

PHYSICOCHEMICAL CHARACTERIZATION OF ASBESTOS AND ATTAPULGITE MINERAL FIBERS BEFORE AND AFTER TREATMENT WITH PHOSPHORUS OXYCHLORIDE *

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ABSTRACT

Among the hydrous silicates belonging to the serpentine, amphibole, and clay mineral families, chrysotile, crocidolite and attapulgite fibers reacted most strongly with phosphorus oxychloride. While the reactivity of crocidolite was linked mainly to the sodium cations of its structure, the reactivities of chrysotile and attapulgite correlated best with their high hydroxyl group content. The TG/DTG curves of chrysotile and attapulgite revealed significant modifications of their dehydroxylation profiles. IR spectra and specific surface measurements confirmed that, most probably, the phosphorylation process created: (a) a phosphorus coating at the surface of the chrysotile fibers, and (b) an obstruction of the pores by phosphorus compounds with the attapulgite fibers.

INTRODUCTION

Among the various hydrous silicate minerals, three families can be selected for their fibrous nature, and their peculiar structural and surface properties. The surface reactivity, mostly consisting of physical and chemical interactions, is controlled both by the chemical composition of the exposed planes, and by the structural organization of the fibers.

The chrysotile asbestos belongs to the serpentine mineral family, as do the antigorite and the lizardite who share the same chemical composition. The basic structure is a sheet of silica tetrahedra, overlaid with a sheet of magnesium hydroxide (Mg–OH). In the case of chrysotile, the differences in the lattice parameters of the silica and brucite layers induce the composite to adopt a curvature, with the Mg–OH groups on the external surface [1].

The amphibole asbestos minerals, i.e. crocidolite, amosite and anthophyllite, are double chains of linked silica tetrahedra that are cross-linked with

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bridging cations. Each chain consists of silica tetrahedra which share two of their three basal oxygens along the fibre axis, the third being common to two apposite-facing single-chain structures [2]. The various amphiboles have the same basic structure, with the bridging cations in well-defined sites. Any variations observed are related to the cation content [3].

Attapulgite is a crystalline hydrated magnesium aluminum silicate which belongs to the clay mineral family. As described by Bradley [4], the structure of attapulgite consists of a double chain of tetrahedrons of silicon and oxygen. The sheets thus formed are held together by magnesium atoms in six-fold coordination; the result is octahedral sheets similar to those of layered clay minerals, but different in that they are continuous in only one direction. This gives to the attapulgus clay its fibrous three-dimensional structure. Water is present in this mineral in three different structural positions: zeolitic water, crystal water and structural water [5].

Adsorption phenomena and the surface reactivity of these hydrous silicate fibers are extremely important. However, refined studies aimed at comparing these physicochemical properties presented some difficulties. After various tests with several compounds, phosphorus oxychloride (POCl_3) was selected for its acidic character and its known reactivity with hydroxyl (O-H) groups of basic character [6]. Since these basic O-H groups are present in the three silicate minerals described above, this study was undertaken in order to gain further insight into these functional groups in both the structural organization and chemical composition of these minerals.

EXPERIMENTAL

The minerals used in this study (three families of hydrous silicates) are listed below.

Serpentine family. (a) chrysotile asbestos, very short fiber from the commercial grade 4T30 (the isolation procedure (Kimmerle, Roberge and Nadeau, unpublished results), based on the procedure of Jolicoeur et al. [7], will be published elsewhere); (b) antigorite, from a collection of the Canadian government.

Amphibole family. (a) crocidolite asbestos; (b) amosite asbestos; (c) anthophyllite asbestos (all three samples were obtained from the Union Internationale Contre le Cancer (UICC)).

Clay family. (a) attapulgite, as contained in the commercial product Attagel[®] (type 40; Engelhard Minerals and Chemicals Corporation, GA, U.S.A.).

Each mineral sample was characterized before and after the POCl_3 treatment, with the following methods: (a) Fourier transform infrared (FTIR) spectroscopy (Model MX-1, Nicolet Instrument Corp., Madison, WI); (b) Thermogravimetry and differential thermal analysis (TG/DTG) (Model TGS-2; Perkin-Elmer (Canada) Ltd., Montréal, Québec, Canada); (c) Zeta

potential (ZP), in 1 mM KCl, pH 7.0 (Zeta-Reader Komline-Sanderson, model ZR-II; Noram, Pointe-Claire, Québec); (d) Specific surface area (SSA), by nitrogen adsorption (Quantasorb, model QS-10, Quantachrome Corp., Syosset, NY). Before the BET analyses, each sample was conditioned overnight at 110°C, under a helium gas stream.

