



# The influence of $\text{Sr}^{2+}$ on the formation of calcareous deposits on freely corroding low carbon steel in seawater

by H. Möller\* and P.C. Pistorius\*

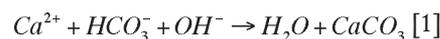
## Synopsis

The corrosion behaviour of a low carbon steel was investigated in synthetic seawaters with and without  $\text{Sr}^{2+}$ . It was found that strontium substitutes for calcium in aragonite, rather than precipitating as discrete strontianite ( $\text{SrCO}_3$ ). The aragonite deposits that formed in the presence of  $\text{Sr}^{2+}$  were finer than those that formed in the absence of  $\text{Sr}^{2+}$ . It is believed that an increase in the strontium content of aragonite induces a decrease in its solubility, which in turn results in a higher nucleation rate of the precipitates. Furthermore, the growth rate of aragonite is decreased by the presence of  $\text{Sr}^{2+}$  in the solution. It is concluded that  $\text{Sr}^{2+}$  is an essential ingredient in any artificial seawater when calcareous deposits are investigated on steel.

Keywords: corrosion, seawater, calcareous deposits, strontium, aragonite.

## Introduction

Seawater is not easily simulated in the laboratory for corrosion-testing purposes<sup>1,2</sup>. Even though the major chemical constituents of seawater are consistent worldwide, the corrosiveness of seawater is affected by various other factors. These include the concentration of dissolved oxygen, salinity, concentration of minor ions and biological activity. It is known that the presence of certain ions occurring in seawater, particularly  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , has a significant influence on the corrosion behaviour of steel<sup>3</sup>. The cathodic reduction of oxygen produces local alkaline surface conditions, which precipitate  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$  by Equations [1] and [2]:



These calcareous deposits are thought to promote a physical barrier against the diffusion of oxygen and thereby decrease the corrosion rate. Cathodic protection of steel immersed in seawater is known to promote the formation of these calcareous deposits<sup>4-7</sup>.

Calcium carbonate in calcareous deposits can exist in the crystalline forms of calcite or aragonite<sup>8</sup>. In the absence of  $\text{Mg}^{2+}$ , calcium carbonate can deposit as calcite and/or aragonite<sup>4,8</sup>. Calcium carbonate formed in the presence of  $\text{Mg}^{2+}$  precipitates exclusively in the form of aragonite<sup>5,8</sup>. This is due to magnesium's inhibiting effect on calcite's nucleation and growth<sup>9</sup>. The  $\text{Mg}(\text{OH})_2$  in calcareous deposits formed during cathodic protection is deposited in the crystalline form of brucite<sup>5</sup>. It has been shown, however, that no or little brucite is formed on steel under freely corroding conditions<sup>1,8,10,11</sup>.

Artificial solutions are commonly used to simulate the corrosion behaviour of materials in seawater. In previous work by one of the authors<sup>1</sup>, it was shown that the aragonite deposits that formed during immersion in natural seawater had a finer morphology than those that formed during immersion in MBL (Marine Biological Laboratory) and ASTM D1141 (American Society for Testing and Materials) synthetic seawaters. It was proposed that the finer deposits caused the slightly lower corrosion rates obtained in the natural seawater. Only compounds with a concentration  $\geq 0.1$  g/L were used in the preparation of the MBL and ASTM D1141 solutions in the previous work. Therefore, the following ions were present in these solutions:  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$  and  $\text{Br}^-$ . Other researchers commonly also use these main species in various combinations in artificial seawater solutions. For example<sup>4-6</sup>, calcareous deposition on cathodically protected steel has been studied using solutions containing mixtures of  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$ . Also, Elbeik and co-workers<sup>10</sup> studied the formation of calcareous

\* Department of Materials Science and Metallurgical Engineering, University of Pretoria, Pretoria, South Africa.

© The Southern African Institute of Mining and Metallurgy, 2007. SA ISSN 0038-223X/3.00 + 0.00. Paper received Jul. 2006; revised paper received Feb 2007.

## The influence of Sr<sup>2+</sup> on the formation of calcareous deposits

deposits on freely corroding steels (zero applied current) in an artificial solution containing only Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. The finer morphology of the aragonite deposits formed in natural seawater compared to the artificial solutions must therefore be due to the presence of another constituent (organic or inorganic) that was not included in any of the synthetic solutions mentioned here. The most notable omission in all of these artificial solutions is Sr<sup>2+</sup>. It is not surprising that this ion is typically absent from artificial solutions, given its low concentration in seawater. The Sr<sup>2+</sup> concentration specified in ASTM D1141 substitute ocean water<sup>12</sup> is only 158 µM (13.8 ppm). This implies that for every Sr<sup>2+</sup> ion dissolved in ASTM D1141 synthetic seawater, there are 346 Mg<sup>2+</sup> and 66 Ca<sup>2+</sup> ions. On the other hand, strontium is mentioned (along with calcium and magnesium) in a few textbooks and papers as being a beneficial constituent in seawater against corrosion<sup>13-15</sup>. It is believed that it is included in the calcareous deposit as a carbonate, thereby assisting in limiting diffusion of oxygen to the steel surface.

Limited solubility information is available for strontianite (SrCO<sub>3</sub>). According to Hartt and co-workers<sup>11</sup>, CaCO<sub>3</sub> is less soluble than SrCO<sub>3</sub>. However, according to Busenberg and Plummer<sup>16</sup>, strontianite has a lower solubility than aragonite and calcite<sup>17</sup> (see Table I). It has also been shown that co-precipitation of Sr<sup>2+</sup> can occur with aragonite<sup>18</sup>. Substitution of calcium by strontium is known to occur more readily in aragonite than in calcite<sup>19</sup>. Furthermore, it has been suggested that substitution of small amounts of strontium in aragonite causes a decrease in its solubility (or an increase in its stability)<sup>20</sup>.

