Comparative effect of chrysotile leaching in nitric, sulfuric and oxalic acids at room temperature

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ABSTRACT

The acid leaching of chrysotile was investigated in different acid media with the aim of quantifying and obtaining insights into the dissolution mechanism. Chrysotile was leached in batch reactors for 1 to 30 days at 25 °C and pH 1 in aqueous solutions of nitric and sulfuric acid and different concentrations of oxalic acid (50, 100 and 200 mmol L^{-1}). The combined analysis of solutions and solids by XRD and FTIR shows different effects: nitric acid induces a strong dissolution after 30 days, lowering the crystallinity of the sample and initiating the transformation of the chrysotile into an amorphous siliceous material. In the case of sulfuric acid, the dissolution is so intense that it is able to destroy the brucitic sheet of chrysotile, leading to an amorphous silica byproduct. Finally oxalic acid is also able to induce amorphization of chrysotile and the precipitation of glushinskite ($MgC_2O_4 \cdot 2H_2O$). As the concentration of oxalic increases from 50 to 200 mmol L^{-1} the amorphization process becomes faster. Finally, the relative effectiveness of acid attack to chrysotile is oxalic acid (9 days) > sulfuric acid (30 days) > nitric acid.

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1. Introduction

Despite the fact that the use of asbestos has been banned in the European Union since 2005 there exist many countries, such as Russia, India and China that mine and commercialize chrysotile. Moreover the intensive use of asbestos in the past, due to its properties as an insulator and its mechanical resistance, has led to a growing concern with its presence in the environment. To prevent adverse effects on humans and biota, it is crucial to identify and understand the degradation processes which are vitally important for the development of decontamination strategies, not only for abandoned mines but also to treat asbestos containing materials (ACMs). Moreover, the mechanism of chrysotile dissolution is also of critical importance for practical aspects of carbon capture and storage (e.g. O'Connor et al., 2002; Park et al., 2003; Park and Fan, 2004). For example, a mixture of weak acids and chemical additives enhanced the dissolution of ground serpentine at low-energy costs while preventing the precipitation of Fe(III) on the surface of the Mg-bearing mineral particles (Park et al., 2003).

Since Hargreaves and Taylor (1946) reported that if fibrous chrysotile is treated with dilute acids, the magnesium can be completely removed, many other studies have focused on leaching with mineral acids (Nagy and Bates, 1952; Fripiat and Mendelovici, 1968; Johan et al., 1974; Allen and Smith, 1975; Papirer et al., 1976). In particular, Pacco et al. (1976) found, by Fourier-transform infrared spectroscopy (FTIR) and

nuclear magnetic resonance (NMR) spectroscopy, that the acid attack produces an ordered fibrous silica gel, retaining the fibrous morphology of the original mineral.

Subsequently, several authors reported the effect of organic acids, such as oxalic (Thomassin et al., 1977) and pyruvic acids (Goni et al., 1979), for leaching in lixiviating magnesium from the chrysotile structure. The complexation capacity of these acids favors the interaction between the hydroxyl groups in the $Mg(OH)_2$ sheet and the hydrogen ions liberated from the acids, thereby eliminating the magnesium hydroxide sheet. Moreover, the effectiveness with which the $Mg(OH)_2$ sheet is broken in acid media has been investigated using other materials, such as titanium chloride (Cozak et al., 1983). Cosak found that titanium is able to cause the morphological transformation of a rolled fiber structure into an open or unrolled amorphous one.

Environmentally friendly policies have led to a growing interest in the transformation of asbestos-containing materials into non-hazardous phases, as displayed by recent literature. Most of these studies transformed chrysotile into an amorphous phase by leaching chrysotile with hydrochloric acid together with a range of thermal or mechanical treatments (e.g. Keane et al., 1999; Wypych et al., 2005; Wang et al., 2006; Liu et al., 2007; Gualtieri et al., 2008; Silva et al., 2011). Other authors (Mirick, 1991; Mirick and Forrister, 1993; Sugama et al., 1998) demonstrated and patented a method that incorporated fluoride ions into the acidic media, which significantly promotes the rate of chemical decomposition of asbestos. Presumably the attack by acids on the chrysotile causes hydrolysis of the outer brucitic sheet in the structure, while fluoride ions favorably

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react with Si in the inner siliceous sheets, thereby destroying the fibrous nature of the chrysotile.

