

Native Copper in Permian Mudstones from South Devon: A Natural Analogue of Copper Canisters for High-Level Radioactive Waste

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ABSTRACT

Native copper (>99.9% Cu) sheets associated with complex uraniferous and vanadiferous concretions in Upper Permian mudstones from south Devon (United Kingdom) have been studied as a “natural analogue” for copper canisters designed to be used in the isolation of spent fuel and high-level radioactive wastes (HLW) for deep geological disposal. Detailed analysis demonstrates that the copper formed before the mudstones were compacted. The copper displays complex corrosion and alteration. The earliest alteration was to copper oxides, followed sequentially by the formation of copper arsenides, nickel arsenide and copper sulphide, and finally nickel arsenide accompanied by nickel-copper arsenide, copper arsenide and uranium silicates. Petrographic observations demonstrate that these alteration products also formed prior to compaction. Consideration of the published history for the region indicates that maximum compaction of the rocks will have occurred by at least the Lower Jurassic (i.e. over 176 Ma ago). Since that time the copper sheets have remained isolated by the compacted mudstones and were unaffected by further corrosion until uplift and exposure to present-day surface weathering.

INTRODUCTION

The use of copper canisters for spent fuel disposal

The Swedish Nuclear Fuel and Waste Management Company (SKB) plan to dispose of HLW encased in a steel inner container within an outer canister of copper [1]. The canisters will be surrounded by compacted bentonite buffer within a repository constructed in granitic host rocks at a depth of 700 m. [1]. SKB has set a performance requirement that the copper canister should isolate the waste for at least 10^5 years until the various radioactive components decay to acceptable levels [1]. Neither the canister nor its corrosion products must have a deleterious effect on other barrier components (backfill and host rock) in order that they remain effective in attenuating radionuclide migration in the event of canister failure.

Copper has been identified in several international waste disposal programmes as a suitable canister material on the basis of its cost and corrosion resistance [1,2,3]. Experimental and theoretical studies demonstrate a wide stability range for metallic copper, and suggest that corrosion effects will be small in the mildly alkaline and reducing environment anticipated for a potential repository site [1]. However, the potential presence of dissolved sulphides in groundwater, or the formation of sulphides through the activity of sulphate-reducing bacteria

may compromise the long-term stability of the copper. This could significantly enhance copper corrosion. Current SKB design concepts consider that both of these factors will be minimal [1]. However, groundwater chemistry may vary significantly, in response to climatic changes (e.g, glaciation and sea level change) on a timescale relevant to PA [4]. The complex interplay of different processes occurring over these long periods of time may not be adequately modelled or reproduced in short-term laboratory experiments. Uncertainties in the long-term predictions of repository performance can be reduced by studying the analogous processes in natural systems (“natural analogues”) that have operated over geological timescales [5].

Previous analogue studies of copper stability

Previous analogue investigations on the corrosion and longevity of copper have focussed largely on the study of buried archaeological or industrial artefacts composed of copper or tin-bronzes [5,6,7]. However, these are not truly representative of repository materials and environments [5]. A detailed investigation was made of the corrosion of a bronze cannon recovered from the wreck of the Swedish man-of-war “Kronan”, which sank in the Baltic Sea during the Battle of Öland in 1676 [3,5,8]. The cannon was buried vertically in tightly-packed, seawater-saturated smectitic clay sediment. It presented the opportunity to study corrosion effects across a redox profile through the sediments, which provides some information that might be broadly analogous to a copper canister enclosed in bentonite. However, the geochemical environment of the Kronan Cannon is considered to be more oxidising than that anticipated within a HLW repository [5].

Whilst buried industrial and archaeological artefacts provide valuable information on processes over the 10 to 10³ year timescale, observations from geological analogues are also required to examine processes and to validate model predictions over the longer timescales required for PA. Very few geological analogues for copper corrosion have been studied in detail. Marcos [9] undertook a natural analogue study of native copper from several geological associations and found the metal remained stable over a broad range of hydrogeological environments. However, none of these environments were really applicable to repository conditions.

