

Discolouration and deterioration of wood in geothermal environments

Wood and wood structures in geothermal areas can quickly discolour and deteriorate, particularly where the wood is treated with preservatives that contain copper. Wood samples were included in a wider BRANZ field test of building materials in geothermal environments to study this effect and look for possible explanations.

NEW ZEALAND has many geothermal systems, particularly in the central North Island. Features such as fumaroles (vents), hot springs and mud pools emit the gases hydrogen sulphide (H_2S) and sulphur dioxide (SO_2), which can speed corrosion of susceptible building and construction materials.

Discolouration of wood, particularly wood treated with copper-containing preservatives, is common in areas with strong geothermal emissions (Figure 1). Although the colour change is mainly cosmetic surface damage, significant reduction of physical and/or structural properties can also happen. Consistent exposure can lead to the formation of deep and large cracks.

Discolouration has been observed in hardwood, softwood, sapwood and heartwood and can happen to standing trees, green logs, green or kiln-dried timber and wood products in service. It is generally caused by microbial, chemical, biochemical, mechanical or photochemical factors. Wood discolouration seen in geothermal environments in the research reported here was seen to be different from that under other conditions.

The expanding uses being found for wood, including a growing range of engineered wood products, means that understanding discolouration and finding ways of preventing it are important research topics.

BRANZ field test

The samples in this test were treated wood, with untreated *Pinus radiata* included as a reference. The treatments were based on



Figure 1. Wood discolouration in an area with strong geothermal influences (south of Sulphur Bay, Rotorua).

copper-bearing preservatives to H3.2 and H4 levels of:

- chromated copper arsenate
- copper azole
- alkaline copper quaternary
- micronised copper azole.

Wood samples approximately 20 × 20 × 100 mm were cut from treated long wood blocks. The four major surfaces were sanded to remove any precipitated preservation chemicals and to give a reasonably smooth and uniform surface.

Field exposure was carried out for 1 year in two geothermal environments in Rotorua:

- Approximately 5 m from an active small fumarole (a natural vent that emits hot sulphurous gases) in the grounds of Scion, a Crown research institute.
- Close to a large geothermal system at Sulphur Bay.

After this 1-year exposure, all wood samples, except the untreated ones, showed surface discolouration and turned blue (Figure 2).

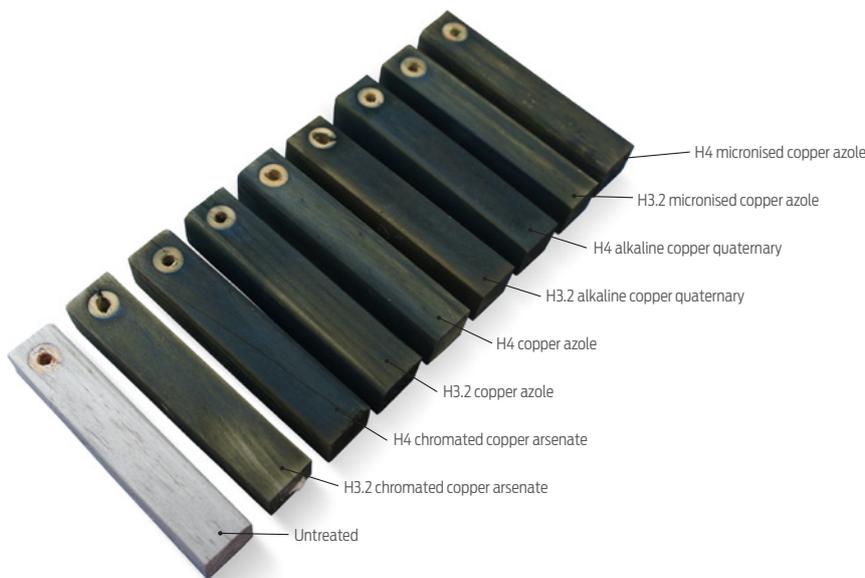


Figure 2. Discolouration of untreated and treated wood blocks exposed at a location approximately 5 m away from a fumarole in Scion campus.

An examination of cross-sections showed that this colour change could affect areas up to around 1 mm deep from the top, directly exposed surface (Figure 3).

The results of the 1-year exposure indicate that discolouration may be connected to the presence of certain preservation chemicals in the wood, since the untreated wood showed no discolouration. Those treatment chemicals in the test have copper ions in common.

The BRANZ field tests also found that the surface of copper samples showed a

regular colour change with the concentration of airborne H_2S released from geothermal sources. The corrosion products formed on the copper samples exposed in areas with strong geothermal influences had a typical blue colour, sometimes brown. These corrosion products were identified as a mixture of sulphide, sulphate and/or oxide of copper.

Based on these results, it is suggested that this type of wood discolouration is caused by the formation of copper sulphide and/or

sulphate. This occurs through interactions between copper in the preservative chemicals and geothermal sulphur-containing gases entering the wood structure.

Looking at the surface with a scanning electron microscope showed some particles randomly distributed on the top surface of the treated wood samples. Most were rich with both copper and sulphur, although oxygen was also detected by energy-dispersive X-ray spectroscopy (EDS). This co-presence of elements implies the formation of copper sulphides, sulphates and/or oxides.

