

ISSUE 627 **BULLETIN**



## THE IMPACT OF GEOTHERMAL ENVIRONMENTS ON METALS AND WOOD

August 2018

- BRANZ conducted field trials in Rotorua to examine how metals degrade in geothermal environments. Different metals showed very different responses.
- The scope of NZS 3604:2011 *Timber-framed buildings* requires a 50 m separation from geothermal hot spots. This will not always reduce corrosion rates to a safe range.
- Wood discolouration is likely to be the result of copper sulphide forming on/in wood treated with copper-based preservatives.

## 1 INTRODUCTION

**1.0.1** Thermal vents, hot springs and other geothermal features release hydrogen sulphide ( $H_2S$ ) and sulphur dioxide ( $SO_2$ ) gases into the environment. These gases can be aggressive towards susceptible building materials. The deterioration of buildings and infrastructure can result in large maintenance and repair costs.

**1.0.2** To assess the performance of metals in geothermal environments, BRANZ established exposure sites at locations across Rotorua (Figure 1). Comparison sites were set up at the semi-rural BRANZ campus at Judgeford and close to breaking surf at Wellington's Oteranga Bay.

**1.0.3** After varying exposure periods, corrosion rates for different metals were measured and the differences between sites compared. The impact of distance from a geothermal feature was assessed. Wood that had changed colour was tested to determine possible reasons for the change.

## 2 CORROSION OF MILD STEEL, ZINC AND COPPER

**2.0.1** Metal samples  $150 \times 100 \times 1-3$  mm were attached to exposure racks with nylon fixings. To minimise the influence of weather and/or geothermal activity changes, samples were examined and corrosion rates measured over three periods:

- December 2014–December 2015
- June 2015–June 2016
- December 2015–December 2016.

**2.0.2** The concentration of airborne  $H_2S$  was measured for 3 weeks in each period. Huge variations were found between sites (Figure 2). The highest concentration – approximately 31.0 parts per billion (ppb) at the wastewater treatment plant site (WWTP) – was around 500 times higher than the lowest – 0.06 ppb in the far west.

**2.0.3** Corrosion rates also varied greatly depending on location. For example, mild steel corrosion below  $200 \text{ g/m}^2/\text{year}$  was measured at two sites in the western area, while a rate of  $3,302 \text{ g/m}^2/\text{year}$  was measured at the wastewater treatment plant site close to Sulphur Bay.

**2.0.4** At the wastewater treatment plant site, a thick corrosion product layer that could easily break off formed on the mild steel (Figure 3). The sample increased from 3 mm to around 5–6 mm thick after a 1-year exposure.

**2.0.5** By comparison, corrosion product layers on the mild steel samples at the west and east city sites were relatively thin and compact, with fewer physical defects.

**2.0.6** The corrosion products on the zinc samples at the west and east city sites developed into relatively uniform, dense and thin layers. This type of corrosion product is expected to grow slowly and to provide protection to the zinc substrate due to it having few physical defects.

**2.0.7** By contrast, high corrosion rates with rough corroded surfaces were seen on the zinc samples exposed at sites with high  $H_2S$  concentrations – for example, the wastewater treatment plant site close to Sulphur Bay.

**2.0.8** The copper samples exposed at the wastewater treatment plant site had very high mass losses of  $443-495 \text{ g/m}^2$  after 1 year. This extremely high corrosion rate is a result of the rapid reaction of copper and sulphur-containing gases and poor protection offered by the corrosion products on the surface. Corrosion products started to crack and flake after approximately 1 month of exposure. Fresh copper substrate was then exposed. Microscopic examination showed a rough surface. This type of corrosion product is unlikely to provide protection to the underlying metal.