Twenty-four hours before the treatment with POCl_3 , a known amount of each fiber was dried at 100°C. Then, following the phosphorylation process carried out in a special reactor and under a nitrogen atmosphere, the phosphorylated samples were heated at 300°C for 2 h [8–10]. For the phosphorus determinations, a Technicon Auto-Analyzer II was used (industrial method no. 94-70).

RESULTS AND DISCUSSION

The main physicochemical properties of the silicates studied here are shown in Table 1, whilst Table 2 summarizes their surface properties and the location of their hydroxyl groups.

Serpentine family

As judged by the percentage of phosphorus retained on the fibers, we observed the strongest reactivity with chrysotile (Table 3). In relation to the treatment, we observed a decrease in the SSA and a shift of the ZP, from a positive to a negative value. For the antigorite sample, only a slight shift in the ZP was observed. FTIR spectra (Fig. 1) show that the phosphorylation process caused some modifications in the area of the Si–O vibrations (1100–800 cm^{-1}). It is believed that these modifications are due to the superimposition of the vibrations of phosphate groups which have vibrations in the area between 1200 and 800 cm^{-1} [10].

TABLE 1

Description of the four hydrous silicates under study

Type of silicate	Mineral family	Ideal formula	Morphology
Chrysotile asbestos	Serpentine	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$	Fibrous
Antigorite	Serpentine	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$	Granular
Amosite asbestos	Amphibole	$(\text{Fe}^{2+}, \text{Mg})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$	Fibrous
Anthophyllite asbestos	Amphibole	$(\text{Mg}, \text{Fe}^{2+})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$	Fibrous
Crocidolite asbestos	Amphibole	$\text{Na}_2\text{Fe}_3^{2+}\text{Fe}_2^{3+}\text{Si}_8\text{O}_{22}(\text{OH})_2$	Fibrous
Attapulgite	Clay	$\text{Si}_8\text{Mg}_2\text{Al}_2\text{O}_{20}(\text{OH})_2(\text{OH}_2)_4 \cdot 4\text{H}_2\text{O}$ $\text{Si}_8\text{MgAl}_3\text{O}_{20}(\text{OH})_3(\text{OH}_2)_3 \cdot 4-5\text{H}_2\text{O}$	Fibrous

TABLE 2

Reactivity of the silicates under study

Type of silicate	Surface properties	Localization of the hydroxyl groups
Chrysotile	Basic and very reactive	On surface and at extremities of fibers
Antigorite	Weakly acidic; slightly basic	Hidden inside layers with a few basic sites
Amosite, anthophyllite, crocidolite	Weakly acidic	Inside layers and at extremities of fibers
Attapulgite	Weakly acidic	Mostly inside channels hidden in the highly crystalline structure

The TG/DTG curves of the chrysotile and antigorite samples (Fig. 2), confirmed that the modifications induced on the chrysotile fibers were significantly more important. The main change was that the dehydroxylation speed of the phosphorylated chrysotile fibers was slowed down (DTG curves between 600 and 800°C). This can be interpreted as a decrease in the porosity of the fibers, and/or as a coating effect of the phosphorus compounds produced by the POCl_3 treatment. Phosphorus compounds are known to have a high thermal stability [11].

Amphibole family

Among those samples, it was observed (Table 3) that the crocidolite fibers had the strongest reactivity (3% phosphorus retained). However, contrary to the chrysotile sample, the phosphorylation process did not appreciably

TABLE 3

Modifications of the physicochemical properties of silicates by phosphorylation

Type of silicate	Phosphorus retained (wt.%)	Zeta potential (mV)		Specific surface area ($\text{m}^2 \text{g}^{-1}$)	
		Before POCl_3	After POCl_3	Before POCl_3	After POCl_3
Very short					
chrysotile	3.6	+ 39	- 26 ^a	38	24 ^a
Antigorite	1.0	- 32	- 36 ^a	4	4
Crocidolite	3.0	- 50	- 55 ^a	8	7
Amosite	1.0	- 51	- 55 ^a	6	5
Anthophyllite	1.0	- 44	- 46	9	9
Attagel	4.8	- 23	- 30 ^a	160	40 ^a

^a A significant shift in properties is noted.

