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Dissolution kinetics and biodurability of tremolite particles in mimicked lung fluids. Effect of citrate and oxalate

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ABSTRACT

The effect of citrate and oxalate on tremolite dissolution rate was measured at 37 °C in non-stirred flow-through reactors, using modified Gamble's solutions at pH 4 (macrophages), 7.4 (interstitial fluids) and 5.5 (intermediate check point) containing 0, 0.15, 1.5 and 15 mmol L^{-1} of citrate or oxalate. The dissolution rates calculated from Si concentration in the output solutions without organic ligands depend on pH, decreasing when the pH increases from −13.00 (pH 4) to −13.35 (pH 7.4) mol g^{-1} s^{-1} and following a proton-promoted mechanism. The presence of both ligands enhances dissolution rates at every pH, increasing this effect when the ligand concentration increases. Citrate produces a stronger effect as a catalyst than oxalate, mainly at more acidic pHs and enhances dissolution rates until 20 times for solutions with 15 mmol L^{-1} citrate. However, at pH 7.4 the effect is lighter and oxalate solutions (15 mmol L^{-1}) only enhances dissolution rates eight times respect to free organic ligand solutions. Dissolution is promoted by the attack to protons and organic ligands to the tremolite surface. Magnesium speciation in oxalate and citrate solutions shows that Mg citrate complexes are more effective than oxalate ones during the alteration of tremolite in magrophages, but this tendency is the opposite for interstitial fluids, being oxalate magnesium complexes stronger. The biodurability estimations show that the destruction of the fibers is faster in acidic conditions (macrophages) than in the neutral solutions (interstitial fluid). At pH 4, both ligands oxalate and citrate reduce the residence time of the fibers with respect to that calculated in absence of ligands. Nevertheless, at pH 7.4 the presence of ligands does not reduce significantly the lifetime of the fibers.

1. Introduction

The world has 200 million tons of identified resources of asbestos. Although the commercial use of these minerals is banned in many countries, nowadays there are still many active mines, being the biggest producers some Eurasian countries like Russia (1000 million tons), and Asian countries like China (400 million tons) and Kazakhstan (210 million tons) (USGS Mineral Commodity Summaries, January 2012). The leading consuming countries in 2007 were, in decreasing order tonnage, China (30%), India (15%), Russia (13%), Kazakhstan and Brazil (5% each), and Thailand, Uzbekistan and Ukraine (4% each). These eight countries accounted for about 80% of world asbestos consumption in 2007 (USGS Mineral Industry Survey, 2003–2007).

Although the vast majority of Asian mines are ultramafic chrysotile deposits, the presence of tremolite is common, as a natural impurity. Despite low concentrations, inhaled amphibole fibers tend to accumulate in the lung tissue and may contribute significantly to the mesothelioma risk of chrysotile miners and millers (Case, 1991; McDonald and McDonald, 1997). National Institute of Occupational Safety and Health (NIOSH) has developed a priority list of 10 leading work-related illnesses and injuries where occupational lung disease is first on the list (silicosis, asbestosis and byssinosis).

Toxicological studies (in vivo) show that interactions between fibrous material and biological environment are strongly dependent on both geometry and crystal chemistry of mineral fibers (Donaldson and Tran, 2004; Maxim et al., 2006; Bulsari et al., 2007; Stettler et al., 2008; Donaldson, 2009; Osmond-McLeod et al., 2011). Another factor that control the tendency of a fiber to cause a disease is the residence time of the particles in the lungs. The residence time is related to the particle biodurability, which is intrinsic for each mineral. The biodurability is the resistance of a particle to chemical dissolution in the body. Therefore to describe the dissolution in the lungs the solvent solution must be similar in composition to those found in the lungs. Thus the use of geochem-

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ical methods, as the traditional dissolution experiments, can be also useful to understand the biological breakdown of the fibers.

A number of studies have reported the dissolution rates of various silicate minerals as siliceous fibers (Scholze and Conradt, 1987), chrysotile (Hume and Rimstidt, 1992; Gunter and Wood, 2000; Oze and Solt, 2010), crocidolite (Werner et al., 1995), talc (Jurinski and Rimstidt, 2001) and tremolite (Mast and Drever, 1998; Oze and Solt, 2010) in simulated lung fluids. Moreover, others studies have confirmed the catalytic effect of organic ligands presents in lung fluids, as oxalate (Mast and Drever, 1998) or citrate (Ramos et al., 2011). These ligands are able to form strong complexes with cations as Al and Mg, promoting the release of these structural cations to solution and consequently enhancing dissolution rates. Therefore, the aim of this study is to evaluate tremolite dissolution rates in mimicked lung-fluids, including citrate and oxalate as a proxy for organic acids in alveolar fluids and to estimate the biodurability of the tremolite particles. Although in vitro experiments do not reproduce the complexity of processes that can occur in human body, they provide a benchmark to understand the degradation of these particles.

