

Marie Strnadova,  
Daniela Podloucka,  
Jiri Hamacek,  
Ales Helebrant  
Department of  
Glass and Ceramics,  
Institute of Chemical  
Technology in Prague,  
Technika 5 no 25,  
CZ-Prague 6  
E-mail: marie.  
strnadova@vscht.cz

# The Effect of Heat Treatment of Glass Fibers on their Phase Composition and Solubility in Simulated Lung Fluid

Dedicated to the 15<sup>th</sup> Conference on Refractory Castables (24./25.05.2005, Prague/CZ)

## Abstract

Some of the insulating materials made of ceramics and glass fibers do not satisfy the present standards, in particular regarding biopersistence. The estimation of their biopersistence is usually carried out using both in-vivo and in-vitro tests. The present testing of glass fibers determined that the risk of carcinogenicity evidently increases with increasing biopersistence. The purpose of this study was to determine a normalized dissolution rate of heated and unheated glass fibers and to discuss the mechanism of glass fibers dissolution in the simulated lung fluids (SLFs) using in-vitro flow-through tests. Corrosion of both heated (crystalline) and unheated (amorphous) glass fibers was investigated. The NR [ $\text{g}\cdot\text{m}^{-2}/\text{day}$ ] (normalized dissolution rate) for unheated and heated glass fibers was determined. This rate (NR) increased with increasing flow rate. Most probable rate controlling mechanism of glass matrix dissolution is the transition of surface reaction products through the solution boundary layer adjacent to the fiber surface. The first results show that

the dissolution rate of the heated glass fibers is lower than of the unheated glass fibers in both of the simulated lung fluids.

## Introduction

In recent years there has been increasing interest in the health effect of inhaled fibrous materials [1,2]. Diseases from asbestos exposure take a long time to develop. Most cases of lung cancer or asbestosis in asbestos workers occur 15 or more years after initial exposure to asbestos. The time between diagnosis of mesothelioma and the time of initial occupational exposure to asbestos commonly has been 30 years or more. Cases of mesotheliomas have been reported after household exposure of family members of asbestos workers and in individuals without occupational exposure who live close to asbestos mines.

In general, it is believed that fibers less than  $0,2 \mu\text{m}$  in diameter and longer than  $10 \mu\text{m}$  are most likely to induce tumors [3].

For these reasons, most of the studies have been conducted to measure the dissolution rates of various inorganic fibers using in vivo and in-vitro tests [4-9]. In vivo and in-vitro

tests are usually executed for determination of dissolution rate of man-made vitreous fibers (MMVF) in physiological solutions. In-vivo tests are conducted on rats. There are suggested three types of in-vivo tests: long-term inhalation, abdominal and tracheal injection. These tests are fairly expensive and time consuming. In-vitro static and flow-through tests are generally used for the testing of glass dissolution; the flow-through process (EURIMA test) was proposed and evaluated as the standard procedure for MMVF by Sebastian *et al.* [10].

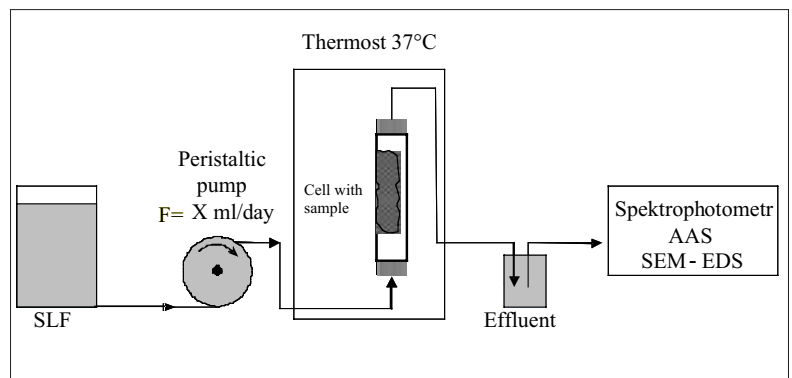
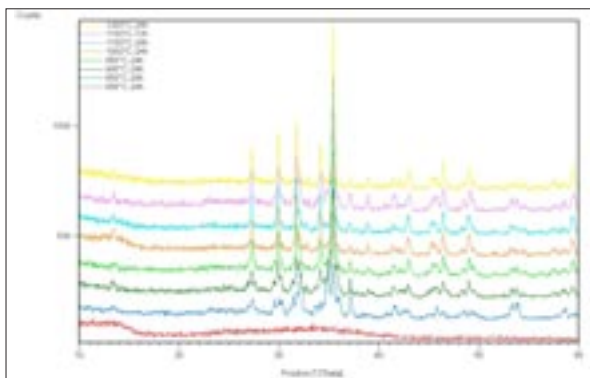
This study presents the results of the dissolution rate of the glass fibers, especially the effect of heat treatment on phase composition and solubility in the simulated lung fluid.

