Which metals are more sensitive to geothermal corrosion?

BRANZ conducted field trials in Rotorua to examine how different metals corrode in geothermal environments. Identical samples were also exposed to a marine environment for comparison. Copper and mild steel suffered serious corrosion in the Rotorua exposure sites, and zinc did too where concentrations of sulphur-containing gases were high. Aluminium and stainless steel corroded more slowly in a geothermal environment than a marine environment.

Thermal vents, hot springs and other features in geothermal areas can release sulphur-containing gases such as hydrogen sulphide (H_2S) and sulphur dioxide (SO_2) into the environment. These gases can be aggressive towards susceptible building and construction materials.

The material deterioration frequently seen in buildings and infrastructure in geothermal regions can result in large repair and maintenance costs. In addition, NZS 3604:2011 *Timber-framed buildings* requires specific engineering design for buildings constructed within 50 metres of a geothermal hot spot.

To assess the performance of metals in a geothermal environment, field exposure sites were established at different locations in Rotorua, roughly in a line from west to east across the city (Figure 1). Two contrasting exposure sites were also set up - one in the semi-rural BRANZ campus at Judgeford, Porirua, and the other close to breaking surf at Wellington's Oteranga Bay.

The metal samples had a typical dimension of 150 × 100 × 1-3 mm. They were set into exposure racks with nylon fixings. To minimise the influence of changes in weather and geothermal activity, corrosion rates were measured over three exposure periods:

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

The samples were regularly retrieved and their corrosion rates measured. The surfaces and cross-sections of samples were also examined with microscopes to see what was happening.

H_2S concentration in air

The concentration of airborne H_2S was measured with passive tube sensors in the first 3 weeks of each exposure period. A huge range was found between exposure sites, with the bottom graph in Figure 2 providing finer detail. The highest concentration of H_2S in Rotorua - 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.

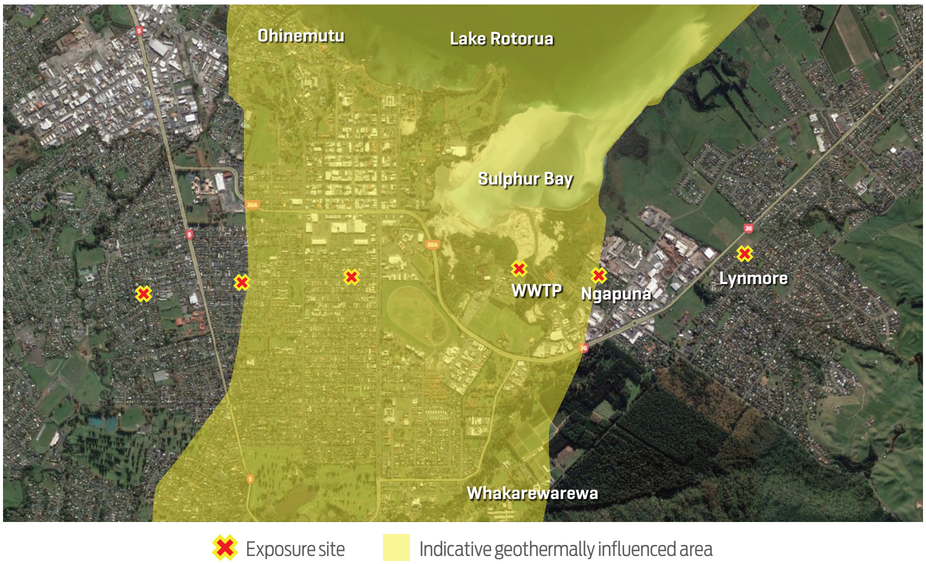

Figure 1. Exposure sites established in Rotorua.

Mild steel, zinc and copper corrosion

The corrosion rates of mild steel, zinc and copper varied greatly based on exposure site location. Mild steel corrosion rates lower than 200 g/m²/year were measured at only two sites, both in the western area. The highest corrosion rates were observed at the wastewater treatment plant site close to Sulphur Bay - 3,302 g/m²/year for mild steel, 84.2 g/m²/year for zinc and 495 g/m²/year for copper.

At the wastewater treatment plant site, a thick corrosion product layer formed on the mild steel sample (Figure 3). The sample thickness had increased from 3 mm to around 5-6 mm after a 1-year exposure, leading to a huge volume expansion. This thick corrosion product layer of around 1-2 mm thickness on each side could easily break off from the sample surface.