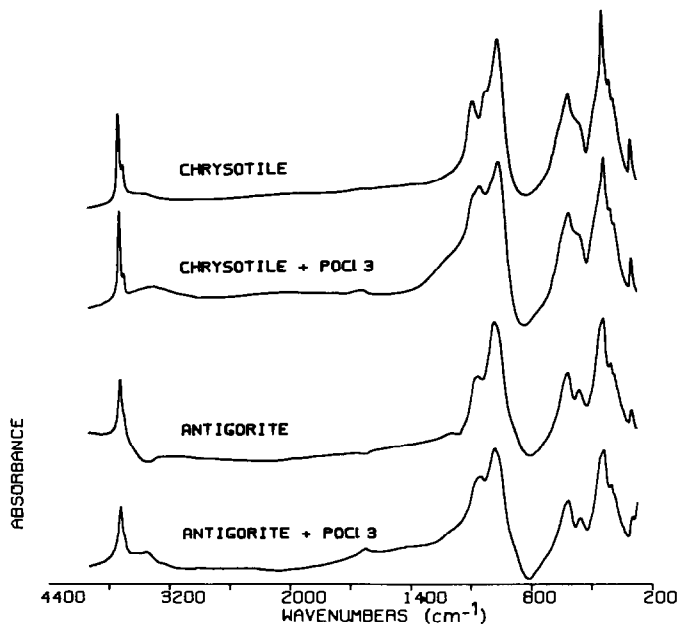


Fig. 1. FTIR spectra of chrysotile and antigorite before and after treatment with POCl_3 vapor.

change the physicochemical properties of these fibers. Having negative ZP and low SSA before the treatment, no significant changes have been observed afterward. However, IR spectra showed small changes in the $1200\text{--}1000\text{ cm}^{-1}$ region (data not shown). Because the thermal degradation of this mineral is often associated with simultaneous weight increases due to the oxidation of Fe^{2+} to Fe^{3+} , and small weight losses due to the dehydroxylation process [12], TG analyses on amphiboles cannot be considered a sensitive method for evaluating chemical modifications.

The strong reactivity of crocidolite during the phosphorylation process was linked to its peculiar chemical nature. Contrary to amosite and anthophyllite fibers, crocidolite (also known as the alkaline amphibole) has sodium cations and ferric iron [13]. Previous studies [14,15] have shown that a phosphatation reaction is an efficient way to protect iron and that such a phosphatation reaction is favored, or even stimulated, in the presence of alkaline ions.

Clay family

Among this mineral family, the commercial product Attagel was selected because attapulgite fibers were not available in large quantities. Basically, this sample is structurally and chemically similar to attapulgite, but contains more carbonates. After the POCl_3 treatment, chemical analyses revealed that

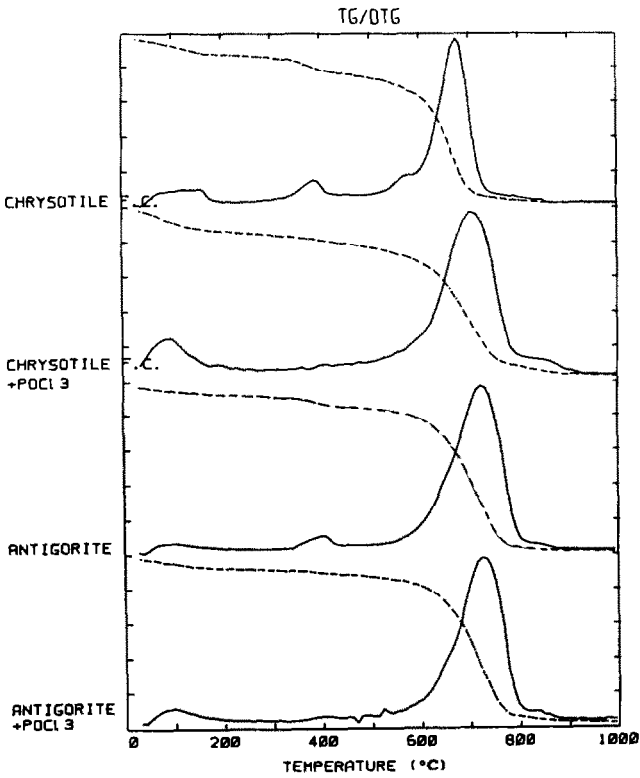


Fig. 2. TG/DTG curves of chrysotile and antigorite before and after treatment with POCl_3 vapor.

4.8% of phosphorus was retained on the fibers (Table 3). The chemical modification was associated with a strong decrease in SSA and an increase in the negative ZP value. The results from Fig. 3 and Table 4 illustrate the

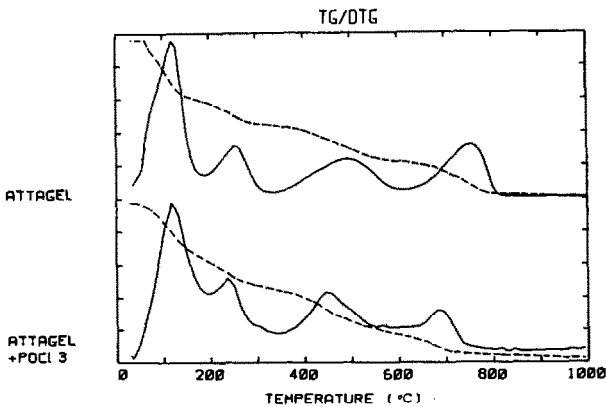


Fig. 3. TG/DTG curves of Attagel before and after treatment with POCl_3 vapor.