## Experimental methods

Glass fibers of composition (in mass %)  $\text{SiO}_2$  62,90,  $\text{CaO}$  30,73,  $\text{MgO}$  5,81,  $\text{Al}_2\text{O}_3$  0,25 and  $\text{Fe}_2\text{O}_3$  0,11 were investigated. These fibers were heated from 800 to  $1200^\circ\text{C}$  for 24 h. X-ray diffraction detected a crystalline phase of the heated fibers. The amount of the crystalline phase was increased with increasing heating temperature. X-ray diffraction detected a crystalline phase of the

Fig. 1 (left)  
X-ray diffraction pattern of heated fibers (main crystalline phase is wollastonite card 27-0088)

Fig. 2 (right)  
Schema of flow-through test



heated fibers (Fig. 1). The flow-through tests were carried out on the fibers heated at 1100°C for 24 h. The chemical composition of unexposed fibers was analyzed using X-rays fluorescence analysis (XRFA). The specific surface 0,136 [m<sup>2</sup>.g<sup>-1</sup>] of the tested material was determined using BET method. As a corrosive medium the simulated lung fluid (SLF) was used. Two types of the SLF were used. The SLF with a pH of 4,5 (intracellular lung fluid- inside of macrophages) and another had a pH of 7,4 (extracellular lung fluid) (Tab. 1). The tests were carried out at 37±0,5°C in flow-through configuration [11]. The experimental arrangement is shown in Fig. 2. It begins with a plastic container containing the simulated lung fluid (left side) connected to a multiple line peristaltic pump and then to the sample cells, which contain an amount of fibers. The cells with the samples are inside of a thermostat, which contains distilled water. At the end of the configuration is a collection bottle. The collection bottles are used to monitor the flow rate which were set on 60 and 120 ml/day, but real rates were calculated after experiment. The real flow rates were 67,135 [ml/day] for the amorphous fibers and 69,124 [ml/day] for the crystalline fibers. The highest are within the range recommended by EURIMA test guideline [10]. The solutions at output were analyzed after time intervals using AAS for Ca and Mg determination, the total amount of Si in the solution was determined by spectrophotometry. The surfaces of exposed fibers were observed by scanning electron microscopy (SEM-EDS).

### Results and Discussion

The results are shown in Fig. 3,4 in the form of the time dependencies of normalized mass release NLi, which is given by the amount of component i in the solution (mi), divided by sample surface (S) and by mass fraction of component i (xi) in the glass fiber. The slope of the tangent characterizes the rate of dissolution at any time. In the case of congruent dissolution, the curves for all components should be the same. Evidently, the dissolution in both SLFs was incongruent. At the beginning of the interaction, for the unheated and for the heated fibers, the selective leaching Ca and Mg was observed in SLF4,5, which was caused by Me<sup>2+</sup>-H<sub>3</sub>O<sup>+</sup> interdiffusion