**2.0.9** Corrosion products on copper samples exposed in the western and eastern areas showed no obvious spallation

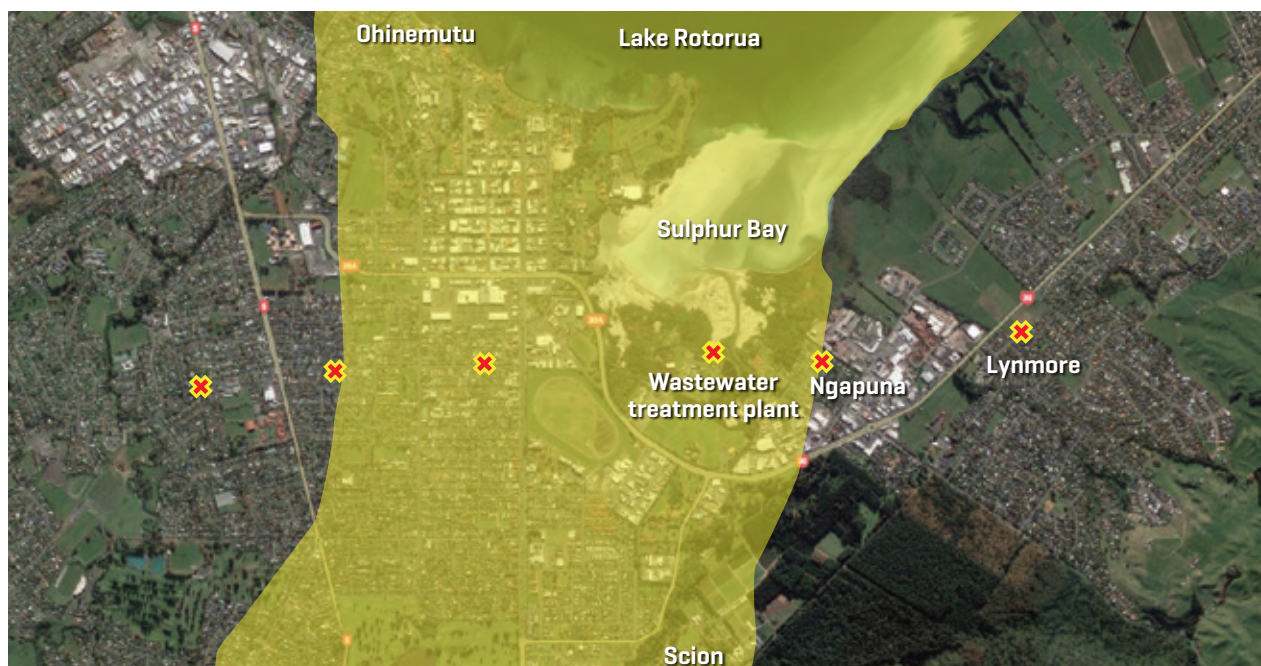


Figure 1. Exposure locations in Rotorua.



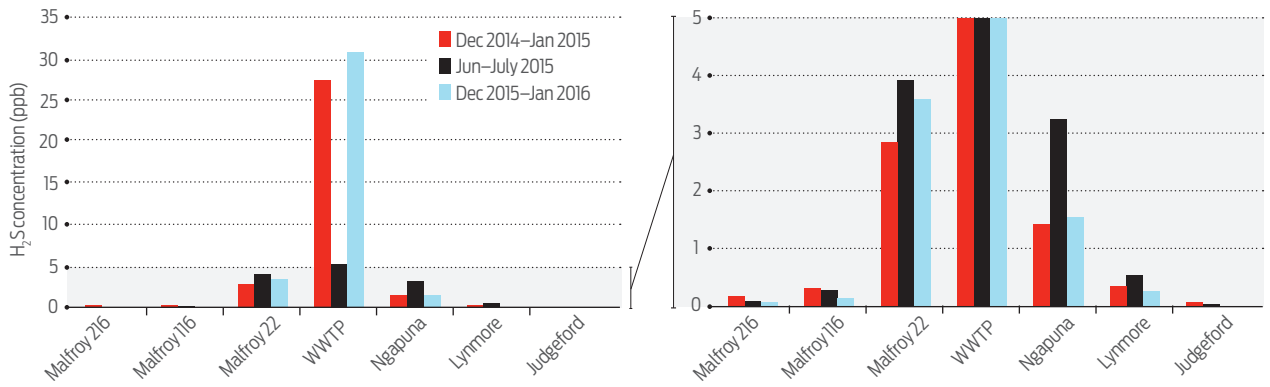


Figure 2. Average H<sub>2</sub>S concentration during a 3-week exposure.

or detachment, contributing to lower corrosion rates when compared with that exposed at the wastewater treatment plant site. However, the corrosion product layer on the copper sample in the east was thicker and more porous than that on the copper in the west. This indicates that a small difference in concentration of sulphur-containing gases could make a large difference in corrosion of copper.