However, the danger of hydrofluoric acid and the use of high temperatures to enhance the transformation reaction increase the cost of the recycling process. As an alternative some other authors have tried to use organic additives to enhance the transformation at ambient temperature. One of the most often used is oxalic acid, because it is present in many soils and lichens secrete it as a metabolite. Favero-Longo et al. (2005) showed that the action of some lichen species (Crustose and Foliose) actively helps the weathering of serpentinite outcrops. These show a natural deactivation (transformation into a non-hazardous material) due to selective Mg-depletion of those chrysotile fibers in contact with lichens. Different techniques (X-ray photoelectron spectroscopy and scanning electron microscopy) have shown a depletion of magnesium on the surface but no X-ray diffraction data are available to demonstrate whether the initial material turns into an amorphous material.

Finally, and despite the vast number of studies dedicated to chrysotile acid leaching, there are many questions about the transformation mechanism that remain unsolved. For instance, is it a question of pH? Is the mechanism same for all mineral acids? Do they have the same effect? Can we improve the transformation rate by increasing the concentration of oxalic acid? The aim of this study is therefore to investigate the mechanism of chrysotile transformation using three different buffered acid media (HNO_3, H_2SO_4 and oxalic acid) adjusted at pH 1, in order to see if all of them are able to turn chrysotile into an amorphous material and obtain some information about the mechanism of this process. The information obtained in this study will help to develop and improve remediation techniques for asbestos-containing materials (ACM).

2. Materials and methods

2.1. Characterization of the mineral sample

All experiments were done using chrysotile collected from Mina Laurel, an old asbestos mine in the Ojén ultramafic massif (Málaga, Spain). The starting material was studied by X-ray diffraction (XRD) and corresponds to chrysotile, without any accompanying minerals. Scanning electron microscopy (SEM) images show mainly fiber bundles, made up of acicular curved structures with a wide variety of length:diameter ratios (Fig. 1). The length of the fibers varies from those that are easily observed with the eye (2–3 mm) to a large quantity of very fine material (length < 2 μm). The composition of individual fibers was obtained by transmission and analytical electron microscopy (TEM–AEM). The average composition obtained from several tens of fibers was used to calculate the chrysotile structural formula, giving $Ca_{0.02}(Al_{0.06}Fe_{0.10}Mg_{2.75})(Si_2)O_5(OH)_4$. The corresponding Mg/Si atomic ratio is 1.38.
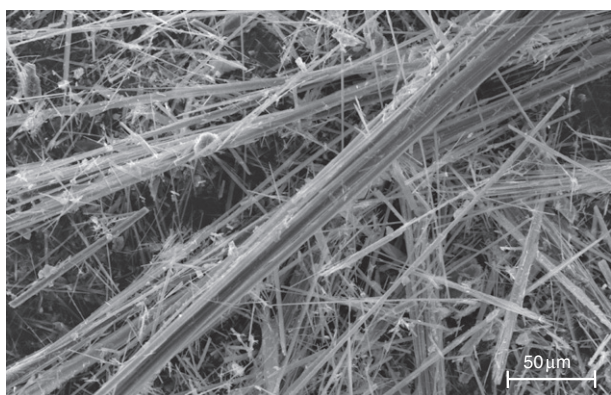

Fig. 1. SEM image of the micromorphology of the chrysotile used as starting material.