There are conflicting views in literature about aragonite-strontianite solid solutions (Sr<sub>x</sub>Ca<sub>1-x</sub>CO<sub>3</sub>). According to Plummer and Busenberg<sup>20</sup>, a miscibility gap occurs over the compositional range 0.0058 ≤ x ≤ 0.875 at 25°C. However, Lucas-Girot and co-workers<sup>21</sup> have recently suggested that substitution of calcium by strontium is continuous from aragonite (x = 0) to strontianite (x = 1). They found that the evolution of the orthorhombic cell parameters as a function of x was linear for the overall domain (0 ≤ x ≤ 1). If a miscibility gap is indeed present, then calcareous deposits containing CaCO<sub>3</sub> and SrCO<sub>3</sub> in separate phases could be possible when the solubility level of strontium substituted in aragonite is exceeded. On the other hand, if a continuous solid solution exists between aragonite and strontianite, only one phase should be present in the calcareous deposits. In the case of corals, opinions differ on whether Sr<sup>2+</sup> directly substitutes for Ca<sup>2+</sup>, or whether it occurs as strontianite<sup>22</sup>. When calcareous deposits on steels are considered, it appears as if no strontium is present in the deposit when the steel is corroding

Table I

**Solubility products for CaCO<sub>3</sub> and SrCO<sub>3</sub>**

Form	-log K <sub>s</sub> (at 25°C)	Reference
Strontianite (SrCO <sub>3</sub> )	9.27	16
Calcite (CaCO <sub>3</sub> )	8.48	17
Aragonite (CaCO <sub>3</sub> )	8.34	17

freely<sup>11,14</sup>. Strontium seems to occur only in the deposit (between 0.006 and 0.14 %) when cathodic protection is applied<sup>11</sup>. It is also not clear from literature whether the strontium in calcareous deposits is only substituted into the aragonite structure or if it occurs as discrete strontianite<sup>11,13-15</sup>.

Gutjahr and co-workers<sup>23</sup> have shown that Sr<sup>2+</sup> causes a significant reduction in the growth and dissolution rates of aragonite. This was attributed to reversible adsorption of Sr<sup>2+</sup> ions at growth sites (kinks).

The objective of this study was therefore to determine the influence of strontium on the formation of calcareous deposits on freely corroding steel. Several effects are possible. Firstly, if SrCO<sub>3</sub> precipitates before CaCO<sub>3</sub>, it might act as nucleation sites for the deposition of the CaCO<sub>3</sub>. Secondly, if strontium substitutes for calcium in aragonite, the lower solubility of this Sr<sup>2+</sup>-containing aragonite might lead to a higher nucleation rate than would be found in Sr<sup>2+</sup>-free aragonite (due to greater supersaturation). A higher nucleation rate, together with a lower growth rate of aragonite crystals in the presence of Sr<sup>2+</sup>, would result in the formation of a calcareous deposit consisting of finer precipitates. Finally, if the morphology of the calcareous deposit is influenced by strontium, it might have an effect on the corrosion rate of the steel.

### Experimental

#### Solutions

The compositions of the artificial seawater solutions used in this study are shown in Table II. The amounts of the various compounds added to the solutions are based on the quantities specified in ASTM D1141 substitute ocean water<sup>12</sup>. Solution 1 contained only NaCl, CaCl<sub>2</sub>, MgCl<sub>2</sub> and NaHCO<sub>3</sub>. These four compounds represent the minimum number of constituents needed to form calcium carbonate as aragonite<sup>8</sup> and was used as a baseline to determine the effect of other ions on the morphology of the deposits. Solution 2 contained all the compounds in the ASTM D1141 specification with a concentration equal to or larger than 0.1 g/L (as was used in the previous paper<sup>1</sup>). Finally, solution 3 had the same composition as solution 2, except that SrCl<sub>2</sub> was also added. The conductivities of all the solutions were similar at approximately 54 mS/cm.

Table II

**Chemical composition (in g/L) of the synthetic seawater solutions used in this study**

Compound	Solution 1	Solution 2	Solution 3
NaCl	28.5	24.5	24.5
MgCl <sub>2</sub>	5.20	5.20	5.20
CaCl <sub>2</sub>	1.16	1.16	1.16
NaHCO <sub>3</sub>	0.20	0.20	0.20
Na <sub>2</sub> SO <sub>4</sub>	-	4.09	4.09
KCl	-	0.70	0.70
KBr	-	0.10	0.10
SrCl <sub>2</sub>	-	-	0.025

## The influence of Sr<sup>2+</sup> on the formation of calcareous deposits

### Material

Low carbon steel (SAE 1006 [UNS G10060]) was used for the experiments. The chemical composition of this steel is given in Table III. The steel was cut into 50 × 25 × 2 mm samples. The surfaces of the samples were ground clean using silicon carbide grinding paper starting with grit P180 and finishing with grit P800. The samples were then rinsed in distilled water and dried with ethanol to remove residual water. The cleaning procedure was performed quickly to avoid premature corrosion. The samples were weighed accurately (to a precision of 1 mg) before the immersion tests in order to conduct weight loss experiments.