Small particles and/or clusters of particles were also seen on the exposed surface of the untreated wood sample. EDS analysis revealed that these particles are quite diverse in their composition. They can be rich either with sulphur, silicon or aluminium, but not with copper. The untreated samples showed no discolouration.

Finely sliced cross-sections of wood were also examined. EDS was used to map the elements present. This method can produce coloured images that show the distribution of specific elements in a specimen.

In areas very close to the top surface, a layer with obvious overlapping of copper and sulphur was seen. In deeper sections, it appeared that distribution of sulphur was more concentrated in the cell wall, with copper in the cavity. However, a closer look revealed that sulphur and copper were also overlapping in the cell wall area. The co-presence of these two elements indicates that they might be combined chemically to form copper sulphides or sulphates in the cell wall areas.

Using X-ray diffraction to identify corrosion products

EDS helped identify potential elements and showed their distributions in the samples. However, this technique cannot identify the phase structure of the unknown material that has the elements detected. For example, the chemical combination of copper and sulphur may form CuS , Cu_2S , CuS_2 or non-stoichiometric $Cu_{2-x}S$. ('Non-stoichiometric' means that make-up of the elements can't be described with a ratio of well defined natural numbers.)

Working out what the unknown crystalline materials are is critical to reveal the

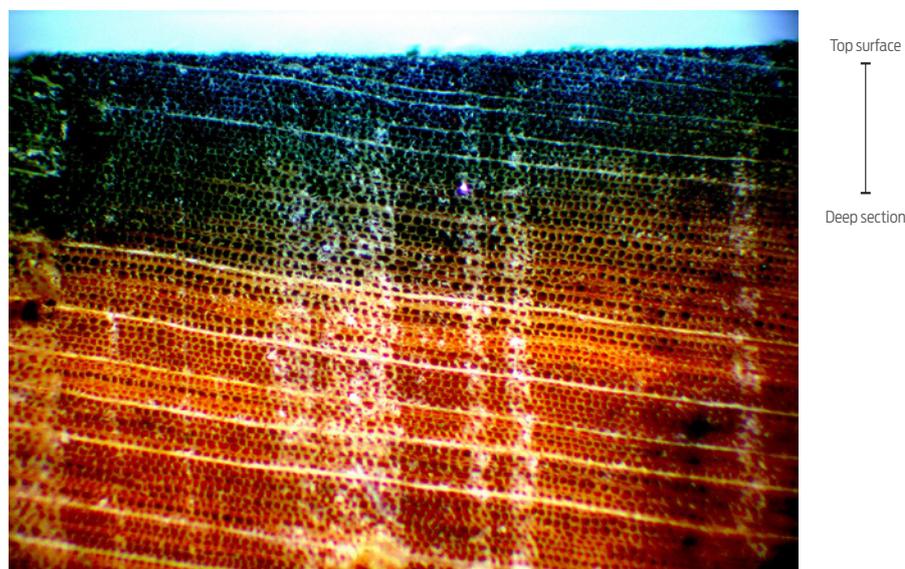


Figure 3. Optical microscopic view [32x] of the cross-section of an H4 micronised copper azole-treated wood block. Discolouration is visible after a 1-year exposure at a location about 5 m from a fumarole in Scion campus.



interactions between treated wood and geothermal emissions. This is where X-ray diffraction comes in.

X-ray diffraction was used on the wood samples after a 1-year exposure. Several new peaks were found with the diffraction pattern collected from the wood samples treated with copper-containing chemicals. These new peaks were identified as copper sulphide. This result is consistent with the earlier analysis, which showed enrichment of copper and sulphur within most small particles on the exposed top surface and overlapping within the cell wall region.

Conclusion

Wood discolouration in strong geothermal environments is likely to be the result of copper sulphide forming on the surface and/or within the structure of the wood. This is based on the following findings:

- Untreated wood showed no discolouration.
- All treated wood samples showed discolouration. The common presence within these four preservatives (chromated copper arsenate, copper azole, alkaline copper quaternary and micronised copper azole) is copper ion.
- Energy-dispersive X-ray spectroscopy analysis revealed particles rich with copper and sulphur on the surface of treated wood. Overlapping copper and sulphur was also found within cell wall areas of the wood.
- X-ray diffraction revealed the formation of copper sulphide in treated wood, not in untreated wood.
- Corrosion products on copper samples exposed to strong geothermal environments have a colour that is typically blue, sometimes brown. This is similar to the wood discolouration seen in this research. Those corrosion products formed on copper were identified as a mixture of sulphides, sulphates and oxides of copper.
- Copper sulphide occurs in nature as the dark indigo blue mineral covellite, and its fine powder is black. This compound was detected with the treated wood in this study.
- Hydrated copper sulphate is blue. This

compound was not detected within treated wood in this study, but its presence cannot be completely excluded since its quantity might be very limited.

More information

Li, Z., Marston, N. & Stokes, K. (2018). *Materials within geothermal environments*. BRANZ Study Report SR393. Judgeford, New Zealand: BRANZ Ltd.

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