**2.0.10** The different metals had different responses to geothermal attack. Copper showed high corrosion rates in areas with low H<sub>2</sub>S concentrations and appeared to be more prone to geothermal attack than mild steel and zinc.

### 3 CORROSION OF ALUMINIUM AND STAINLESS STEEL

**3.0.1** The field trial found that atmospheric corrosion of aluminium and stainless steel [AISI 304] is limited in geothermal environments. Examination of the exposed metal surfaces did not find significant corrosion products – just a few small black spots that could be cleaned off. There was no visible attack to the substrate underneath the spots.

**3.0.2** These metals had higher mass losses when exposed to a severe marine environment, with severe corrosion under or close to the nylon fasteners where salt particles could be trapped. This indicates that chloride-containing sea salt particles are more corrosive to them. Aluminium also appeared to be degraded by erosion from wind-blown sand and salt particles.

### 4 THE PERFORMANCE OF ALUMINIUM-ZINC ALLOY-COATED STEEL

**4.0.1** The aluminium-zinc [Al-Zn] alloy coating used in the research is typically 55% aluminium, 43.5% zinc

and 1.5% silicon by weight. Al-Zn alloy-coated steel is widely used in New Zealand as roof and wall claddings, spouting, downpipes and fencing.

**4.0.2** Samples were exposed in three locations:

- Approximately 5 m from a small fumarole [a natural vent emitting sulphurous gases] in the grounds of Scion, a Crown research institute not far from the Whakarewarewa thermal area, Rotorua.
- At the wastewater treatment plant site approximately 200 m south of Sulphur Bay near the southeastern corner of Lake Rotorua.
- In a severe marine environment at Oteranga Bay on Wellington's south coast.

**4.0.3** The microstructure of Al-Zn alloy coating has an aluminium-rich phase and a zinc-rich phase [Figure 4]. The aluminium-rich phase forms into dendrites – tiny metallic crystal structures that look a bit like snowflakes or trees. The zinc-rich phase occupies the regions between the dendrites and is therefore often called the interdendritic phase. The dendrites constitute approximately 80% of the coating volume. An intermetallic layer is normally formed to bond the coating to the steel substrate. Silicon can also be present in the microstructure as needle-like particles in the interdendritic regions.

**4.0.4** After a 2-year exposure in a geothermal environment, sample surfaces did not show heavy rusting – just a few small, random rust spots [Figure 5a]. This indicates that the alloy coating has been consumed locally and some parts of the steel substrate have then been exposed to the environment.

**4.0.5** Heavy rusting was seen close to unprotected cut edges [Figure 5b]. This indicates that the exposed steel was not protected by the cathodic protection effect normally lent by a zinc coating.



Figure 3. Corrosion products on the mild steel sample exposed at the wastewater treatment plant site for 1 year.

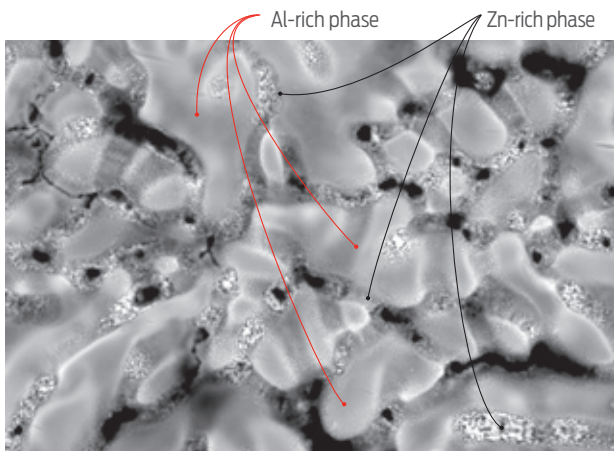


Figure 4. Typical surface structure of Al-Zn alloy coating.

**4.0.6** Spot rusting and grey/white patches were occasionally seen on samples exposed to the severe marine environment (Figure 5c). Rusting was limited to very small areas close to the bottom cut edge. Damage seen in some areas on the top surface of the marine-exposed sample was the result of mechanical impact from wind-blown sand or salt.

**4.0.7** When Al-Zn coated steel is exposed to the atmosphere, corrosion begins in the zinc-rich region at the outer surface. Corrosion products create a barrier, so corrosion normally slows over time. This can provide sacrificial protection to cut edges in many environments. The aluminium only provides protection when it is activated, such as in marine environments.

