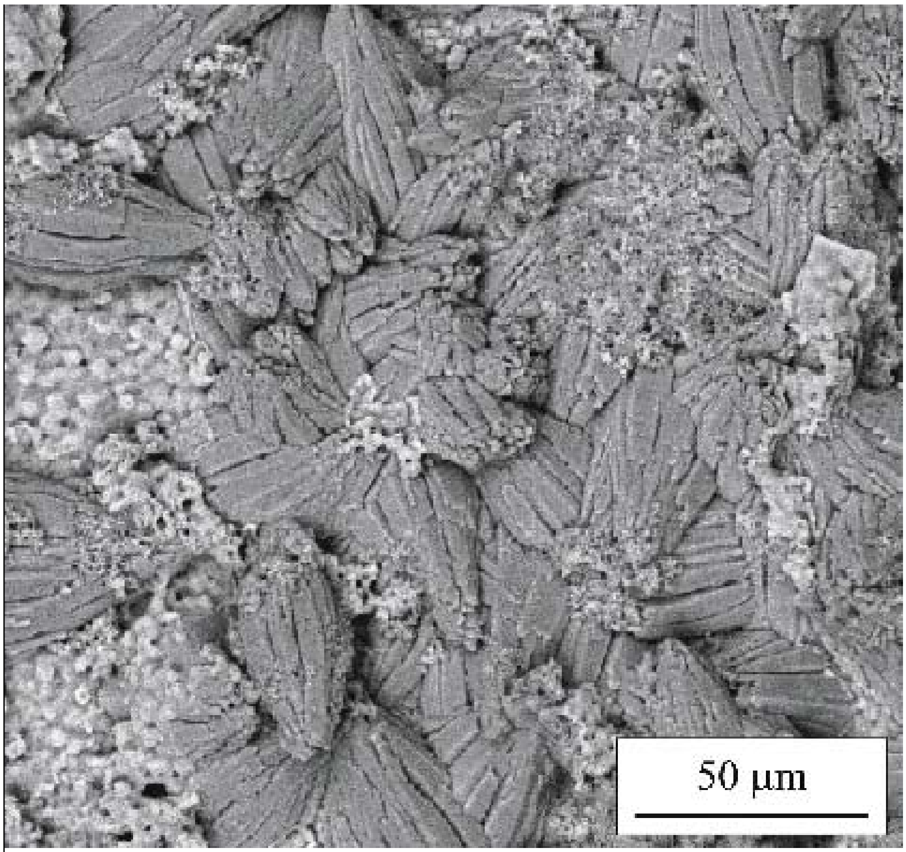
SEA(LING) THE RUST

Most people are familiar with the image of stranded ships rusting away – their hulks lying stranded on rocks. Rust never sleeps and rust is particularly active if steel is exposed to sea water. The question is often asked why sea water is more corrosive than, for instance, pure river water. The answer is that it isn't. High purity water can be more corrosive than sea water.



→ 1 *When you next swim in the ocean, spare a thought for the complex combination of chemicals in which you are immersed and how they interact to affect something as apparently simple as the rusting of a shipwreck.*

Published results from five years of testing mild steel in very pure river water showed slightly higher corrosion rates than five years of corrosion in sea water. In both cases, the rate of metal loss was around one-tenth of a millimetre a year. The simple idea of "salt water bad – fresh water good" does not hold true for the corrosion of mild steel.

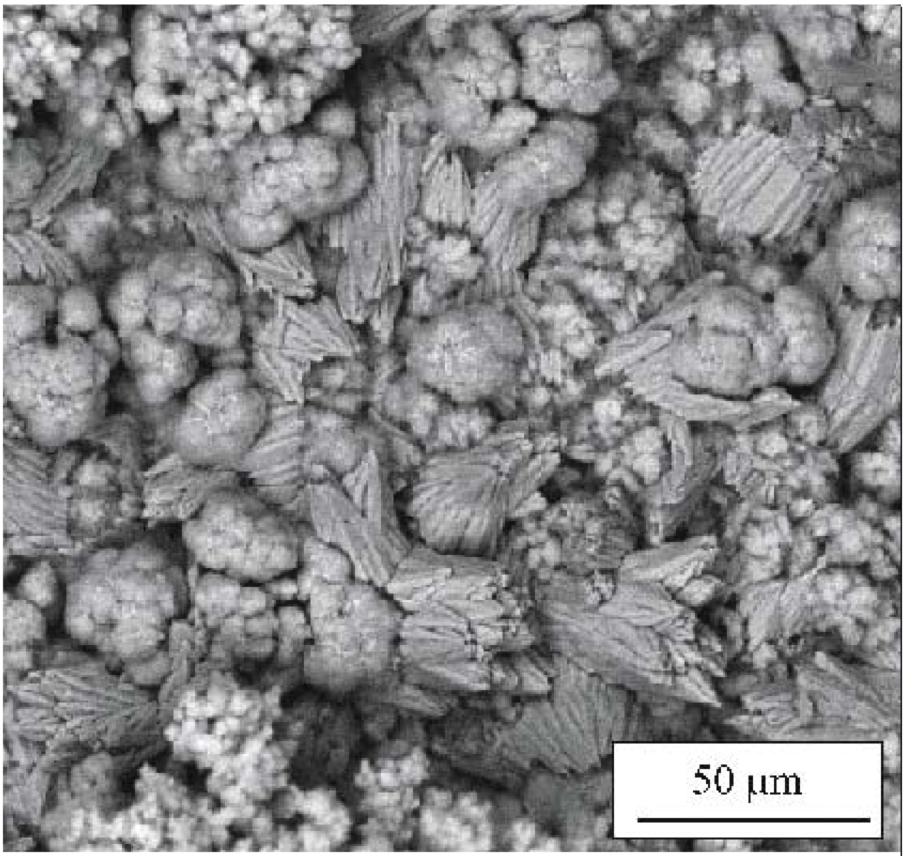
In a series of annual projects, Hein Möller, a lecturer in Materials Science and Metallurgical Engineering at the University of Pretoria, studied how the salts in sea water affect corrosion.