THE LITTLEHAM MUDSTONE FORMATION NATURAL ANALOGUE SITE

Geological background

The geology of the site is detailed elsewhere [10] but a brief summary is given here. The occurrence of rare native copper from Littleham Cove (south Devon), on the southwest coast of England, was originally recorded by Harrison [11]. It occurs in thin sheets associated with diagenetic concretions (containing high concentrations of uranium, vanadium and other metals with arsenic) hosted by mudstones and siltstones of the Upper Permian (230-250 Ma) Littleham Mudstone Formation. These rocks are exposed in the sea cliffs and beach at Littleham Cove - between Budleigh Salterton and the River Exe, where they are overlain directly by Triassic strata (figure 1). They consist mainly of continental (“red bed”) mudstones and siltstones (representing

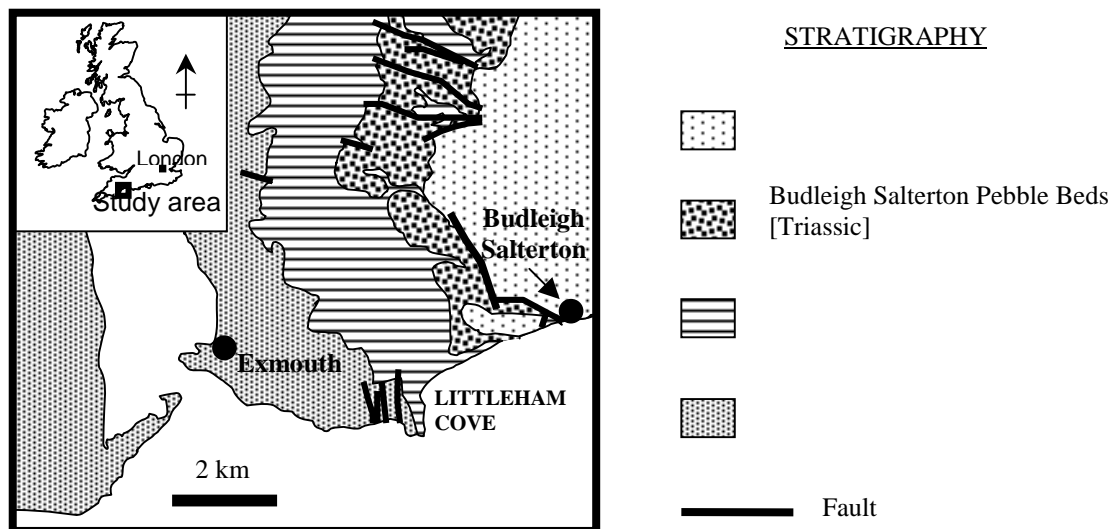


Figure 1. Location map and simplified geology of the Littleham Cove site.

overbank flood deposits, levee and crevasse splay deposits, and ephemeral lake deposits) and minor thin channel and sheet flood sandstones. These were laid down within an alluvial floodplain or flood basin near the western margin of the Wessex Basin. This complex basin developed across much of central southern England (and adjacent offshore areas) from the Permian to the Tertiary and is filled by thick sequences of Mesozoic and Tertiary strata [12].

The concretions have nucleated within pale green reduction spots developed within the red-brown ferruginous mudstone and siltstone matrix, and vary in morphology from simple spheres to complex and stellate forms [11]. Earlier studies, on these and similar feature elsewhere, suggested that the reduction spots formed locally around detrital organic fragments during burial diagenesis [see 10]. Reduction is also seen along more permeable sandy laminae, sand-filled desiccation cracks in the mudstone, and along fractures associated with small faults - implying that reducing pore fluids also permeated through the strata.

Analytical details

Archived materials at the British Geological Survey [11] were re-examined together with new material collected from the site [10]. Five copper-bearing concretions were examined in detail as polished sections. They were initially examined under a petrological microscope in reflected light. More detailed petrological observations were made by backscattered scanning electron microscopy (BSEM), using an energy-dispersive X-ray microanalysis (EDXA) to aid mineral identification. Quantitative microchemical data and X-ray maps of elemental distribution were obtained by wavelength-dispersive electron probe microanalysis (EPMA). The bulk rock and clay mineralogy of the host rocks were determined by X-ray diffraction analysis (XRD). Full analytical details are given elsewhere [10].