**4.0.8** Corrosion of Al-Zn coated steel appears to follow this general pattern when exposed to geothermal environments, though with some differences.

**4.0.9** X-ray spectroscopy found enrichment of sulphur and oxygen in the zinc-rich surface areas and attacks to them after exposure to a strong geothermal environment. Loose corrosion products rich with zinc sulphide formed on zinc exposed to geothermal environments do not provide good substrate protection. These zinc-rich areas are consumed quickly, producing physical and structural defects. Sulphur-containing gases can then enter the inner part of the coating or the steel substrate through the defects.

**4.0.10** This process may happen more quickly than in marine environments. Iron-rich corrosion products can form at the coating-steel substrate interface (Figure 6). The huge stresses generated by the volume expansion produce more physical defects in the coating such as bubbles and/or cracks (Figure 7). During extended exposure, severe, localised attack to the steel substrate leads to larger volume expansion, more damaged areas and finally coating failure with the formation of iron-rich rust on surface areas.

## 5 DISTANCE EFFECTS OF CORROSION IN GEOTHERMAL ENVIRONMENTS

**5.0.1** Buildings constructed within 50 metres of a geothermal hot spot are outside the scope of NZS

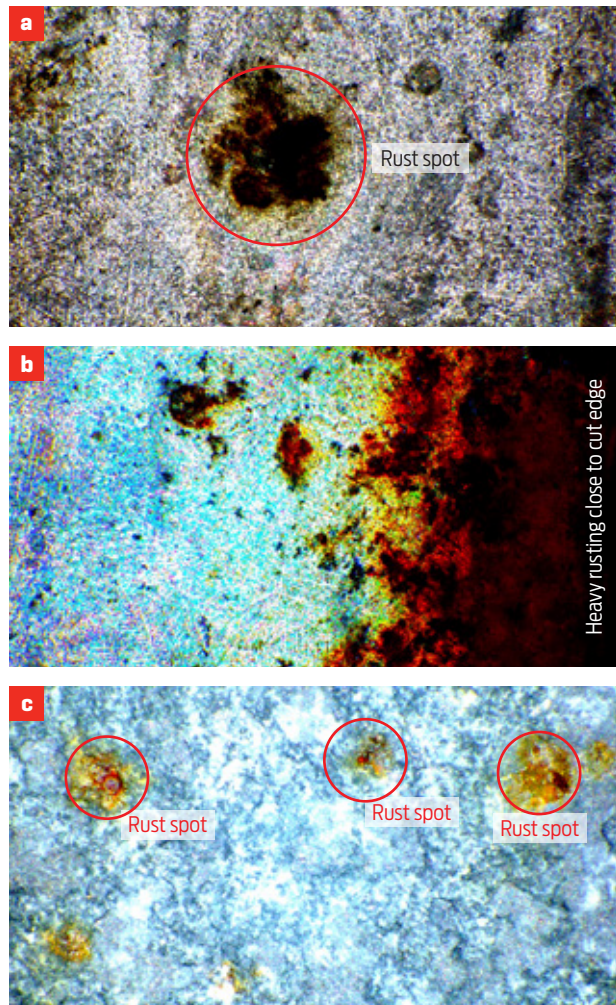


Figure 5. Surface of Al-Zn alloy coating after a 2-year exposure at [a] approximately 5 m from a fumarole [Scion campus] [b] the wastewater treatment plant approximately 200 m south of Sulphur Bay and [c] Oteranga Bay [severe marine].

3604:2011 and require specific engineering design (SED). How appropriate is the 50 m distance?

**5.0.2** One rack holding mild steel, zinc and copper samples was fixed approximately 5 m from a small fumarole in the Scion campus. A second was located approximately 50 m east and a third approximately 60 m southwest.

**5.0.3** A separation of 50–60 m from the geothermal source was shown to significantly decrease the corrosion rate of all three metals tested, by up to 10 times in some cases (Figure 8 shows the results for mild steel). This is likely related to lower airborne concentrations of sulphur-containing gases – H<sub>2</sub>S concentrations 50–60 m from the fumarole could be 5–10 times lower than that at the fumarole itself.

