Synthesis of Imogolite: A Tubular Aluminium Silicate Polymer

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Summary Heating weakly acidic dilute solutions containing hydroxyaluminium orthosilicate complexes gives a fibrous polymer, each fibre consisting of tubes about 2·2 nm external diameter and 1·0 nm internal diameter, essentially identical with those of the natural mineral, imogolite.

IMOGOLITE[1] is a naturally occurring hydrated aluminium silicate, which can be seen in high resolution electron micrographs to have the form of long tubes of about 2·2 nm external and 1·0 nm internal diameter, with a length of up to several micrometers. First recognized in 1962 as a component of Japanese ash and pumice soils, imogolite has subsequently been shown to be widely distributed in recent (800—30,000 years old) volcanic deposits, and to occur also as a minor component in some soils derived from crystalline rocks.

On the basis of electron diffraction pattern, composition, and the proven presence of orthosilicate anions, it has been proposed[2] that the walls of the tubes have a structure like that of a single sheet of gibbsite [$Al(OH)_3$] with orthosilicate groups replacing the inner hydroxy surface of the gibbsite tube. This gives an empirical formula $(HO)_3Al_2O_3SiOH$, which is also the sequence of atoms encountered on passing from the outer to the inner surface of the tubular model.

Since certain features in its natural occurrence suggested that this unique polymer might form from solution, the possibility of its synthesis has been successfully explored in conditions analogous to those in which gibbsite crystallizes. Imogolite tubes in a highly dispersed condition appeared in dilute solutions containing hydroxy-aluminium silicate complexes heated for a few days. The product was formed in the pH range 5·0—3·1 in solutions having various Si to Al ratios, but reaction was most rapid and nearly complete at pH $<4·5$ when a slight excess of silica over the theoretical requirement was present to inhibit boehmite (γ-AlOOH) formation. In a typical preparation, a solution containing 1·40 μmol cm^{-3} SiO_2 as monomer and 2·4 μmol cm^{-3} $AlCl_3$ was adjusted to pH 5 with NaOH, acidified by adding 1 μmol HCl and 2 μmol acetic acid per cm^{-3} of solution, then maintained near the boiling point. Imogolite was detected in the clear solution after one day, and approached a maximum yield in five. Its presence was recognized by its i.r. spectrum,[3] fibrous morphology, and electron diffraction pattern, all of which indicated a product only slightly less regular than the best natural specimens. Macroscopically, the formation of imogolite was indicated by a more than tenfold increase in the bulk of the centrifuged gel obtained on making the solution alkaline. Such imogolite gels typically contain about 0·1% of solids by weight, and presumably incorporate an open network of cross-linked imogolite tubes.

In the course of this work it has been observed that, even under conditions unfavourable for formation of the regular structure of imogolite, hydroxyaluminium cations react with silicic acid to give sols stable below about pH 5; the disperse phase in these appears to have structural analogies with imogolite, as indicated by its diffuse electron diffraction pattern, and its i.r. spectrum. Poorly ordered compounds of this type must play an important role in the transport of aluminium and silicon in acid soils and natural waters.

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