



*Authigenic native copper plate with curled edges from the Littleham Mudstone Formation.*

**T**he Swedish concept for the storage of spent nuclear fuel is encapsulation in copper canisters. These canisters will be buried in a deep geological repository excavated in granitic rock at a depth of 400 to 700 metres, and backfilled with bentonite clay. At these depths, it is envisaged that the groundwater will be chemically reducing and copper will be immune to corrosion in the absence of dissolved sulphides. As a natural analogue for the long-term stability and corrosion behaviour of copper canisters in a clay environment, we have studied the mineralisation and alteration of authigenic native copper at Littleham Cove, near Budleigh Salterton in south

Devon. Previous analogue studies of the longevity of copper metal have examined the corrosion of man-made objects exposed in different environments for long periods of time. These include bronze-age artefacts, a seventeenth-century bronze cannon (recovered from the wreck of the Swedish man-of-war 'Kronan') buried in smectitic clay on the Baltic seabed, and early twentieth-century lightning conductor earth plates buried in soil. None of these environments are really applicable to repository conditions, nor do they encompass the long timescale required for performance assessment. However, the authigenic native copper sheets in mudstones from south Devon

# The corrosion of native copper

## A natural analogue for the durability of canisters for spent nuclear fuel

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Courtesy Svensk Kärnbränslehantering AB

*Schematic diagram of a copper canister for storage of spent nuclear fuel.*

Devon. The copper occurs as unusual plates, containing greater than 99.4 % copper by weight, within reduction spots and reduced bands in the Littleham Mudstone Formation (early Triassic).

A target life of 100 000 years is required for the copper canister to contain and isolate the waste — the timescale considered in performance assessment for the radioactivity to decay to levels that present an acceptable risk. Extrapolations of short-term experimental data to predict the behaviour of the canisters over such long periods will always have some degree of uncertainty. To increase confidence in these predictions and the understanding of the long-term behaviour of repository materials, we are using natural analogues to bridge the gap between laboratory timescales and the very long durability expected from a repository design.

are accompanied by uranium mineralisation, and have been buried in a water-saturated clay environment for many millions of years. They therefore potentially provide a more appropriate natural analogue for studying the long-term corrosion behaviour of copper canisters for spent nuclear fuel enclosed within a bentonite buffer.

The Littleham Cove native copper occurs in uraniferous and vanadiferous concretions containing a complex assemblage of copper oxides, copper-nickel-cobalt-arsenides, copper sulphides, montroseite (vanadium oxide) and roscoelite (vanadian mica). There are also trace amounts of clausthalite (lead selenide), uranium silicate, native silver, gold, electrum, and other gold-copper-zinc alloys. Each copper sheet comprises several tightly stacked laminae of metal, each 0.1–5.0 mm thick, forming composite plates up to 160 by 90 mm in diameter and up to 5 mm thick. They

often have curled edges, curving in the same direction, which appears to be an *in situ* feature of their growth. The copper sheets grew along more permeable sandy laminae in the mudstone. They also replaced earlier low-angle cross-fibre calcite veins that may be related to hydrofracturing by overpressured porewaters. The copper displays complex corrosion, alteration and subsequent mineralisation. Alteration is dominated by copper oxides and consists mainly of coarse-grained cuprite ( $\text{Cu}_2\text{O}$ ) (with minor tenorite,  $\text{CuO}$ , and paramelaconite,  $\text{Cu}_4\text{O}_3$ ), which replaces the copper and is indicative of an early stage of oxidative alteration. Cuprite alteration was followed by a complex sequence of mineralisation (*see box*).

Although the copper-nickel-arsenide-sulphide mineralisation locally replaces metallic copper and cuprite corrosion products, elsewhere this mineralisation forms accretionary layers on the copper with little corrosion of the underlying substrate. Corrosion and replacement of the metal is often asymmetrical, affecting only one surface of the altered copper laminae.

Similar copper-nickel-cobalt arsenide mineralisation forms around roscoelite-montroseite-rich cores, in zoned concretions ('fish-eyes') within the mudstones. These preserve uncompacted detrital grain frameworks relative to the host mudstones. The copper plates may be locally deformed by differential compaction around these concretions. These observations indicate that the native copper sheets and the associated cuprite and copper-nickel-arsenide-sulphide mineralisation formed prior to the maximum burial and



*Uraniferous–vanadiferous ‘fish-eye’ concretions in the Littleham Mudstone Formation, Littleham Cove, south Devon.*

compaction of the Littleham Mudstone Formation (which would have occurred by the early Jurassic).

There is little evidence of further alteration until post-Tertiary uplift and erosion exposed the copper-bearing concretions to supergene alteration in the near-surface weathering environment. Our observations imply that, after early burial and diagenetic alteration, the copper has been preserved without further alteration, in a water-saturated clay, for over 176 million years. The study shows that copper can be stable in a clay environment over timescales well in excess of that considered in performance assessment for radioactive waste disposal. ■

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**The sequence of copper-nickel-arsenide-sulphide mineralisation**

- (i) Copper arsenides (including algodonite,  $\text{Cu}_6\text{As}$ , domeykite,  $\text{Cu}_3\text{As}$ , and koutekite,  $\text{Cu}_5\text{As}_2$ , and several unidentified copper arsenides). Minerals with a low copper to arsenic ratio formed first to be replaced by phases with a higher ratio as mineralisation progressed.
- (ii) Nickel arsenides; initially niccolite ( $\text{NiAs}$ ), then more extensive maucherite ( $\text{Ni}_{11}\text{As}_8$ ) and other minor nickel arsenides.
- (iii) Minor copper-nickel-cobalt arsenides, chalcocite ( $\text{Cu}_2\text{S}$ ) and rare covellite ( $\text{CuS}$ ).
- (iv) Clausthalite ( $\text{PbSe}$ ) and uranium silicate (possibly coffinite).

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