**5.0.4** Even the reduced concentrations away from the fumarole were still far higher than non-geothermal locations. These lower H<sub>2</sub>S concentrations were more than 25 times higher than those at BRANZ's semi-rural campus at Judgeford.

**5.0.5** Mild steel samples 5 m from the fumarole suffered severe corrosive attack (Figure 9a) with cracking and spalling. By contrast, corrosion product layers on mild steel samples exposed 50–60 m away showed no

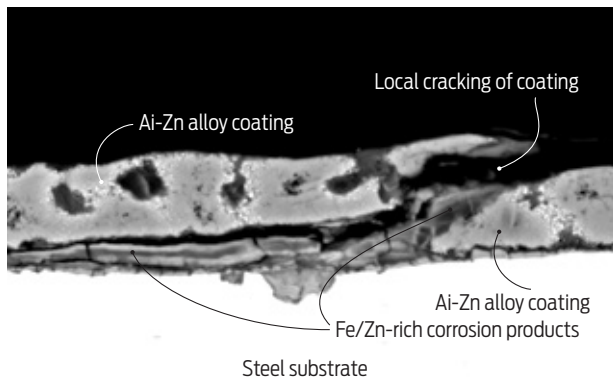


Figure 6. Cross-sectional view of a Al-Zn alloy coating after a 2-year exposure to a strong geothermal environment.

significant detachment or spallation, although there were some cracks (Figure 9b). Corrosion product layers with better protective capabilities had formed.

**5.0.6** The corrosion layer on the zinc sample 50–60 m from the fumarole (Figure 9d) was much thinner than that on the zinc sample 5 m from the source (Figure 9c).

**5.0.7** Corrosion products on copper samples close to the fumarole detached and spalled with nodules/clusters formed (Figure 9e). Spallation and/or detachment were not seen on the copper samples 50–60 m away (Figure 9f).

**5.0.8** These findings do not mean that the atmosphere 50–60 m from the source falls into medium or low corrosion risk categories. [Categories are defined in ISO 9223:2012 *Corrosion of metals and alloys – Corrosivity of atmospheres – Classification, determination and estimation.*] The corrosion rate of mild steel 60 m southwest of the fumarole was 443–551 g/m<sup>2</sup>/year, placing this environment into the C4 High category (Table 1). For copper, corrosivity 50–60 m from the fumarole was even greater, coming above the limits for the CX Extreme category.

**5.0.9** At the wastewater treatment plant site, first-year corrosion rates were 3,044–3,443 g/m<sup>2</sup>/year for mild steel, 65.6–88.6 g/m<sup>2</sup>/year for zinc and 443–517 g/m<sup>2</sup>/year for copper. In the 1980s, BRANZ measured a first-year corrosion rate of mild steel of 2,293 g/m<sup>2</sup>/year at a site nearby, approximately 400 m southwest of Sulphur Bay. All these measurements indicate that the area 200–400 m south or southwest from Sulphur Bay could be classified in the CX Extreme corrosivity category.

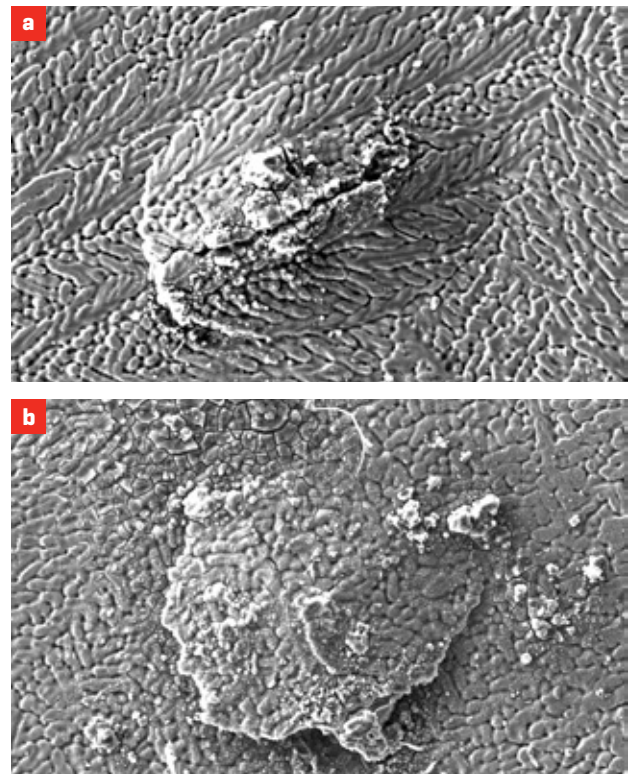


Figure 7. Failures seen on Al-Zn alloy coatings exposed to a strong geothermal environment: (a) bubbling/cracking, (b) lifting up.