Sea water in the laboratory

In the first project, conducted in 2004, Materials Science and Metallurgical Engineering students completed a laboratory project as part of their final-year module on Corrosion. The investigation by undergraduate students Hanré Froneman and Theodor Boshoff (since published as a refereed paper in the *Journal of the South African Institute of Mining and Metallurgy*) showed that the bicarbonate in sea water could precipitate as calcium carbonate (limestone) while the metal is corroding.

This limestone stifles further corrosion: for artificial sea water (made by using only sodium chloride – table salt) the corrosion rate was four times higher than for natural sea water and microscopy showed that limestone indeed precipitated on the surface of the steel samples corroding in sea water.

This seems straightforward enough – we have all seen limestone encrusting the heating elements of domestic kettles and it seems reasonable to assume that such a crust would shield the steel from the



→ 2 The star-shaped aragonite (limestone) crystals are much larger on the surface of mild steel that has corroded for three weeks in strontium-free artificial sea water (above) than in the presence of strontium (→ 1). The micron marker in the bottom right of each picture shows the magnification: 50µm is roughly the diameter of a human hair.

corrosive sea water. Examining the rusted samples by electron microscope, however, it became clear that most of the corroded surface was not covered by limestone. There were only isolated, microscopic patches of limestone.

How this can give such a dramatic effect on the corrosion rate is linked to the basic steps involved in the corrosion of any metal. The first step is the chemical change that takes place in the steel, from a neutral metal to a charged cation that precipitates as rust, or dissolves in the water. The second step is a supporting reaction (or reactions) to receive the electrons released when the metal dissolves as cations.

Without a reaction – termed a cathodic reaction – to take up the electrons, corrosion would stop. In sea water (and other natural waters) the main cathodic reaction is the reduction of dissolved oxygen; the oxygen molecules react at the surface of the corroding metal surface, taking up electrons and forming hydroxide ions as the product. This means that the alkalinity of the water increases just where the oxygen reacts on the surface of the rusting metal. The increased alkalinity is the trigger for limestone to precipitate. In this way the cathodic reaction stifles itself.

From microscopic examination of the rusted metals, coverage of only a small fraction of the metal surface with limestone is sufficient to decrease the corrosion rate considerably – for reasons that are imperfectly understood, some parts of the metal surface have a greater tendency to act as cathodic regions than others. If these areas receive a coating of limestone, the corrosion rate is much lower. This is why water that contains only table salt is more corrosive than real sea water – real sea water contains dissolved bicarbonate and dissolved calcium, which precipitate where oxygen is reduced on the surface of the rusting metal.

More dissolved ions are, however, involved than just calcium and bicarbonate. Sea water contains more magnesium than calcium. The magnesium does not precipitate on its own, but (as Hein showed) if one makes artificial sea water containing only sodium, chloride, calcium and bicarbonate, the nature of the limestone precipitate changes completely. It assumes a different crystallographic structure (calcite, rather than aragonite) and the corrosion rate is higher.

Subtler still is the effect of dissolved strontium. Sea water contains about eight parts per million (ppm) strontium – much less than sodium (1.1%), chloride (1.8%), magnesium (1200 ppm) or calcium (400 ppm). Yet, artificially mixed sea water without strontium gives larger aragonite (limestone) crystals than sea water that does contain strontium.

In the photographs, the star-shaped precipitates are the aragonite crystals; the finer-grained background is the iron hydroxide (rust). Careful microanalysis reveals that the aragonite contains a small amount of strontium – as strontium carbonate, which precipitates with the calcium carbonate that makes up the bulk of the aragonite.

It turns out that others have researched the presence of strontium carbonate in aragonite deposits extensively (coral reefs are large aragonite deposits that contain strontium carbonate). The relative proportion of strontium is thought to be an indicator of the temperature at which the coral was deposited. From this body of work by others, the observation is made that strontium slows down the growth of aragonite. This seems to be the main reason for the much smaller aragonite crystals that form when the water contains strontium.

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