### Immersion

Immersion tests were performed in continuously aerated solutions using three samples per solution. The volume of the solution was 2500 ml. Aeration was achieved by using a small air pump, which also contributed to uniform experimental conditions by stirring. All experiments were conducted at room temperature (20°C). The samples were immersed in the various solutions for either 3 hours, 5 days or 21 days. The water in the test cells was refreshed every 7 days for the longer exposure time. Before examination in a scanning electron microscope (SEM), the samples were coated with a sputtered layer of gold in order to reduce charging effects.

The corrosion products on the samples used for the weight loss experiments were removed with Clarke's solution<sup>24</sup> prior to weighing. A scale-free sample was also tested in Clarke's solution to verify that minimal metal loss occurred during this treatment.

## Results and discussion

### Characterization of calcareous deposits

Figure 1 shows images of small precipitates that formed on steel during immersion for 3 hours in solution 1 (Figure 1a), solution 2 (Figure 1b) and solution 3 (Figure 1c). The deposits in Figure 1a and Figure 1b were identified by EDS (Energy dispersive spectroscopy) as calcium carbonate. Obviously, no strontium-containing deposits could be formed in the strontium-free solutions (1 and 2). However, the precipitates in Figure 1c were identified as calcium carbonate containing some strontium (see Figure 2a for EDS results). This contradicts the findings presented by other researchers<sup>11,14</sup> who found no strontium in calcareous deposits that formed on freely corroding steel. No strontianite (SrCO<sub>3</sub>) precipitates were detected on the sample. It therefore seems that strontium was substituted into the aragonite crystals, rather than precipitating as strontianite.

Table III

**Chemical composition (in wt%) of SAE 1006 (UNS G10060) steel**

C	Mn	Si	Al	Cr	Ni	V	Fe
0.038	0.25	0.02	0.045	0.008	0.001	0.007	Balance

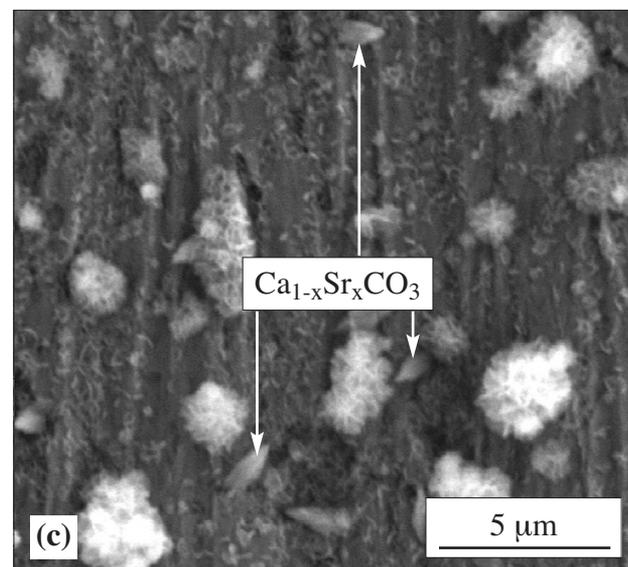
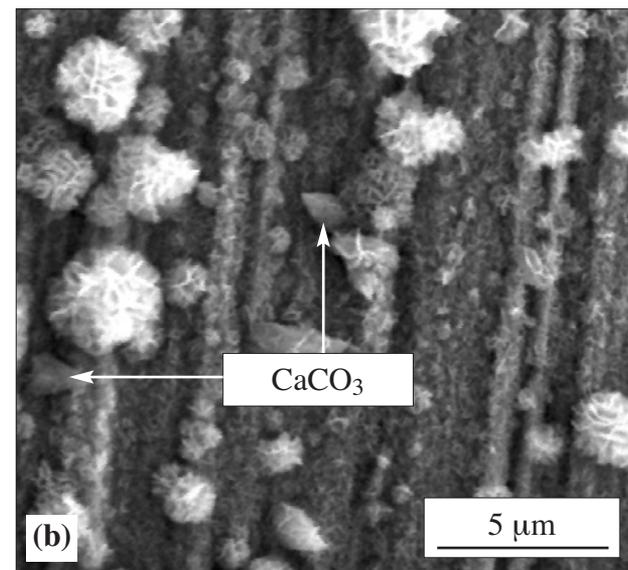
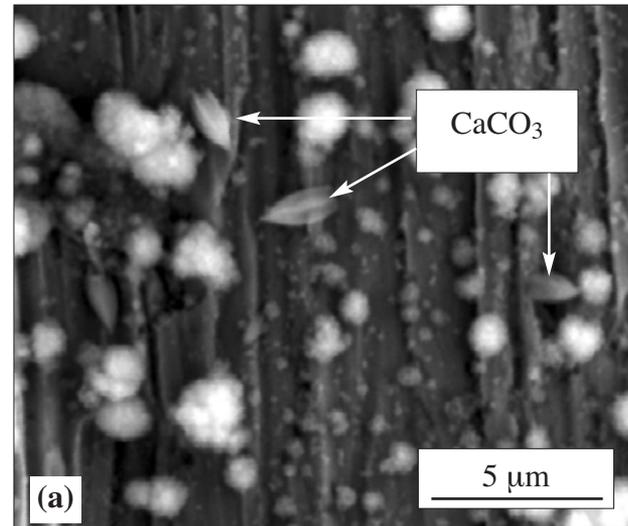


Figure 1 – (a) SEM image showing aragonite deposits that formed during immersion for 3 hours in solution 1, (b) SEM image showing aragonite deposits that formed during immersion for 3 hours in solution 2, (c) SEM image showing aragonite deposits that formed during immersion for 3 hours in solution 3

## The influence of Sr<sup>2+</sup> on the formation of calcareous deposits

To further test this hypothesis, samples were immersed for 3 hours in a solution with similar composition to solution 3, except that the Sr<sup>2+</sup> concentration was increased 10 times (solution 10Sr). Again, only Sr-containing aragonite precipitates were observed by SEM (no SrCO<sub>3</sub>), but, as the EDS results in Figure 2b indicate, strontium substitution for calcium occurred to a greater extent in this solution.