Petrological observations

The red-brown mudstone and siltstone host rocks are composed mainly of detrital quartz sand and silt with a clay matrix dominated by major illite. Some beds contain smectite as the

major clay mineral. Other minor to trace detrital components include detrital K-feldspar, plagioclase, chloritized mica and iron-titanium oxides. Finely disseminated iron and titanium oxide (probably largely authigenic hematite and anatase) are present throughout the matrix, which is sometimes cemented by calcite. Green reduction spots in the mudstones have an altered mineralogy, in which fine framboidal pyrite is formed at the expense of hematite, and chlorite is formed at the expense of smectite (in the case of smectitic host rock).

Native copper (>99.9% Cu), containing small inclusions of silver (>99.9% Ag), occurs within the concretions as thin discoidal plates (figure 2a) up to 160 x 90 mm in diameter, and up to 4 mm thick. Each plate is a composite of several stacked thin sheets of copper, which vary in thickness from <0.1 to 2 mm (e.g. figure 2b). The copper sheets have grown along, or sub-parallel to, thin siltstone bedding laminae in the mudstones, and along microfractures cutting the same bedding laminae. Inclusions of corroded quartz sand grains and relicts of cross-fibre calcite veining indicate that the sheets grew by replacement of clastic material

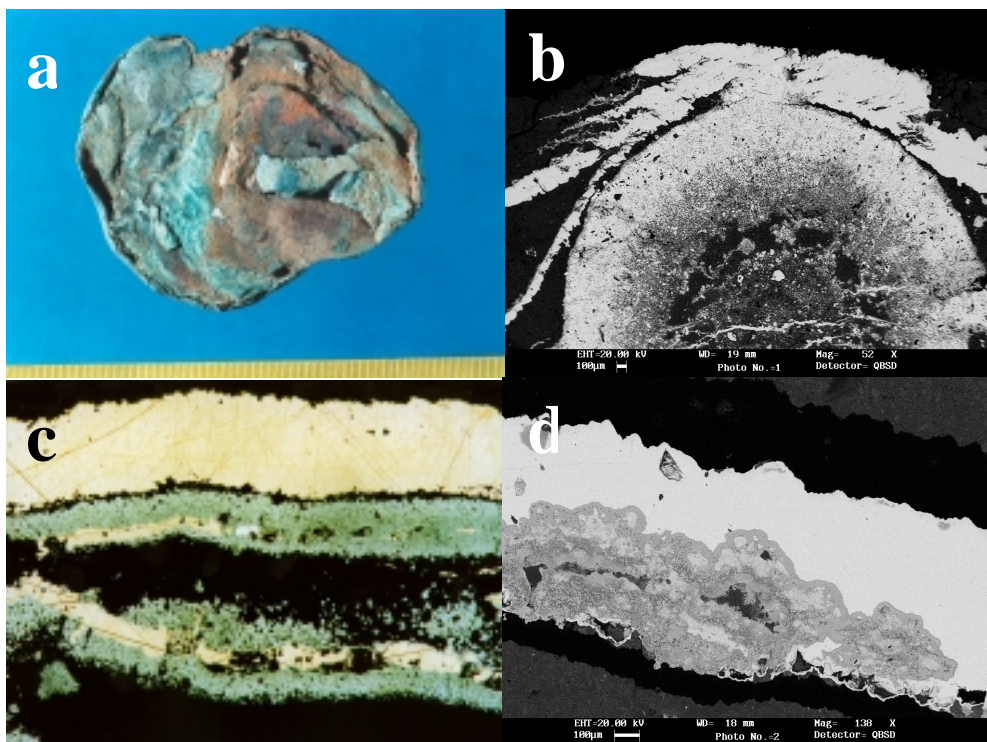


Figure 2. [a] Typical native copper plate with residual light grey clay matrix still attached (field of view is 12 mm wide). [b] BSEM image showing compactional deformation of copper sheets (bright) around a spherical banded concretion of nickel arsenide (bright) enclosing a core of vanadian illite (dark) containing bright grains and thin sheets of native copper (bright). [c] Reflected light photomicrograph showing asymmetric alteration of copper sheet to nickel arsenide (field of view is 2.6 mm wide). [d] BSEM image showing alteration of copper sheet to cuprite (dull grey), overlain by a thin fringe of nickel and copper arsenides (bright).