By comparison, the corrosion product layers on the mild steel samples exposed at the west and east city sites were relatively compact, with fewer physical defects such as spallation or detachment.

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 provide protection to the underlying zinc substrate and to grow slowly due to the absence of a lot of physical defects. Corrosion rates measured for zinc in the west and east of Rotorua were even lower than that measured at the semi-rural Judgeford site, where H_2S levels were exceedingly low.

By contrast, high corrosion rates in the zinc samples were seen at sites with high H_2S concentrations. The corroded surface of the zinc sample exposed at the wastewater treatment plant site was rough. It had a large number of clusters growing from underlying pit-like features.

The copper samples exposed at the wastewater treatment plant site had very high mass losses of 443-495 g/m² after 1 year of exposure. This extremely high corrosion rate is a direct result of the fast interaction of copper and sulphur-containing gases and poor protection offered by the corrosion products remaining on the surface. Corrosion products started to crack and detach partially as flakes after approximately 1 month of exposure. Consequently, fresh copper substrate would continue to be exposed to the corrosive environment. Examination under a microscope showed a very rough surface with large nodules and deep pit features. This type of corrosion product is unlikely to provide good protection to the underlying metal.

Corrosion products on copper samples exposed in west and east areas showed no obvious spallation or detachment, contributing to lower corrosion rates when compared with that exposed at the wastewater treatment plant. However, the corrosion product layer on the copper sample in the eastern region was thicker and more porous than that on the copper in the western area. The sizes of clusters and particles were also larger. This indicates that a small difference in concentration of airborne sulphur-containing gases would be enough to make a large difference in atmospheric corrosion of copper.

The corrosion rate measurement and observation of the form and structure of the corrosion products indicated that different

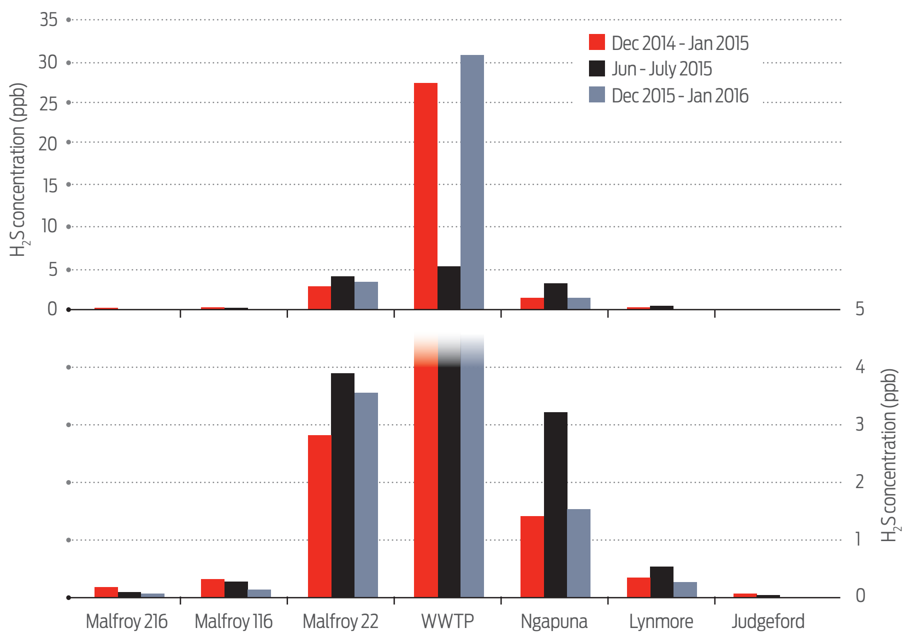

Figure 2. Average H_2S concentration during a 3-week exposure.