The effect of Sr<sup>2+</sup> on the morphology of aragonite can be seen in Figures 3a–c. Figure 3 shows images of the calcareous deposits that formed on the steel during immersion for 5 days in solution 1 (Figure 3a), solution 2 (Figure 3b) and solution 3 (Figure 3c). The morphology of the aragonite deposits that formed in solution 2 is marginally finer than those that formed in solution 1. This implies that the combination of K<sup>+</sup>, SO<sub>4</sub><sup>2-</sup> and Br<sup>-</sup> does not have a significant effect on the morphology of deposited aragonite on freely corroding steel. However, it is seen that finer aragonite deposits were formed in the Sr<sup>2+</sup>-containing solution (Figure 3c). The calcareous deposits that formed in this solution compare more favourably with those that were formed in natural seawater<sup>1</sup>.

The observation that finer aragonite deposits are formed in the Sr<sup>2+</sup>-containing solution can be attributed to a combination of two factors. Firstly, the nucleation rate of aragonite was increased by substitution of Sr<sup>2+</sup>, due to the lower solubility of Sr<sup>2+</sup>-containing aragonite<sup>20</sup>. The higher nucleation rate of aragonite in solution 3 is evident when comparing Figure 3c with Figures 3a and b, showing the much larger area density of carbonate particles for solution 3. The second factor is the influence of Sr<sup>2+</sup> on the growth rate of aragonite. Gutjahr and co-workers<sup>23</sup> have demonstrated that certain divalent cations, such as Sr<sup>2+</sup>, Ba<sup>2+</sup>, Zn<sup>2+</sup> and Cu<sup>2+</sup> cause a considerable decrease in the growth rate of

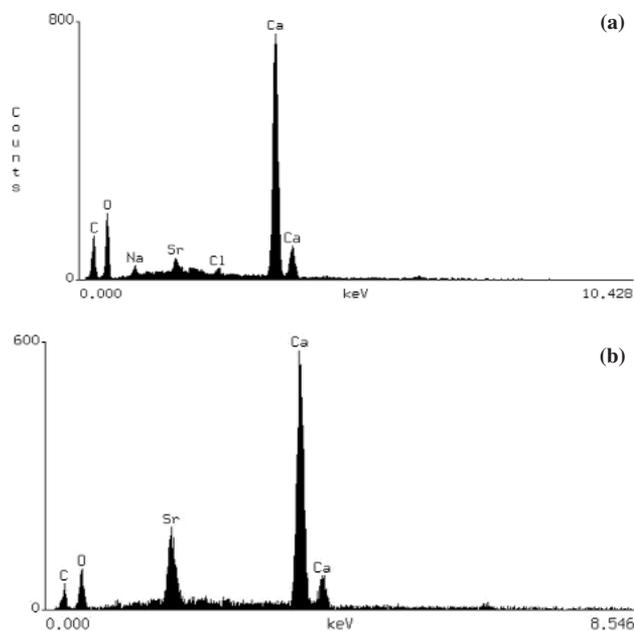


Figure 2—(a) EDS analysis of an aragonite precipitate that formed on steel after immersion in solution 3 showing a peak indicating the presence of strontium in the precipitate, (b) EDS analysis of an aragonite precipitate that formed on steel after immersion in solution 10Sr (solution containing 10 times the standard quantity of Sr<sup>2+</sup>)

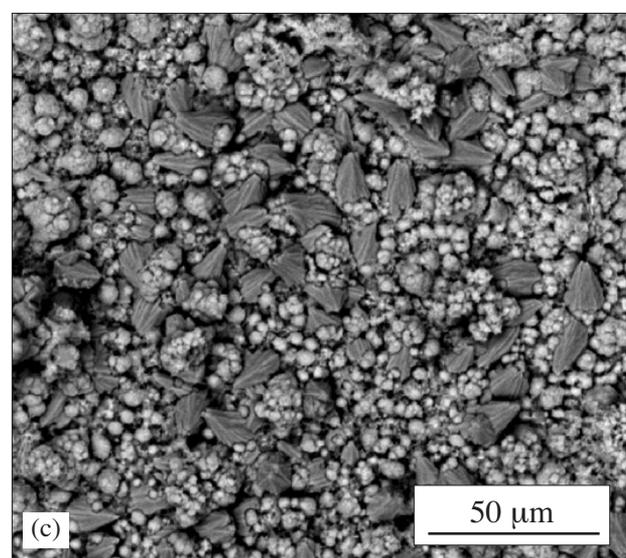
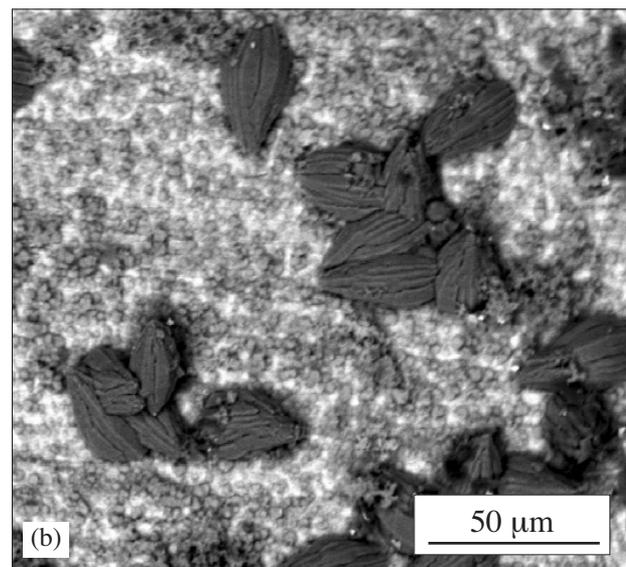
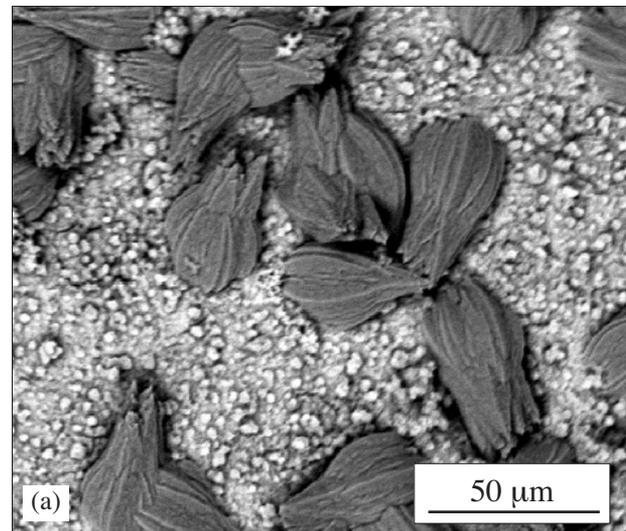


