



VERY MUCH THE little brother for kaolin, halloysite ( $\text{Al}_4(\text{Si}_4\text{O}_{10})(\text{OH})_8 \cdot 4\text{H}_2\text{O}$ ), differs in that it usually contains water molecules between the two-layer aluminosilicate structural units – a similarity to the major smectite group mineral, montmorillonite.

This water is easily removed to yield a dehydrated form of halloysite. Because of the considerable difference in ionic size between aluminium and silicon in this two-layer structure, directional bending of the silica layer occurs.

This leads to the development of hollow tube-like crystal forms reflected in yet another piece of scientific jargon. Halloysite is classified as a *solenosilicate* – a small group of minerals exhibiting similar crystal form.

A better known solenosilicate is chrysotile that owes its fibrosity to the same phenomenon of directional bending of the crystal lattice layers. In contrast with chrysotile, however, halloysite's tube-like form is much shorter and microscopic rather than visible with high aspect ratio fibres. Inclusions of other substituting elements in the halloysite crystal structure serve to inhibit bending and rolling of the silicate sheets.

### Applications going up market

In terms of market uses halloysite has traditionally been sought after for fine high quality tableware manufacture – hard and soft porcelain as well as bone china. The New Zealand halloysite, first exploited as filler for paper primarily for the domestic market, came to prominence in the early 1970s when quality South

# Tubular clays

Rare, sophisticated, and upmarket, halloysite leads on the catwalks of clay. *Gerry Clarke* explains how this unique mineral shows much promise for new generation markets

Korean halloysite was in short supply and Japanese demand growing.

The reactivity of halloysite, greater surface area compared with kaolinite, and its fine particle size permits manufacturers to produce vitreous products with very high translucency.

The key is the proper and effective dispersion of halloysite in the ceramic body so avoiding larger aggregated particles that remain and cause opacity in vitreous bodies. In this regard halloysite is far more efficient than is kaolinite.

Later, applications in technical and advanced ceramics evolved. The main market in the technical sector is for use in molecular sieves for water adsorption and gas separation.

Other areas are in the manufacture of honeycomb catalyst supports in car exhaust systems, other catalyst applications and filters. Increasing uses in the so-called advanced ceramics field essentially replaced metal parts in electronic and heat resistant applications.

In very recent years a new piece of jargon has become everyday language

reflecting the emergence of high-value ultra-small engineered applications – nanotechnology – and with it a clutch of “nano” companies looking for mega profits (see *IM February '08 p.60*).

Halloysite, because of its characteristic tube-like crystal form and reactivity, has a range of potential nano applications that hold the promise for substantial growth. Whilst some are in the developmental stage there are a range of patents in the wings.

### How rare is halloysite?

Geologically and commercially halloysite is rare. Whilst halloysite is widely reported as a minor, mineralogically interesting, constituent in kaolinitic clay mineral assemblages, its accumulation in commercially significant proportions is so rare it is only known as such in a very few countries.

This is because the conditions for its formation are uncommon and the resulting accumulations easily worn and eroded if unprotected. Tending not to survive over time many halloysite deposits are

geologically very young and not very extensive.

Essentially the mineral forms by the relatively low temperature alteration of feldspar. It has been suggested that halloysite may be a precursor to kaolin as a weathering product which, to some extent, may explain further why it is rare.

In other words, for halloysite accumulations to persist in nature, some persistent and unusual geological conditions are required to halt its degradation.

Somewhat special conditions have given rise to the exceptionally large commercial deposits in northern New Zealand and mid-western USA. The ages of these deposits are quite distinct with parent rocks formed at the opposite ends of Phanerozoic time.

The best known commercially-established halloysite deposits are situated some 240km north of Auckland at Matauri Bay in New Zealand's North Island. They are the alteration product of volcanic rocks that were formed in the most recent of geological times, up to 5.4m. years ago, in the Pliocene to Quaternary periods.

Over time these volcanic rocks succumbed to hydrothermal alteration caused by warm percolating primary fluids superimposed by deep and intensive surface weathering in a humid climate – a kind of natural in-situ sweating process.