along coarser sandy laminae pre-existing bedding-parallel microfractures. This reflects mineral deposition from fluids moving along the more permeable pathways in the mudstone. Fine disseminated grains (5-100 μm) and very thin sheets of copper also occur within the cores

of complex uraniferous-vanadiferous concretions. These concretions comprise cores of vanadian illite or roscoelite ($KV_2AlSi_3O_{10}[OH]_2$) intergrown with montroseite ($VO \cdot OH$), surrounded by haloes of nickel arsenides (including maucherite, Ni_3As_2 ; niccolite, $NiAs$; and rammelsbergite, $NiAs_2$). Minor amounts of copper, copper-nickel and nickel-cobalt arsenides (e.g. algodonite, Cu_6As ; and chalcocite, Cu_2S), pyrite and uranium silicate (probably coffinite, $U[SiO_4]_{1-x}[OH]_{4x}$), together with traces of fine grained galena (PbS) and clausthalite ($PbSe$) are intergrown with the nickel arsenides. Trace amounts of fine grained gold and gold-copper alloys are also present in the matrix and nodules.

The copper sheets display compactional deformation around the more competent concretions (figure 2c), indicating that both grew very early during sediment diagenesis before any significant burial compaction of the strata. There is a close paragenetic relationship between copper and nodule development. The inclusion of thin copper sheets and fine copper inclusions in the cores of the nodules indicates that copper deposition started before concretion growth. However, copper sheets external to concretions are thicker, suggesting that copper growth continued during and/or after concretion growth.

The copper displays complex corrosion and alteration. Often this affects the sheets asymmetrically, with alteration on one side of the sheet whilst the opposite surface is unaffected (figure 2b and d). In a composite stack of several thin sheets, the corrosion is commonly on the same surface in each successive sheet. The reason for this characteristic corrosion is not yet clear. The earliest formed alteration product is copper oxide (principally cuprite, Cu_2O with minor tenorite, CuO). The cuprite forms colloform corrosion layers that “eat” into the copper metal (figure 2d). This was followed by the formation of copper arsenides (including algodonite and unidentified minerals). These are closely associated with the dissolution of native silver inclusions in the copper, and form fringes on the cuprite and copper surfaces. The copper arsenide alteration was followed by the deposition of extensive rims of dull-grey nickel arsenide similar to maucherite in composition, accompanied by minor chalcocite. Thin alteration fringes of bright nickel arsenides (including niccolite), and sometimes accompanied by copper arsenide, copper-nickel arsenide and uranium silicate form later alteration layers. A similar sequence of mineral deposition is seen in the growth of the associated uraniferous-vanadiferous concretions, indicating a close temporal relationship between the two features. Where the copper has been exposed to surface weathering, thin films of secondary copper sulphates, carbonate and chloride minerals are formed.

CONCLUSIONS

Petrographical studies indicate that the copper sheets formed early during the burial history of the strata, prior to maximum compaction. The earliest alteration was to copper oxides indicating oxidizing porewater conditions. Subsequent sulphide and arsenide alteration products imply a more reducing environment as burial progressed. The association of the copper sheets with cross-fibre calcite veining suggests that they may have developed under overpressured porewater conditions which may have been generated during dewatering of the sediments during burial. Similarly, the copper oxide, arsenide and sulphide alteration products are also early, forming pre-compactional concretions as well as on the copper sheets. Reconstruction of the burial history of the Wessex Basin [12] indicates that these rocks would have achieved their maximum depth of burial by at least the end of the Lower Jurassic.

Therefore, the copper sheets and their alteration products are older than 176 Ma. The copper suffered alteration during the early burial history of the mudstones. However, the copper has been effectively isolated within the compacted clay matrix and unaffected by corrosion, retaining 30-80% of its original thickness, since that time -despite the probable presence of highly saline and reducing porewaters. Corrosion only recommenced when the rocks were uplifted and exposed to near surface weathering (probably only during the last few thousand years). These observations lend support to predictions of the long-term stability of copper in compacted bentonite.

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