## 6 DISCOLOURATION OF WOOD

**6.0.1** Discolouration of wood, particularly wood treated with copper-containing preservatives, is common in geothermal environments (Figure 10). Although the change is mainly cosmetic, consistent exposure can result in large, deep cracks.

**6.0.2** Part of the BRANZ field test examined this phenomenon. Wood samples approximately 20 × 20 × 100 mm with treatments based on copper-bearing preservatives to H3.2 and H4 levels were used, with untreated *Pinus radiata* as a reference. The treatments were:

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

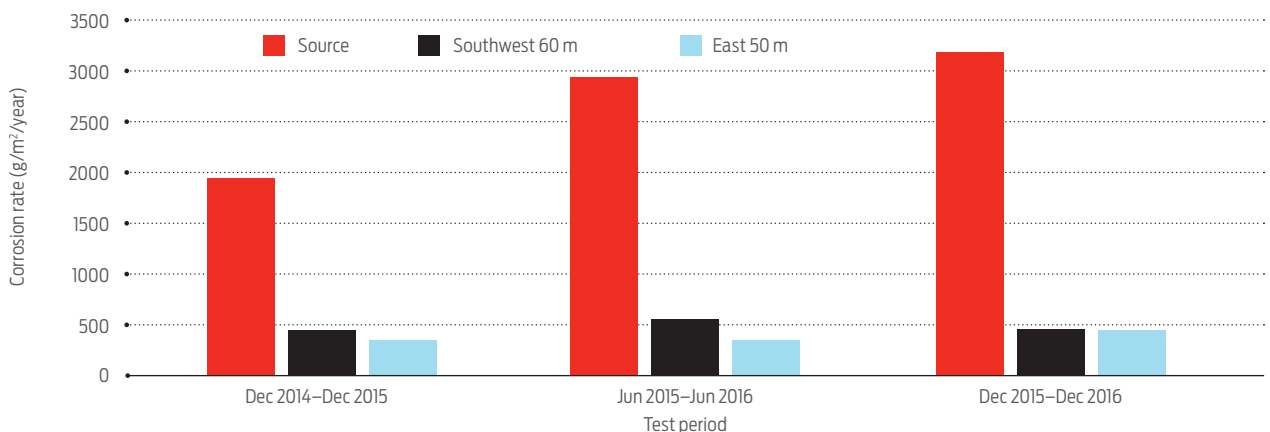


Figure 8. First-year corrosion rate of mild steel exposed at three locations around a fumarole in the Scion campus.