Figure 3—(a) SEM image showing coarse aragonite deposits that formed during immersion for 5 days in solution 1, (b) SEM image showing coarse aragonite deposits that formed during immersion for 5 days in solution 2, (c) SEM image showing fine aragonite deposits that formed during immersion for 5 days in solution 3

## The influence of Sr<sup>2+</sup> on the formation of calcareous deposits

aragonite crystals. The transition metals (Cu<sup>2+</sup>, Zn<sup>2+</sup>) show a stronger inhibition than Sr<sup>2+</sup>, but their concentrations in seawater are too low to have the same individual effect as strontium. Table IV shows the concentrations of these ions that are needed to cause a 50% reduction in the growth rate of aragonite (C<sub>50%</sub>), as well as the concentrations of the ions in ASTM D1141 synthetic seawater (C<sub>D1141</sub>). Table V shows the approximate % reductions in growth rate of aragonite caused by these ions at the concentrations in ASTM D1141 synthetic seawater. It is seen from Table V that Sr<sup>2+</sup> (at typical seawater concentrations) can reduce the growth rate of aragonite by as much as 65%.

In order to further investigate the effects of strontium substitution on the morphology of aragonite, samples were also immersed for 5 days in the solution containing 10 times the standard quantity of Sr<sup>2+</sup> (i.e. solution 10Sr). The calcareous deposits formed in this solution (Figure 4) were much finer than in any of the other solutions after 5 days (note the difference in magnification used in Figures 3 a–c and Figure 4). Again, no strontianite precipitates were observed on this sample. It is seen from Table V that the Sr<sup>2+</sup>-concentration of this solution can reduce the growth rate of aragonite crystals by 95%. Interestingly, a few small precipitates containing Sr and S were observed on the Sr-containing aragonite precipitates (see Figures 5a and b). These precipitates are tentatively identified as SrSO<sub>4</sub> (celestite). It is not too surprising that celestite was formed on the steel in this solution—some marine organisms (such as acantharians) use celestite as a skeleton<sup>25</sup>. It is known that celestite is under-saturated in seawater (approximately 30% of saturation<sup>26</sup>), but it must be remembered that this specific solution contained an order of magnitude larger Sr<sup>2+</sup>-concentration than seawater.

Table IV

**Ion concentrations needed to cause a 50% reduction in the growth rate of aragonite<sup>23</sup>, compared with the composition of ASTM D1141 synthetic seawater<sup>12</sup>**

Ion	C <sub>D1141</sub> Concentration in ASTM D1141 solution <sup>12</sup> (μM)	C <sub>50%</sub> Concentration for halving growth rate <sup>23</sup> (μM)	C <sub>D1141</sub> : C <sub>50%</sub>
Sr <sup>2+</sup>	158	63	2.51
Cu <sup>2+</sup>	0.16	1.0	0.16
Zn <sup>2+</sup>	0.051	0.63	0.081
Ba <sup>2+</sup>	0.38	7.9	0.048
Mg <sup>2+</sup>	5.5 x 10 <sup>4</sup>	∞	0

Table V

**Calculated reduction in aragonite growth rate (based on literature data<sup>23</sup>) by certain divalent ions at the concentrations in ASTM D1141 synthetic seawater**

Ion at C <sub>D1141</sub> concentration	% Reduction in aragonite growth rate <sup>23</sup>
Sr <sup>2+</sup>	65
Cu <sup>2+</sup>	15
Zn <sup>2+</sup>	5
Ba <sup>2+</sup>	3
Mg <sup>2+</sup>	0
10 x Sr <sup>2+</sup>	95