2. Materials and methods

2.1. Characterization of the mineral sample

All the experiments were carried out with tremolite collected in an old serpentine quarry next to K29 of A-395 road, in Sierra Nevada (Granada, SE Spain). X-ray diffraction (XRD) analysis shows a pure tremolite phase without accessory/companying minerals. We have not grinded the sample to avoid crushing the initial size of the fibers. The natural tremolite was pretreated to enrich the sample in fine particles (<4 μm equivalent spherical diameter) by repeated sedimentation–suspension in water. The supernatant was dried in an oven at 40 °C and the particles were recovered with acetone. Finally, it was stored in a polyethylene bottle as the starting material. Chemical analysis of major elements was performed by X-ray fluorescence (XRF). The calculated structural formula corresponds to a tremolite:

$$Ca_{1.84}Na_{0.17}(Mg_{5.08}Fe^{2+}_{0.17})(Si_{7.88}Al_{0.12})O_{22}(OH)_{2.23}$$

The corresponding atomic ratios Mg/Si, Ca/Si and Na/Si are respectively 0.645, 0.233 and 0.0216. Scanning electron microscopy (SEM) images show mainly prismatic and acicular structures that forms fiber bundles, with a wide variety of ratios length:diameter. The material is very friable and a very large number of extremely fine fibers are observed (Fig. 1). The specific surface area was measured by BET using a 5-point N_2 adsorption isotherm obtaining a value of 0.49 $m^2\ g^{-1}$ with an associated uncertainty of at least 10%.

2.2. Flow through dissolution experiments

Dissolution experiments were performed in single-pass, non-stirred, flow-through cells, which facilitated the measurement of the dissolution rate under fixed saturation state conditions by modifying flow rate, initial sample mass and input solution concentration. The reactors were fully immersed in a thermostatic water-bath held at a constant temperature of 37 ± 1 °C. The flow rate was controlled with a peristaltic pump that injects the input solution into the bottom chamber of the cell (0.02 mL min^{-1}). The tremolite sample is confined within the upper chamber (reaction zone) by using two membrane filters: a 5 μm nylon mesh plus a 1.2 μm Durapore membrane at the bottom and a 0.45 μm Durapore membrane at the top. The total volume of the cell was 46 mL and the solid mass added to each cell was approximately between 0.1 and 0.5 g to yield a solid:solution ratio between 2 and 10 g L^{-1}.

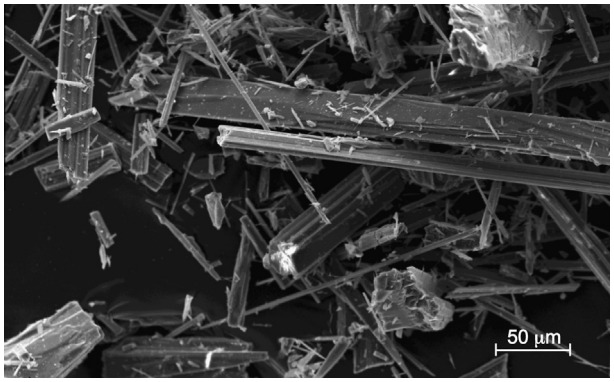

Fig. 1. SEM image of the micromorphology of the tremolite used as starting material.

In each run, the flow rate and the input pH were held constant until steady-state conditions were achieved. The steady state was assumed to prevail when the Si output concentration remained fairly constant, differing by less than 6% between consecutive samples (Rozalen et al., 2008). Reaction times were from 1000 to 1800 h depending on the pH and citrate/oxalate concentration. At steady state, dissolution is expected to proceed under far-from-equilibrium conditions. All the experiments consisted of a single stage; the cell was dismantled after the steady state was achieved.

After sampling every 24 h, the pH of the output solutions were immediately measured at room temperature by using a Crison combination electrode standardized with pH 4.01 and 7.00 buffer solutions. The reported accuracy was ±0.02 pH units. The difference in the pH value between both room and experimental temperature was less than the accuracy of the measurement, thus no temperature correction was applied (Ramos et al., 2011). An aliquot was separated for oxalate or citrate analysis. Then the output solutions were acidified to pH 3 with HNO_3 to prevent the precipitation of Mg-bearing phases during storage for further analyses.

The Si concentration in every output solution was determined by colorimetry, using the molybdate blue method (Grasshoff et al., 1983) with a detection limit of 5 ppb and a 5% associated error. The concentration of oxalate was measured by ion chromatography (IC) using a Metrohm 761 Compact Ion Chromatograph with a Metrosep A Supp 4-250 column with chemical suppression. The eluent was prepared with 1.7 mmol L^{-1} $NaHCO_3$ and 1.8 mmol L^{-1} Na_2CO_3. The detection limit is 0.007 mmol L^{-1} and the associated error 5%. Citrate was also measured by IC with a Metrosep Organic Acids column. The eluent was prepared with 0.5 mmol L^{-1} H_2SO_4/15% acetone. The detection limit is 0.03 mmol L^{-1} and the associated error 3%.

2.3. Simulation of lung fluids

The composition of the input solutions mimics the fluids found in the human lung, the so-called Gamble's solution. In this study the solutions were prepared by using the formulation of Jurinski and Rimstidt (2001) with additional modifications (Table 1). Saline solutions have the same molar composition, but Mg and Ca salts were substituted by Na salts to avoid structural cations of tremolite. Phosphate salts were also avoided, because phosphate is an important interference in the Si analysis.

When fibers are respired the particles can come into contact with both macrophage cytoplasm and interstitials fluids (Collier et al., 1992). We have chosen three working pHs: 4 (corresponding with macrophages), 5.5 (middle check point) and 7.4 (correspond-

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