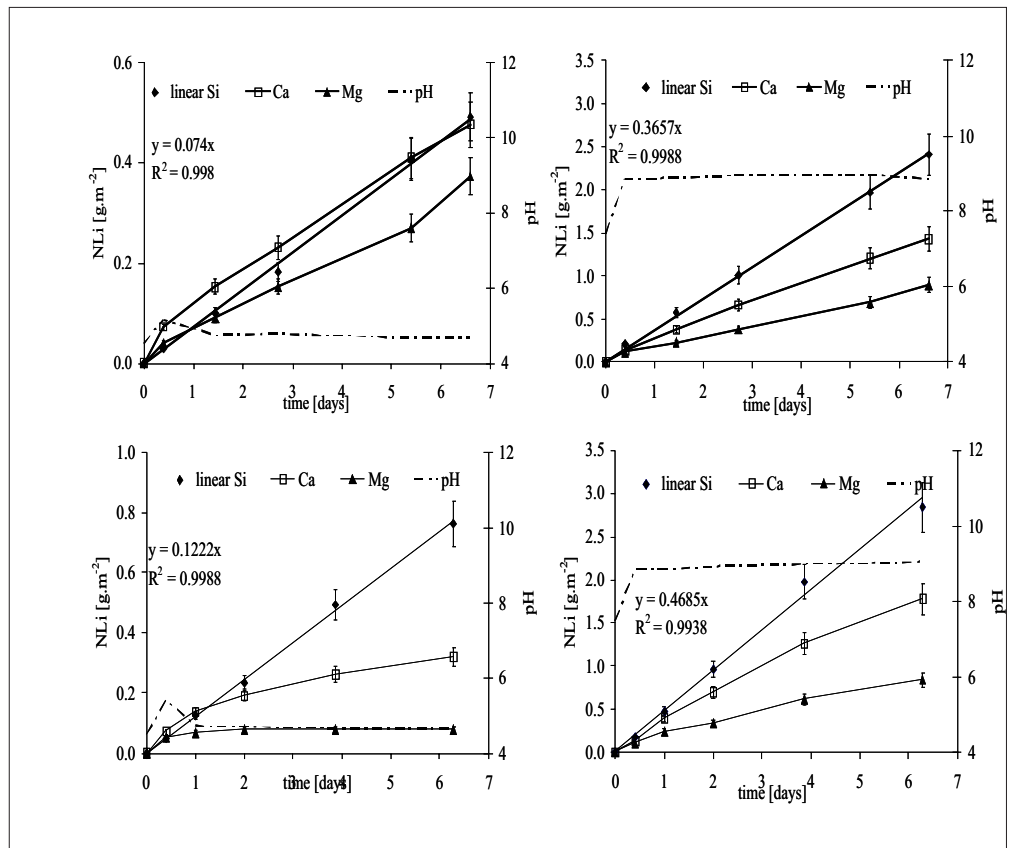


Fig. 3 The time dependencies of normalized mass release of element i of unheated fibers (two upper graphs are for adjusted flow rate 60, lower 120 ml/day)

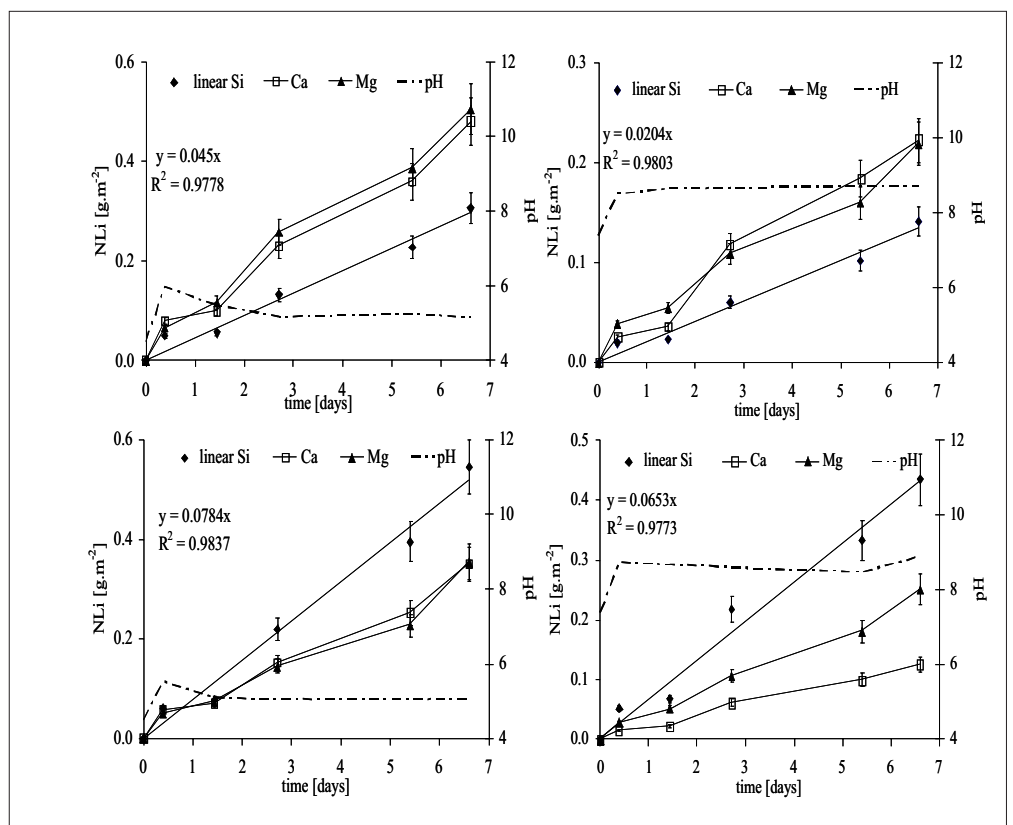
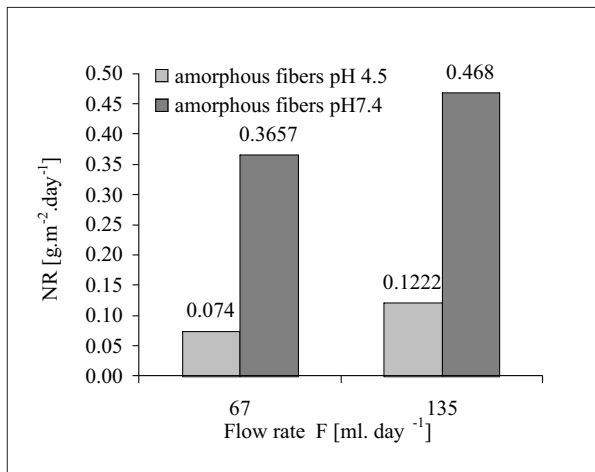
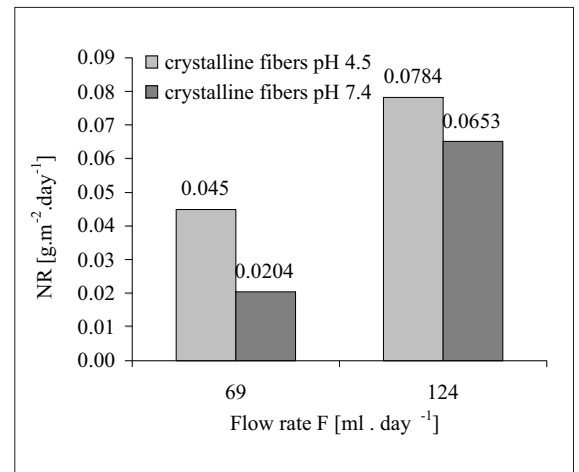


