.: +82 2 880 4321; fax: +82 2 877 7376.
E-mail address: namsn76@gmail.com (S.-N. Nam).

0304-3894/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jhazmat.2013.11.004

Pathogenic mechanisms by the physical properties of asbestos are related to the size and length of the fibers, morphology (i.e., asbestiform or non-asbestiform), etc. [4]. Thus, if any treatment technique can achieve the "detoxification" of asbestos through both chemical (i.e., decomposition) and physical destruction, it should be the target goal of treatment, regardless of which property would play an important role in inducing toxicity to life.

In South Korea, the most common use of asbestos occurred in the 1960–70s by the government-led project "New Village Movement". As a part of the project, straw roofs in rural areas had been replaced with asbestos-cement roofing slates, and most of them are now obsolete and are being removing according to the Waste Asbestos Management Plan (2012–2021). According to the Korea Waste Statistics 2009, it was reported that 16 million tonnes of ACWs would be cumulatively generated by 2016. Currently, the Waste Management Law of South Korea classifies ACWs containing greater than 1 wt.% of asbestos as "Specific Hazardous Waste", which must be disposed of only by controlled landfill in accordance with safety regulations. Regarding interim treatments before landfill, few thermal or mechanochemical techniques such as high-temperature incineration, or solidification with cement are legally permitted [5]. However, the confining and displacement of ACWs in landfill do not essentially destroy asbestos, and yet provide a load to landfill sites for several decades or for a permanent period, especially in a small country like South Korea. Thermal treatment involves the conversion of asbestos into non-asbestiform materials by melting the compositional elements at temperatures ranging from ca. 800 to 1400 °C or above [6,7]. Similarly, microwave heating applies high power to inert asbestos materials [8]. Despite the efforts to lower operating costs, thermal treatments or microwave application are still energy-intensive and cost-demanding. Therefore, new or different treatment techniques need to be considered for significant amounts of ACWs. One approach, which was studied, is a chemical method using caustic acids [9,10] or alkalis to transform the crystalline structures to noncrystalline forms or to decompose the constituents of asbestos. In fact, such chemical treatment is not a discovery, but a novel technology which has been applied a great deal in various media [10–16]. Of the acidic agents, sulfuric acid is known to be the most effective attacking chemical and this was also experimentally observed in our previous tests [17]. Therefore, in this research, sulfuric acid (H_2SO_4)-based chemical dissolution was used and in order to enhance or complete the breakage of chemical bonds thermal process (i.e., heating) was incorporated to the process of chemical digestion. Furthermore, sulfuric acid, one of the most widely applied chemicals in many industrial processes, accounts for about 20% (89,000 tonnes discharged in 2009) of the entire waste acids discharged annually in South Korea, so the reuse or recycling of waste sulfuric acid is strongly desirable [9].

Therefore, the main objective of this research is to evaluate the treatability of asbestos-containing roofing slate waste using low-temperature thermochemical treatment and to demonstrate the feasibility of reusing waste sulfuric acid as a replacement for a commercial acid. Concentration of acid and heating temperature applied in this study were chosen mainly for practical reasons such as estimated costs per tonne of ACWs, comparable to other treatment methods [18]. The authors expect that the results shown in this research would give an insight to future guidelines with regard to the disposal of asbestos-containing wastes.

2. Experimental methods

2.1. Asbestos materials

Asbestos-containing (roofing) slate wastes (hereafter, ACS) were taken from a government-registered hazardous waste treating company. Waste materials were shipped polyethylene double-packed to a HEPA filtration equipped laboratory, and were briefly rinsed with tap water in order to remove the attached dirt such as soil and moss. After drying them at room temperature, the slate samples were ground with a blade mill for 3 min and sieved to get a particle size below 0.5 mm. The presence of chrysotile asbestos was identified and confirmed by XRD, SEM and PLM analytical techniques. The raw fiber materials of chrysotile asbestos obtained from a mine located in Jecheon city, South Korea were used without any further purification process.

2.2. Thermochemical treatment

Based on preliminary tests, the sulfuric acid was determined to be effective at concentrations above 5 N [17]. Thermochemical experiments were performed as follows: 5 g of the ACS sample was placed in 10 mL of 5 N H_2SO_4 in a porcelain crucible with a small lip (i.e., solid/liquid = 500 g/L) and heated at 100 °C for 10 and 24 h. During the treatment, a porcelain lid was covered to prevent gas emissions, and the gases were gently emitted through a lip and were trapped in a potable air cleaning system. The treated residual product was 0.45 μm pore-sized filtered in a vacuum filtration unit while rinsing with deionized water ($\Omega \geq 18.2$) until the pH of the filtrate was neutralized, and the filtrate residues were dried overnight at 100 °C. The dried samples were then analyzed in powder form for further characterization (XRD, PLM, SEM/EDS). The waste sulfuric acid was obtained from an electronic company in South Korea, and the concentration of the acid was determined by the acid-base titration method using NaOH. Detailed descriptions on the waste sulfuric acid were included in Section 3.4.

2.3. Analytical techniques

Regarding solid materials, the chemical compositions of the untreated chrysotile and slate powder below 500 μm were measured with X-ray fluorescence (XRF-1700, Shimazdu Co. Ltd, Japan). In order to examine the changes in the crystalline phases of asbestos, the powdered samples were analyzed by X-ray diffractometer (XRD: RIGAKU Ultima III, Japan) with CuKα radiation (λ = 0.1584 nm) generated at 40 kV and 25 mA. The XRD spectrum was obtained in the 5–75 degree range of 2θ and the obtained diffraction patterns were compared with the JCPDS archives in the PDXL software program. Polarized light microscopy (PLM: DP72, JP/BX51 Olympus, Japan) using dispersion staining, extinction, etc., was also used in order to confirm if chrysotile remained after acidic digestion, or if asbestiform remained or was not detectable. The microstructures and/or compositional changes of the treated asbestos waste were observed using scanning electron microscopy with an electron dispersion spectrum (SEM/EDS: Shimadzu Co., Ltd., Japan). In addition, the concentration of magnesium, silicon, calcium, and iron extracted into solution were measured using inductively coupled plasma-optical emission spectrometry (ICP-OES, Horiba Jobin Yvon Ultima, Japan).

3. Results and discussion

3.1. Characterization of untreated asbestos samples

Table 1 shows the chemical compositions of natural chrysotile asbestos and an ACS sample measured by X-ray fluorescence. Raw chrysotile is mostly composed of about 42 wt.% MgO and 36 wt.% SiO_2 together with 4 wt.% Fe_2O_3 and 1 wt.% Al_2O_3 which may be contained due to replacements of Mg and Si, respectively as reported in the literature [19]. Since ACS materials are mixtures of asbestos with cement, their chemical matrices are similar to