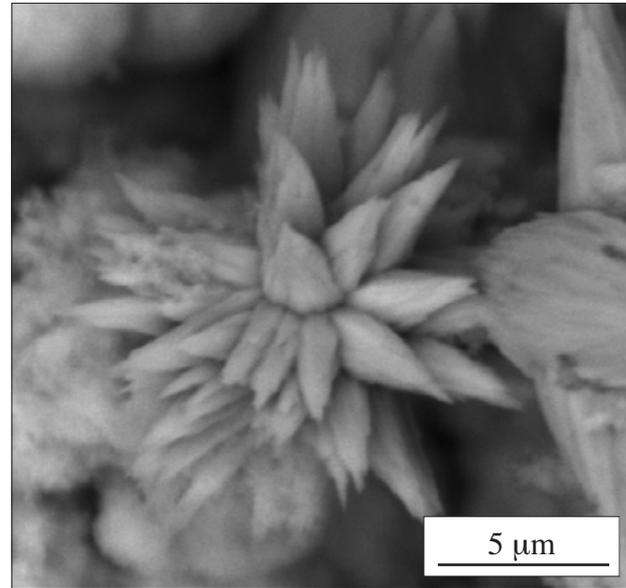


Figure 4—SEM image showing fine aragonite deposits that formed during immersion for 5 days in solution 10Sr

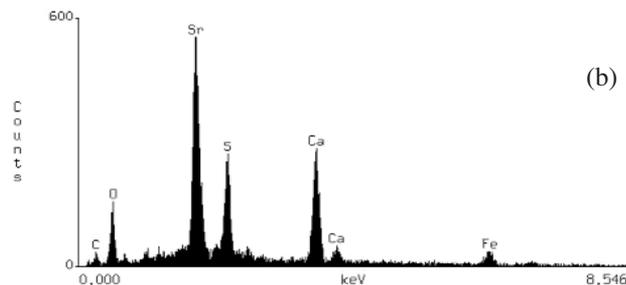
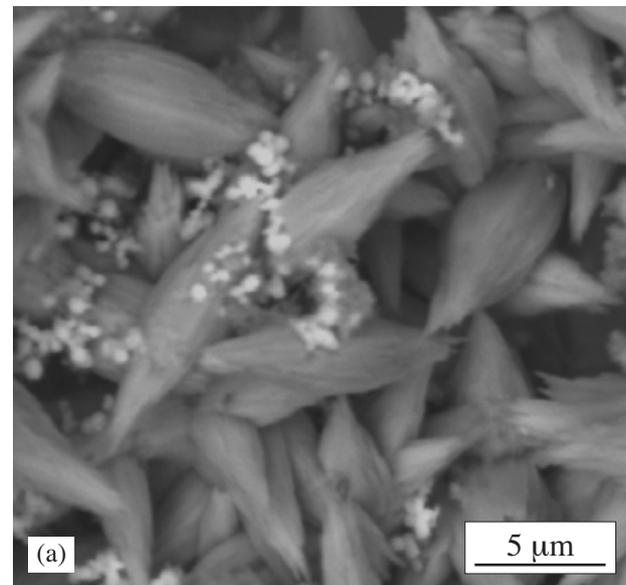


Figure 5—(a) SEM image showing possible celestite precipitates on the Sr-containing aragonite deposits that formed during immersion for 5 days in solution 10Sr; (b) EDS analysis of the small precipitates in Figure 5(a) indicating the possibility of celestite formation after immersion in solution 10Sr for 5 days. The presence of CaCO<sub>3</sub> is due to the small size of the celestite

## The influence of Sr<sup>2+</sup> on the formation of calcareous deposits

To ascertain whether individual SrCO<sub>3</sub> precipitates could be detected when no aragonite was present on the steel surface, samples were also immersed in Sr<sup>2+</sup>-containing solutions without any Ca<sup>2+</sup>. The first solution was similar in composition to solution 3 (containing the standard quantity of Sr<sup>2+</sup>), but without any Ca<sup>2+</sup> (designated as solution 1Sr\_0Ca). The second solution was similar to solution 10Sr, but without any calcium (designated as solution 10Sr\_0Ca). No SrCO<sub>3</sub> precipitates could be observed by SEM even after immersion for up to 18 days in solution 1Sr\_0Ca. This suggests that the Sr<sup>2+</sup> concentration of seawater is too low to allow the precipitation of strontianite on freely corroding steel (also see the equilibrium calculations below). However, SrCO<sub>3</sub> precipitates were observed after immersion for 5 days in solution 10Sr\_0Ca (see Figures 6a and b), even though none of these deposits was detected in the equivalent Ca<sup>2+</sup>-containing solution 10Sr (Figures 4 and 5). All the results therefore strongly suggest that strontium would rather be substituted for calcium into the aragonite structure than precipitate as strontianite in the presence of Ca<sup>2+</sup> (further support for these conclusions is given below based on equilibrium calculations).

Support for the results in this paper is also available in literature on coral aragonite. It has been suggested that the strontium concentration in corals exceeds the thermodynamic

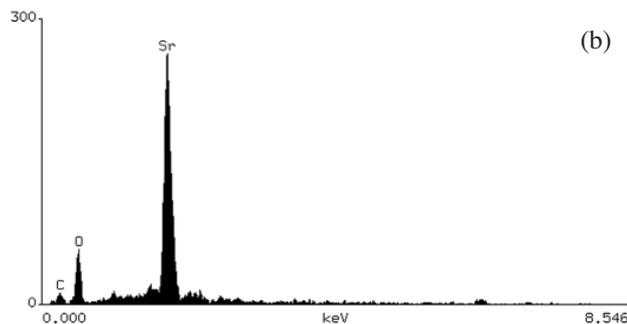
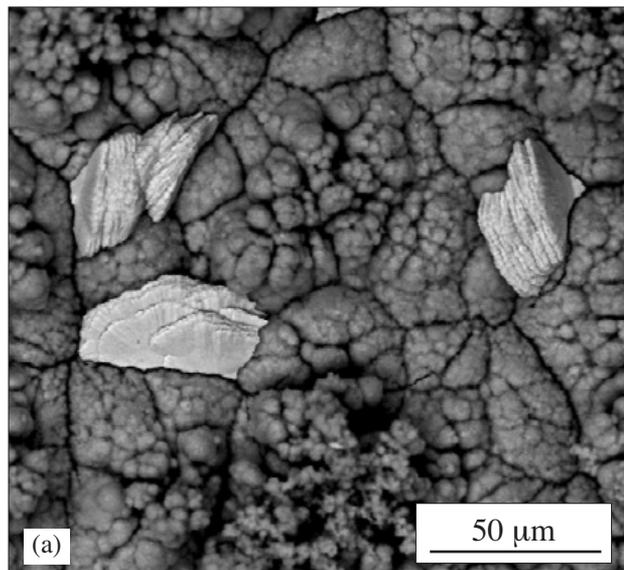