Fig. 4 The time dependencies of normalized mass release of element i of heated fibers (two upper graphs are for adjusted flow rate 60 and lower 120 ml/ day)

**Fig. 5 (left)**  
The normalized dissolution rate of the unheated fibers



**Fig. 6 (right)**  
The normalized dissolution rate of the heated fibers



Component	Conc. [mg/l]	Component	Conc. [mg/l]
NaCl	7120	H <sub>2</sub> NCH <sub>2</sub> CO <sub>2</sub> H (glycine)	118
NaHCO <sub>3</sub>	1950	Na <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> ·2H <sub>2</sub> O (citrate)	152
CaCl <sub>2</sub>	22	Na <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>6</sub> ·2H <sub>2</sub> O (tartrate)	180
Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O	373	NaC <sub>3</sub> H <sub>3</sub> O <sub>3</sub> (pyruvate)	172
Na <sub>2</sub> SO <sub>4</sub>	79	C <sub>3</sub> H <sub>6</sub> O <sub>3</sub> lactic acid (90%)	156
MgCl <sub>2</sub>	99	HCl (diluted 3:5) [ml]	4.1 <sup>a</sup> /0.04 <sup>b</sup>

**Tab. 1** Composition of simulated lung fluid (SLF). Denotes: SLF with pH=4,5 (a), SLF with pH=7,4 (b)

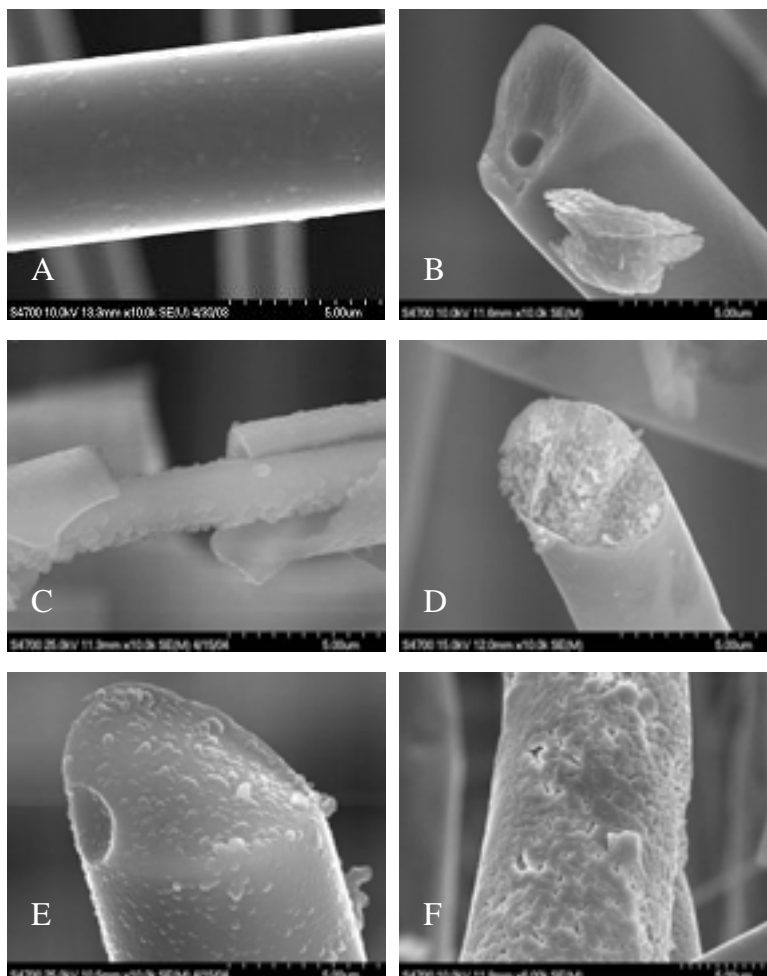
in fiber surface. On the other hand for the unheated fibers, the lower NLMe values then the NLSi ones indicate the back precipitation of Ca and Mg at longer times of interaction in both solutions. The lower NLMe values then the NLSi were indicated for the heated fibers in SLF (4,5-7,4) only for flow rate 69 [ml/day] but for the higher one the opposite is true.