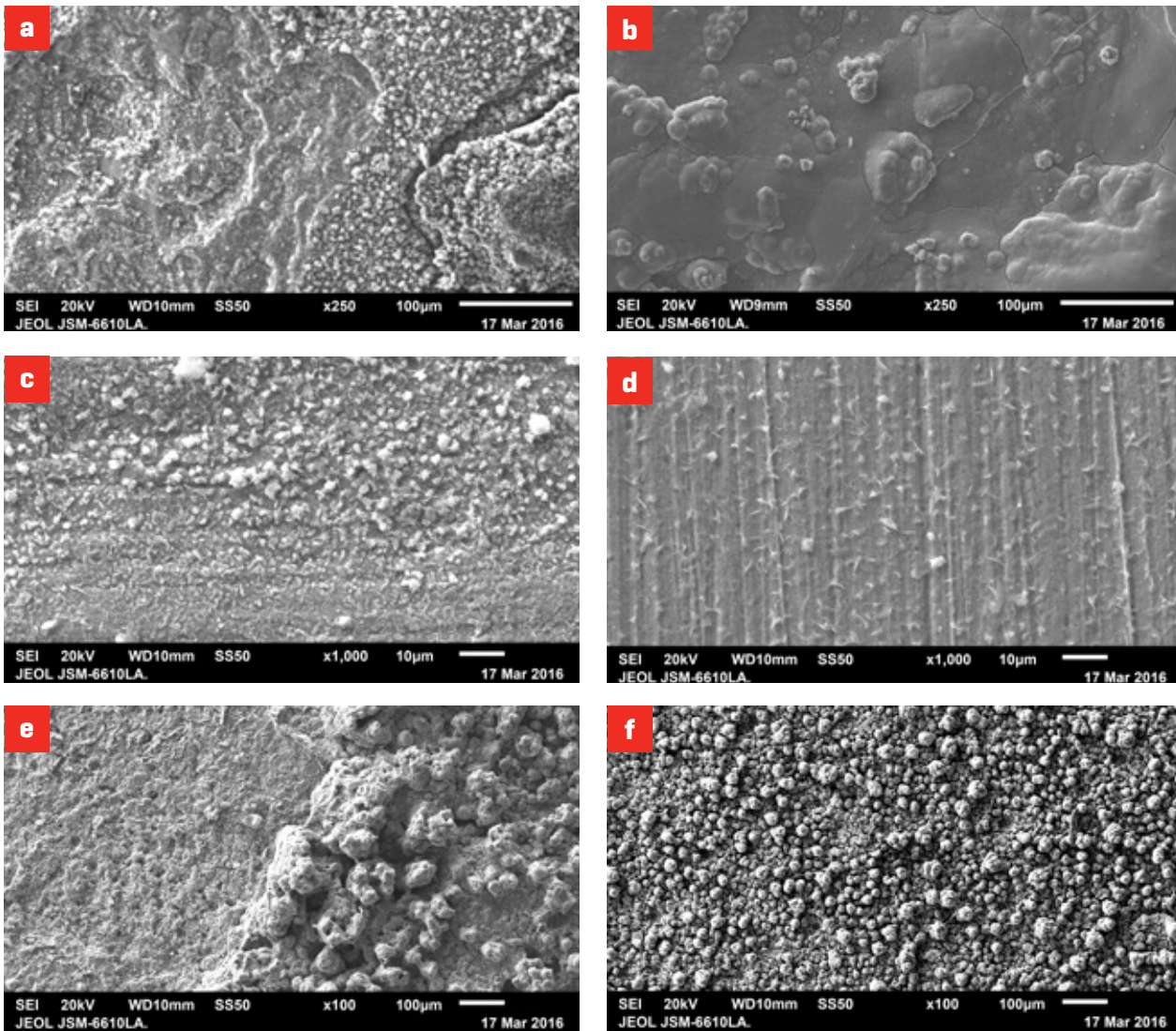


Figure 9. Surface of metal samples exposed for 1 year: [a] mild steel at 5 m from a fumarole, [b] mild steel at 50 m, [c] zinc at 5 m, [d] zinc at 50 m, [e] copper at 5 m, [f] copper at 50 m.

Table 1. Corrosivity category determined according to ISO 9223:2012.

Metal	Location	Corrosivity category		
		Dec 2014–Dec 2015	Jun 2015–Jun 2016	Dec 2015–Dec 2016
Steel	Source [5 m]	CX Extreme	CX Extreme	CX Extreme
	Southwest [60 m]	C4 High	C4 High	C4 High
	East [50 m]	C3 Medium	C3 Medium	C4 High
Zinc	Source [5 m]	CX Extreme	CX Extreme	CX Extreme
	Southwest [60 m]	C3 Medium	C3 Medium	C3 Medium
	East [50 m]	C3 Medium	C3 Medium	C3 Medium
Copper	Source [5 m]	>CX Extreme*	>CX Extreme*	>CX Extreme*
	Southwest [60 m]	>CX Extreme*	>CX Extreme*	>CX Extreme*
	East [50 m]	CX Extreme	CX Extreme	>CX Extreme*

\* The CX category applies to corrosion rates of 50–90 g/m<sup>2</sup>/year. In this study, the first-year corrosion rate of copper could be around 5 times higher than this upper limit.

**6.0.3** Field exposure was carried out in two environments:

- Approximately 5 m from the Scion fumarole.
- Close to a large geothermal system at Sulphur Bay.

**6.0.4** After 1 year, all treated wood samples turned blue [Figure 11]. An examination of cross-sections showed a colour change up to 1 mm deep [Figure 12].