While the degree of alteration varies from place to place in the region the commercial clay mineralisation has been described as unique with a high proportion of halloysite, 50%, in the soft upper layer clay fraction that averages 15 metres in thickness. Occurring with the halloysite is fine silica, kaolinite, allophane and minor feldspar.

The re-emerging commercial halloysite deposits in the USA's mid-west are situated some 100km south of Utah's Salt Lake City. They lie along the Rocky Mountains' Wasatch Front in a region known as the Tintic Mining District.

They are the alteration product of very fine sedimentary rocks that were laid down at a time when life was only just beginning, around 600m. years ago, in the Cambrian period.

Extensive and very fine soft clay sediments accumulated to a thickness of around 80 feet on a shallow sea floor. Over time these soft clays were covered

by thick sequences of mud that ensured they remained undisturbed for hundreds of millions of years.

At some point in time later the water level fell as it began to recede and finally disappear. But, as it did so the clay was buried in limestone derived from the surrounding mountains. The clay was thus entombed and remained undisturbed for another 34m. years or so when geothermal processes raised the regional temperature and caused the original clay to alter to produce, relatively recently, extensive halloysite deposits – again, a kind of in-situ sweating process.

### **Imerys Tableware NZ steady**

The Matauri Bay deposits of New Zealand have been in continuous operation since 1969. In mid-2000, the small New Zealand China Clays Ltd was acquired by Imerys SA, France, renamed Imerys Tableware NZ Ltd, and folded in with the group's Asia Ceramics Division.

In its new guise the company continues as a small volume niche operation with 85% of current production of 15,000 tpa going into tableware applications and the balance into technical ceramics.

Two 12-hour shifts and 35 nationals are all takes to serve 23 countries from Germany to South America although the largest volume goes to customers in Asia. Operational capacity remains 20,000 tpa.

Fine particle size, 96% less than two microns for the New Zealand product, combined with low iron and titania provides excellent fired whiteness and translucency.

Halloysite in application also owes its high performance in considerable measure to its crystal morphology. On the microscopic scale crystals most commonly form tubes but also occur as laths and rolled, prismatic, sub-spherical and platy forms. Crystal morphology provides characteristic rheological properties that are quite different to those of the regular flat platelets exhibited by high quality kaolin.

Recent innovations may be summed up as increased focus on working with individual customers that has led to what the company describes as some outstanding ceramic formulations.

On the nanotechnology front the company has also made progress with the production of a silica-free prototype

halloysite for research in the geopolymer area.

### **Atlas Mining treads water**

The halloysite operations belonging to Atlas Mining Co. are on hold pending the outcome of an independent report on the company's mine waste material and its process requirements (see *IM February '08*, p.18).

Atlas Mining has been developing the halloysite deposit formerly operated by Anaconda subsidiary, Filtrrol Corp, in Juab county, Utah, USA. However, the company ran into difficulty last October when it declared some financial reported irregularity and doubts concerning the existing operational infrastructure to deliver saleable product.

Atlas Mining's objective is to focus on the higher value developing technical market outlets rather than traditional ceramics applications for which, the company asserts, its superior raw material is well suited.

Atlas had expected to be in production by now with its 30,000 tpa wet process plant in operation. Underground reserves of 300,000 tonnes are supplemented by substantial quantities of previously mined material lying on the surface as waste.

The company is now looking to construct a second processing plant that will likely be a wet process geared to processing the more easily accessible, and loss costly to reclaim, mine waste material. This arrangement also offers flexibility in that operations, once started, will be able to continue in times of bad weather.

### **And elsewhere**

Halloysite production is recorded elsewhere but nowhere near the same operational scale. Examples are in Poland and Turkey. Poland's Halloysite Mine Dunino Ltd (Kopalnia Halozyto Dunino Sp.z o.o.), established in 1998, has a surface mining operation near Krotoszyce, Legnica province. Crude annual halloysite output is just 3,000 tonnes sold for ion adsorption applications in the rare earths industry.

In Turkey, Esan Eczacibasi Endustriyel Hammaddeler San Tic AS has kaolin and halloysite mines at Balikesir and Canakkale north of Izmir in the extreme west of the country. Crude annual halloysite production is 3,000 tonnes. 