The NLSi time dependence was linear in all cases. The dissolution rate of the fiber NRSi [g·m<sup>-2</sup>/day] was determined as the slope of linear fit of experimental data. The lower rates of dissolution at pH = 4,5 are in good agreement with minimum of glass dissolution rates observed in slightly acidic solutions (e.g. [12]).

The higher dissolution rates at higher solution flow rates can be explained using a simple mathematical model [13] assuming that the dissolution consists of two subsequent steps: surface reaction and transport of surface reaction products through the solution layer adjacent to the fiber surface. Then the dissolution rate of glass can be calculated using equation (1):

$$NR_{Si} = \frac{dm_{Si}}{x_{Si} S dt} = \frac{k^+ D/h}{k^+ + D/h} (c_s - c) \quad (1)$$

where  $k^+$  is the surface reaction rate constant,  $D$  is the diffusion coefficient of surface reaction products through the solution boundary layer,  $h$  is the thickness of the diffusion layer and  $c_s$  and  $c$  are saturated and actual concentration of Si in the solution. Constant NRSi values allow the assumption that the steady state was achieved very soon. The measured concentrations in solution were



**Fig. 7** Micrographs of fibers: A: unheated B: heated before exposure; C: unheated D: heated pH 4,5 after 7 days in SLF; E: unheated F: heated pH 7,4 after 7 days in SLF

approximately the same for all flow rates. Values of  $c_s$ ,  $k^+$  and  $D$  should be the same in the same solution. Then only the lower value of  $h$  could be responsible for the higher dissolution rate NRSi.

This assumption is in agreement with the chemical engineering models considering the decrease of boundary layer thickness with increased solution flow rate. Furthermore, considering that the surface reaction is faster than the transport of its products through the solution layer, the equation (1) can be simplified to Noyes-Nernst's equation (2) assuming that  $k^+ \gg D/h$ :

$$NR_{Si} = \frac{D}{h}(c_s - c) \quad (2)$$

The normalized dissolution rate of the unheated (amorphous) fibers was lower in the SLF which had a pH of 4,5 and higher of the heated (crystalline) fibers in the SLF with pH 7,4. This is in a good agreement with earlier studies about glass behavior in the acid and alkaline solutions. The normalized dissolution rates of the heated (crystalline) fibers were lower in both of the SLFs than for the unheated fibers Figs. 5, 6. The NRSi was increased with the increasing flow rate in all cases.

The calculations using the geochemical code PHREEQC [14] showed the possibility of back precipitation of dissolved components in the form of silicates during the interaction. Therefore, another control mechanism of dissolution could be the transport of dissolved components through the precipitated layer,

which can be described formally by the same equations.

The corroded fibers and corrosive products were determined by SEM (Fig. 7). This analysis confirmed the assumption of back precipitation.

## Conclusions

The MMVF were developed as asbestos substitutes. There is a concern that some of the MMVF may also present health risks. These results showed the important differences in solubility of the glass and crystalline fibers and may indicate that the so called bio-soluble fibers could become less soluble and therefore potentially carcinogenic during the time of their use as a thermally insulating material. Based on this study and earlier experiments should be definitely recommended that these fibers can be used up to 800°C without crystallization problems.

## Acknowledgement

This study was part of research program MSM 6046137302 „Preparation and research of functional materials and material technologies using micro and nanoscopic methods“.

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