

NOTES

SURFACE MODIFICATION OF CHRYSOTILE ASBESTOS UNDER THE INFLUENCE OF ALUMINIUM TRICHLORIDE

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It is well known that the introduction of Al into the serpentine structure with replacement of Mg by Al ions causes a shrinkage of the octahedral sheet (Smith, 1954; Roy and Roy, 1954). At the same time, the replacement of Si by Al ions leads to a contraction of the layer thickness. This contraction has been attributed to the net ionic charges in the tetrahedral and octahedral sheets. Replacement of Si by Al makes the tetrahedral sheet negative. Thus, adjacent sheets of the structure have ionic attraction in addition to the normal OH...O bonding (Brown, 1972; Brindley, Oughton and Youell, 1951). The results we are presenting are in agreement with those just described, but the system employed is quite unusual.

In order to increase the surface reactivity of chrysotile asbestos, it is a common procedure to hydrolyze the outer hydroxide sheet. The silicic sheet is much more favorable for the type of surface modifications we are currently performing in our laboratory (Papirer and Donnet, 1973).

Chrysotile has been treated by an organic solution (toluene-nitrobenzene 80/20) of AlCl₃ or AlCl₃ + HCl, with a concentration of 2 × 10⁻² mole l⁻¹. The amount

of reagent used is such that 1 g of asbestos is in contact with 1.5 × 10⁻³ mole of reagent. Other experimental details are shown in Table 1.

After treatment at 80°C under agitation, the asbestos is separated by filtration, purified by repeated solvent washing and dried. In order to carry out the chemical surface modification, the hydroxide sheet is hydrolyzed in an aqueous dispersion and in the presence of a complexing agent for the Mg ions. Such a procedure is sufficiently mild to eliminate only the external brucite layer.

It appears that the Mg is much more easily extractable from the treated chrysotile than from the initial one. Apparently, part of the hydroxide sheet has been destroyed during the AlCl₃ attack, thus Mg is more readily liberated. This behavior may point to a structural change which had occurred on the chrysotile surface during the treatment. Therefore, we examined the samples with X-ray powder diffraction; typical results are given in Table 1.

Some of the diffraction lines of the initial chrysotile either disappear or become weaker; the (202) reflection is no longer present in samples 3 and 4. The (020), (202),

Table 1. X-ray diffraction patterns of AlCl₃ treated chrysotile (Debye-Scherrer patterns)

Initial		1 AlCl ₃ + HCl (1 h)		2 AlCl ₃ + HCl (5 h)		3 AlCl ₃ (2 h)		4 AlCl ₃ (4 h)		Clinochrysotile indexation
d (nm)	I/I ₀	d (nm)	I/I ₀	d (nm)	I/I ₀	d (nm)	I/I ₀	d (nm)	I/I ₀	
0.737	10	0.737	10	0.737	10	0.776	6	0.737	10	002
				0.708	10	0.708	10	0.525	0.5	
0.460	6	0.455	5	0.452	6	0.455	4	0.450	4	020
						0.395	0.5			
				0.378	3	0.378	3			
0.370	10	0.367	10	0.363	10	0.363	10	0.364	10	004
		0.332	0.5	0.329	1	0.329	0.1	0.329	0.1	
								0.313	0.1	
								0.290	0.1	(130) or (201)
								0.273	1	202
0.260	1	0.265	2	0.263	2	0.260	2	0.260	1	202
0.254	2	0.254	2	0.253	2					
0.248	7.5	0.250	5	0.245	6	0.250	4	0.250	5	
		0.240	0.1	0.240	1			0.237	0.5	
0.221	0.5									204
0.210	0.5	0.211	2	0.208	1	0.213	1	0.211	1	204
								0.198	0.5	
						0.186	0.1	0.188	1	
0.192	2	0.185	1	0.180	0.1	0.182	1	0.182	2	008
0.176	1.5	0.176	1.5	0.173	1			0.176	0.5	206
								0.171	1	
0.155	6	0.155	6	0.153	3	0.155	5	0.154	3	060
								0.152	0.5	
								0.150	0.5	
0.132	2	0.132	2	0.132	1.5	0.133	2	0.132	1	402

(060) lines are weakened. Some new lines appear; more precisely, the (001) reflection is doubled. The intensities of these lines vary as a function of the durations of the treatment. Lines are also characteristic of mineral impurities already present in the initial sample, or formed during the treatment. Particularly, the line related to 0.332 nm, and a series of low intensity lines (sample 4) indicate that the impurity is probably β Fe₂O₃·H₂O which has been formed from the ferrous impurities existing in the initial chrysotile sample. The duplication of the lines of the series of reflection (002) (004) (008) shows an evolution of the *c* parameter. The basal spacing decreases from a value of 0.737 nm for the clinochrysotile to 0.708 for the end product. Other parameters, *a* and *b*, remain practically unchanged, with perhaps a slight reduction of the value of the parameter *b*, and a small diminution of the intensity of the lines (0*kl*0). The treatment influences the parameter *b*, but without destroying the structure of the layer (conservation of the tubular morphology). Moreover, the results of chemical analysis clearly indicate fixation of a non negligible amount of Al, (about 5.10⁻⁴ mole g⁻¹), whereas Mg is displaced. Further details will be given elsewhere (Papirer, Dovergne, Leroy, 1976). Apparently, Al atoms take the place of Mg atoms in the octahedral sheet and of Si atoms in the tetrahedral sheet leading to progressive formation of a mineral enriched in Al. Both the crystallographic measurements and the chemical analysis point to a modification of the surface layers of the chrysotile structure; the reaction product going towards amesite.

In conclusion, we have shown that the treatment of chrysotile with an organic solution of AlCl₃ leads to a structural modification of the surface layers of the asbestos.

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