Figure 6— (a) SEM image showing SrCO<sub>3</sub> precipitates that formed during immersion for 5 days in solution 10Sr\_0Ca, (b) EDS analysis of a SrCO<sub>3</sub> precipitate in Figure 6 (a) that formed on steel after immersion in solution 10Sr\_0Ca

solubility level of strontium substituted in aragonite<sup>20,27</sup>. For this reason, Gregor and co-authors<sup>28</sup> suggested that some coral skeletons might contain strontium as discrete SrCO<sub>3</sub> and as Sr substituted for Ca in aragonite. However, Finch and co-workers used XRD and Sr K-edge Extended X-ray Absorption Fine Structure (EXAFS) results to propose that a variety of corals precipitate a metastable, strontium-supersaturated aragonite with strontianite below detection levels<sup>27,29,30</sup> (even for the same material used previously by Gregor and co-workers<sup>27,28</sup>). Furthermore, they suggested that the diffusion kinetics of the metastable aragonite is so slow that diffusion-related decomposition will not occur within geological timeframes<sup>27</sup>. For example, by using the diffusivity of strontium in calcite, and assuming a similar diffusivity in aragonite, they estimated that the nucleation of nm-size strontianite domains in aragonite would require time periods of approximately 10<sup>17</sup> years.

Finally, as stated earlier, Lucas-Girot and co-workers<sup>21</sup> have recently suggested the existence of continuous solid solutions between strontianite and aragonite. This could also be a plausible explanation for the absence of discrete strontianite in corals and in calcareous deposits.

Figure 7 shows images of the calcium carbonate deposits that formed on steel immersed for 21 days in solution 1 (Figure 7a), solution 2 (Figure 7b) and solution 3 (Figure 7c). Again, the aragonite deposits are finer in the Sr<sup>2+</sup>-containing solution 3 than in the other two solutions. The deposits that formed in solutions 1 and 2 are again similar, confirming the results found after immersion for 5 days.

### Equilibrium calculations

Preliminary equilibrium calculations were performed with FactSage 5.4<sup>31</sup>, to evaluate the possible effects of strontium on aragonite formation. A Pitzer aqueous solution model (FACT-PITZ) was used, together with pure solid species from the general FACT database. All possible solid phases (carbonates, oxides, and chlorides) were included in the calculation, with the exception of dolomite and MgCO<sub>3</sub>, which are not practically observed (even though they are predicted to be stable in contact with seawater in the case of dolomite, and for slightly alkalized seawater in the case of MgCO<sub>3</sub>).

The compositions of solution 2 and 3 (Table II) were used, for a temperature of 25°C (since this is the temperature at which the Pitzer model is valid). The effect of alkalization at cathodic areas was simulated by adding various additional amounts of NaOH.

Figure 8 shows the results for solution 2, which contains no strontium. As the figure indicates, aragonite is predicted to be the first precipitate to form; brucite forms once the pH rises to approximately 9.3 (and brucite formation then buffers the pH close to this value for further additions of NaOH). The predictions for solution 3 were identical if SrCO<sub>3</sub> was considered as a separate phase: that is, it is predicted that SrCO<sub>3</sub> does not precipitate as a separate phase, in line with the experimental observations.

In the absence of any data on the SrCO<sub>3</sub>-CaCO<sub>3</sub> solid solution, this was modelled as an ideal solution. The predictions where this ideal solid solution was considered as a stable phase, for seawater containing strontium (solution 3), are given in Figure 9. The amount of precipitate