2.2. Experimental setup

Acid leaching experiments were carried out at room temperature in batch reactors using a solid/solution ratio of 2 g L^{-1}. Five sets of experiments were performed using inorganic buffered solutions at pH 1, namely HNO_3 (0.1 mol L^{-1}) and H_2SO_4 (0.05 mol L^{-1}) and organic buffered solutions with 50 mmol L^{-1}, 100 mmol L^{-1} and 200 mmol L^{-1} of oxalic acid (series Ox50, Ox100, Ox200) at pH 1 (Table 1).

For every set, 6 different batch reactors were prepared, placing 0.08 g of chrysotile directly in acid-cleaned PP bottles and adding 40 mL of buffer solution. The reaction vessels were shaken every day to prevent the reaction being controlled by diffusion. After the appropriate reaction time for each batch (1, 2, 5, 9, 19 or 30 days), the residual solids were centrifuged for 15 min at 5000 rpm and the supernatant filtered through a 0.45 μm filter into a previously acid-cleaned polyethylene bottle for solution analysis.

The solutions were analyzed for pH and total dissolved Si, Mg and oxalate. The pH of the solutions was measured at room temperature with a CRISON micropH 2000 pH-meter, using a standard Crison pH 52–03 dehydrated membrane electrode, standardized against pH 4.01 and 7.00 Crison buffer solutions at room temperature. The reported accuracy was ±0.02 pH units. The Si concentration in the samples was determined by colorimetry, using the molybdate blue method (Grasshoff et al., 1983) with a Visible/UV spectrophotometer at 825 nm. The detection limit is 5 ppb for Si and the associated error is 5%. The Mg concentration in every solution was determined by ion chromatography using a Metrohm 883 Basic IC Plus Ion Chromatograph with a Metrosep C3-250 column. The eluent was prepared with 3.5 mmol L^{-1} HNO_3. The detection limit is 1 ppb with 3% associated error. Finally, the concentration of oxalate was measured using a Metrohm 883 Basic IC Plus Ion Chromatograph, with a with a Metrosep A Supp 4–250 column and chemical suppression. The eluent was prepared with 1.7 mmol L^{-1} $NaHCO_3$ and 1.8 mmol L^{-1} $NaCO_3$. A sodium oxalate solution was used as a standard. The detection limit is 0.9 ppm and the associated error is 5%.

Once the experiments were completed, the solid samples were washed with distilled water, centrifuged three times and finally dried at 40 °C in capped bottles to avoid dispersion of the fibers, and stored to proceed with analysis by X-ray diffractions (XRD) and FTIR.

Powder XRD was used to determine changes in mineralogy before and after leaching. Back-loaded powder mounts were run on a PANalytical X'Pert Pro diffractometer with an X'Celerator detector, operated at 45 kV and 40 mA, with Ni filtered CuKα radiation. Patterns were recorded from 4 to 70 2θ degrees. Minerals were identified using PANalytical X'Pert HighScore Plus v.2.2a and the ICDD PDF-2 database.

FTIR was used to determine changes in crystal chemistry before and after leaching. FTIR spectra were recorded in absorbance mode in the 4000–400 cm^{-1} range using a Perkin Elmer Spectrum One spectrometer with a spectral resolution of 4 cm^{-1} from the average of 100 spectra. The sample was prepared in KBr pressed pellets by

Table 1
Stability constants of oxalic acid (H_2Ox) and aqueous Mg^{2+}-oxalate complexes calculated at 25 °C.

Reaction	Constant	Reference
$H_2Ox = HOx^- + H^+$	$pK_1 = 1.27$	[a]
$HOx^- = Ox^{2-} + H^+$	$pK_2 = 4.26$	[a]
$Mg^{2+} + Ox^{2-} = Mg(Ox)_{aq}$	$logK_1 = 2.10$	[b]
$Mg^{2+} + 2Ox^{2-} = Mg(Ox)_2^{2-}$	$log\beta_2 = 6.67$	[b]

[a] EQ3/6 database (Wolery, 1992).
[b] Prapaipong et al. (1999).