TABLE 4

Thermogravimetric profile of Attagel before and after phosphorylation (results are expressed as wt. % loss)

Type of silicate	Dehydration			Dehydroxylation Structural hydroxyl groups
	Zeolite water	Crystallisation water		
		First step	Second step	
Attagel (untreated)	6.2	2.4	3.8	3.6
Attagel (phosphorylated)	4.9	2.3	3.8	2.3

thermogravimetric profile of Attagel before and after the phosphorylation process. Observed were: (a) a decrease in zeolite water; (b) no modification of the crystallization water; (c) a modification of the dehydroxylation pattern; and (d) a reduction of the weight loss.

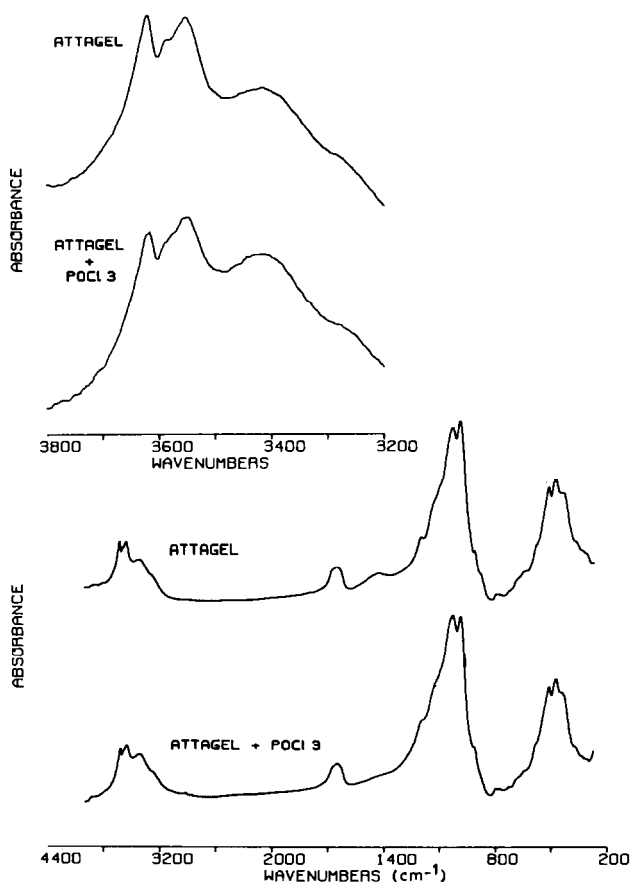


Fig. 4. FTIR spectra of Attagel before and after treatment with POCl_3 vapor.

The FTIR spectra before and after the POCl_3 treatment are illustrated in Fig. 4. An extended view of the vibration bands between 4000 and 3000 cm^{-1} , which correspond to the vibrations of hydroxyl (O–H) groups, is also illustrated. According to Vanscoyoc et al. [16], the band at 3616 cm^{-1} corresponds to the vibrations of structural O–H, while the bands at ~ 3550 and 3404 cm^{-1} correspond to the vibrations of crystalline O–H groups, linked by one or two hydrogen bonds respectively. The comparison of the spectra before and after the phosphorylation process showed: (a) the presence of phosphate groups in the area of the vibrations of Si–O groups (between 1200 and 800 cm^{-1}); (b) there is a decrease in the relative intensity of the band at 3616 cm^{-1} (structural O–H groups), when compared to the vibrations at 3550 and 3404 cm^{-1} (crystalline O–H groups). These results confirm our TG/DTG data and favour the interpretation that it is mainly the structural O–H groups (basic character) that react with the POCl_3 vapor.

CONCLUSIONS

From our data, one can observe that among all the hydrous silicates treated with POCl_3 , significant physicochemical modifications were demonstrated only for chrysotile asbestos and attapulgite. For the crocidolite fibers, despite the coupling of phosphate groups to the alkaline cations and ferric iron species, none of the physicochemical properties studied seemed to have been extensively modified. The modifications observed with chrysotile and attapulgite fibers were linked to the strong reaction of the structural O–H groups of these minerals with POCl_3 , namely: (a) the O–H groups at the surface of the chrysotile fibers; (b) the O–H groups in the open channels of the attapulgite fibers. Respectively, the phosphate compounds retained on the fibers form either a voluminous surface coating, or block the pores (channels) of the crystalline structure. Because the reduction in the biological activity of a fiber rich in O–H groups can be linked to modifications of these functional groups [6,8,9], experiments are now in progress to evaluate further the *in vitro* biological effects of these modified fibers.

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