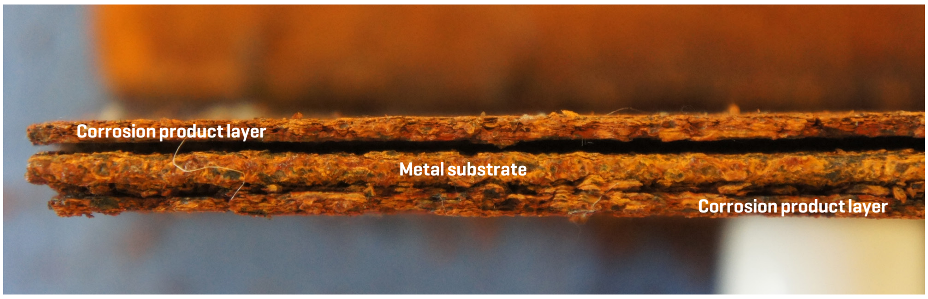

Figure 3. Corrosion products on the mild steel sample exposed at the wastewater treatment plant site for 1 year.

metals had quite different response to geothermal attack. Copper showed high corrosion rates in the west and east areas with (very) low H_2S concentrations and appeared to be more prone to geothermal attack than mild steel and zinc.

To verify this, the corrosion rates measured at Judgeford (where airborne H_2S concentration was extremely low) were used as a baseline to calculate corrosion rate ratios (Table 1). In geothermal environments with low H_2S concentrations, there was no increase of mild steel and zinc corrosion rates. However, there was an increase of copper corrosion rate, and the ratio was quite similar to the H_2S concentration ratio.

More recent BRANZ field research over 2016-2018 (see Study Report 458) confirmed that mild steel, zinc and copper all had severe corrosion when exposed in an area with strong geothermal influence - Tikitere, which had the highest concentrations of H_2S and SO_2 among all exposure sites. Corrosion occurred at lower rates at sites distant from a large-scale geothermal source.

However, copper still showed relatively high corrosion rates (35.6-49.9 g/m^2/year) even in areas with relatively weak geothermal influences (low concentrations of H_2S and SO_2). This was similar to the earlier studies and again indicated that copper has a higher sensitivity to the attack of airborne sulphur-containing gases compared to mild steel and zinc.

Aluminium and stainless steel

The field trial found that atmospheric corrosion of aluminium and stainless steel (AISI 304) is very limited when exposed in areas with strong geothermal influences. Close examination of the metal surfaces after exposure did not find any significant corrosion products. Only some small black spots were seen, and these could be cleaned chemically. There was no visible severe attack to the metal substrate underneath these spots.

Corrosion rate measurements indicated that these materials had higher mass losses when exposed to the severe marine environment, indicating that chloride-containing sea salt particles are more corrosive to them. Degradation of aluminium also appeared to be a result of the mechanical erosion by wind-blown sand and airborne chloride-containing salt particles.

Severe corrosion and rusting was seen on the aluminium and stainless steel samples under and/or very close to the nylon fasteners. These areas could trap sea salt particles for long periods. Pitting was also seen on the ground-facing surface of AISI 304 stainless steel where sea salt particles had been deposited.

Table 1. Metal corrosion sensitivity to airborne H_2S.

EXPOSURE SITE COMPARISON	H_2S CONCENTRATION RATIO	CORROSION RATE RATIO		
	DEC 2014 – JAN 2015	MILD STEEL	ZN	CU
216 Malfroy Rd (west) vs Judgeford	3	0.7	0.6	2.1
Lynmore (east) vs Judgeford	5.7	1.1	0.4	4.6

Conclusion

Measurements of corrosion in the metal samples indicate that different metals have different resistance to H_2S-induced attack in geothermal environments. Copper is more sensitive than mild steel and zinc. It appears to be sensitive to the presence of even very low concentrations of H_2S in the atmosphere.

Zinc appears to be less prone to atmospheric corrosion from sulphur-containing gases of relatively low concentrations compared with mild steel and copper. Above these lower concentrations of gas, corrosion in zinc can be accelerated.

In contrast, aluminium and stainless steel were much more resistant to atmospheric geothermal attack. These materials suffered greater corrosion in a marine environment.

More information

BRANZ Study Report SR393 *Materials within geothermal environments*

BRANZ Study Report SR458 *Atmospheric corrosivity of the Bay of Plenty region*

BRANZ Research Now: Geothermal corrosion #2 *Distance effects of corrosion in geothermal environments*

BRANZ Research Now: Geothermal corrosion #3 *Discolouration and deterioriation of wood in geothermal environments*

BRANZ Research Now: Geothermal corrosion #4 *The performance of aluminium-zinc alloy coating in geothermal environments*