**6.0.5** The discolouration may be connected to the preservation chemicals containing copper ions, since the untreated wood showed no discolouration. [The field tests found that copper metal samples also changed colour after exposure to sulphur-containing geothermal emission.]

**6.0.6** Observation and testing with a scanning electron microscope, X-ray spectroscopy and X-ray diffraction found:

- randomly distributed particles rich with copper, sulphur and oxygen on the wood surfaces
- in areas close to the surface, a layer with copper and sulphur overlapping
- the presence of copper sulphide in the samples.

## 7 CONCLUSIONS

**7.0.1** Different metals appear to have different resistances to sulphur-containing species-induced attack in geothermal environments:

- Copper is more sensitive than mild steel and zinc. It appears to be sensitive to even very low concentrations of H<sub>2</sub>S in the atmosphere.
- Zinc appears to be less prone to atmospheric corrosion from sulphur-containing gases at relatively low concentrations compared with mild steel and copper. Above these lower concentrations, corrosion in zinc can be accelerated.
- Aluminium and stainless steel were much more resistant to atmospheric geothermal attack. These materials suffered greater corrosion in a marine environment.
- Al-Zn coated steel appears to corrode more quickly in strong geothermal environments than marine environments.

**7.0.2** The 50 m separation from geothermal hot spots required by NZS 3604:2011 is not always enough to reduce corrosivity into a safe range:

- The corrosion rate of a mild steel sample 60 m from a



Figure 10. Wood discolouration in an area with strong geothermal influences.

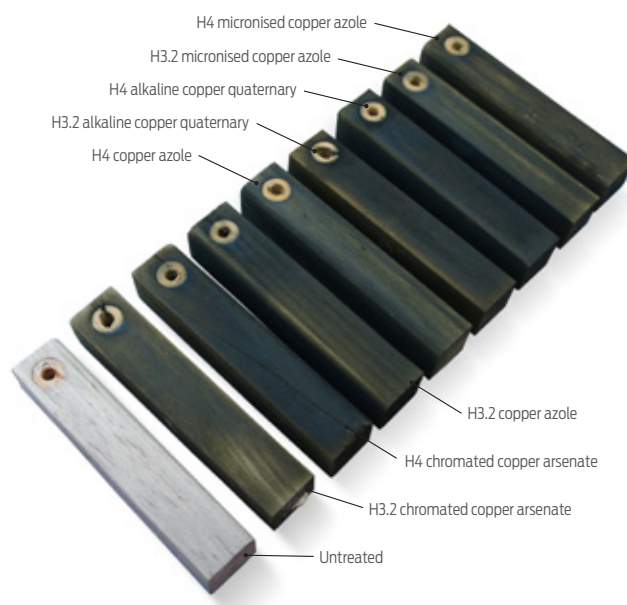


Figure 11. Discolouration of untreated and treated wood blocks from a site approximately 5 m from a fumarole in the Scion campus.

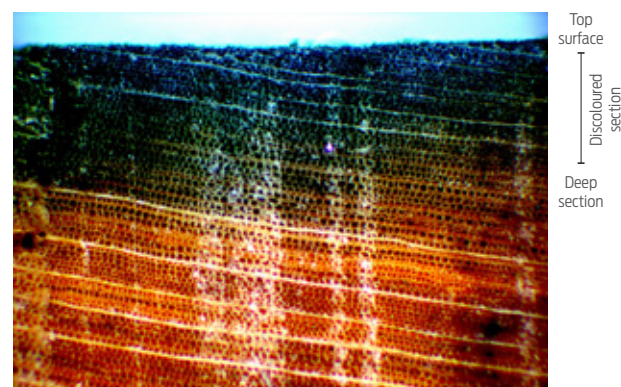


Figure 12. Optical microscopic view [32 $\times$ ] of the cross-section of an H4 micronised copper azole-treated wood block.

small fumarole was in the C4 High corrosivity category.

- The corrosion rate of a copper sample 50–60 m away exceeded the upper limit of the CX Extreme category.
- 200 m south of Sulphur Bay, corrosion rates for mild steel, zinc and copper could all be classified CX Extreme.

**7.0.3** Within approximately 500 m of an active geothermal feature, atmospheric corrosivity is strongly influenced by many factors, including feature size, emission capability, chemistry of the geothermal feature and weather.

**7.0.4** 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 wood treated with copper-based treatments.

## 8 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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