## The influence of Sr<sup>2+</sup> on the formation of calcareous deposits

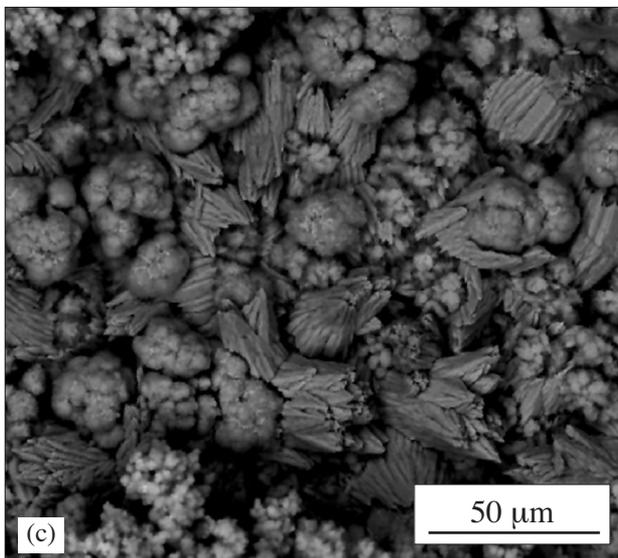
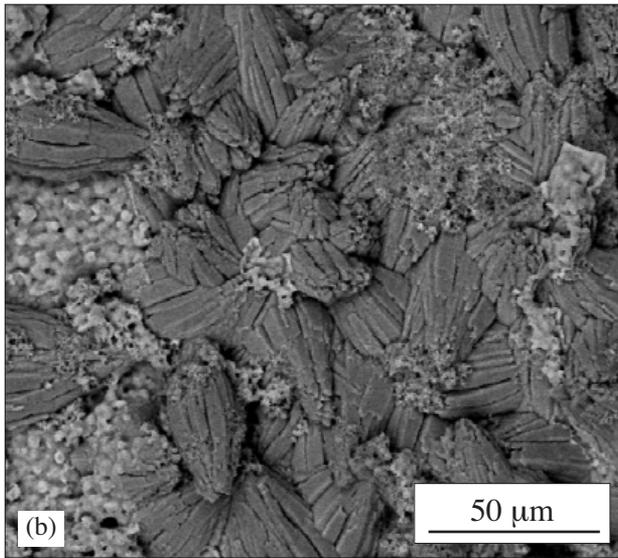
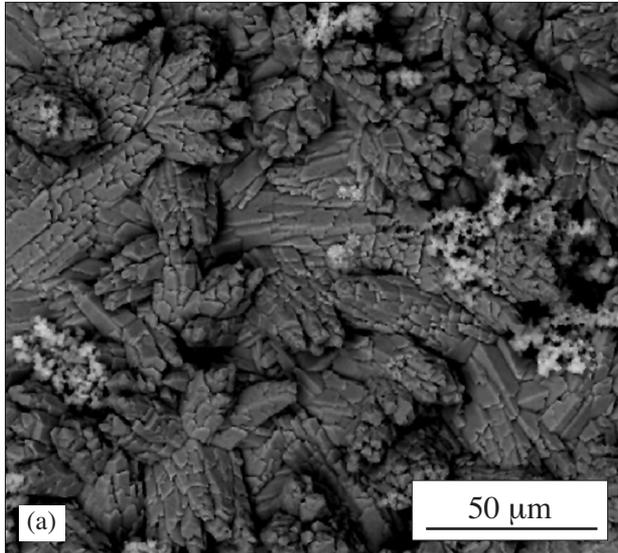


Figure 7—(a) SEM image showing aragonite deposits that formed during immersion for 21 days in solution 1, (b) SEM image showing aragonite deposits that formed during immersion for 21 days in solution 2, (c) SEM image showing aragonite deposits that formed during immersion for 21 days in solution 3

is similar to that of the Sr<sup>2+</sup>-free solution (Figure 8), but with the difference that the aragonite precipitate was predicted to contain SrCO<sub>3</sub> in solid solution—as shown by the lower graph in Figure 9. What is not immediately obvious from comparison of Figures 8 and 9 is that precipitation of the strontium-containing aragonite precipitate is predicted to occur at a slightly lower pH than the strontium-free aragonite precipitate. This is illustrated by Figure 10, which replots the results of Figures 8 and 9 as functions of pH. The strontium-containing aragonite forms at a slightly lower pH, which illustrates the greater stability of this precipitate compared with SrCO<sub>3</sub>-free aragonite.

### Corrosion rates of SAE 1006 steel in the various solutions

The corrosion rates of the samples were calculated by using average weight loss measurements after immersion for 21 days in the different artificial seawater solutions of Table II. The average limiting current density for oxygen reduction on the steel surface ( $i_L$ ) was also estimated from the weight loss measurements by assuming that the corrosion current density of the steel ( $i_{corr}$ ) is equal to  $i_L$ . The results are shown in Table VI. The corrosion rates of the steel immersed in the various solutions are seen to be similar, but somewhat lower in the strontium-containing solution.

### Conclusions

The conclusions of this study are:

- Strontium is present in the calcareous deposits that were formed on freely corroding steel during immersion in Sr<sup>2+</sup>-containing artificial seawater. This contradicts the findings presented by other researchers in earlier studies.
- No strontianite (SrCO<sub>3</sub>) precipitates were detected on any of the samples that were immersed in solutions containing both Ca<sup>2+</sup> and Sr<sup>2+</sup>.

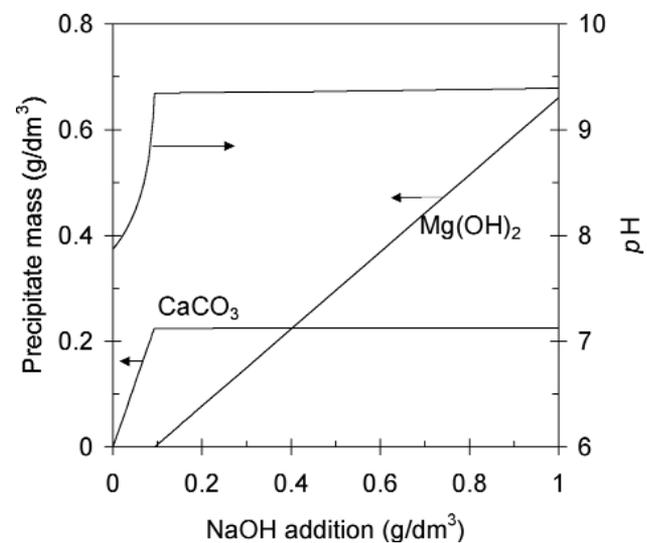


Figure 8—Calculated changes in amounts of solid precipitates and pH, for different levels of addition of NaOH to solution 2

## The influence of Sr<sup>2+</sup> on the formation of calcareous deposits

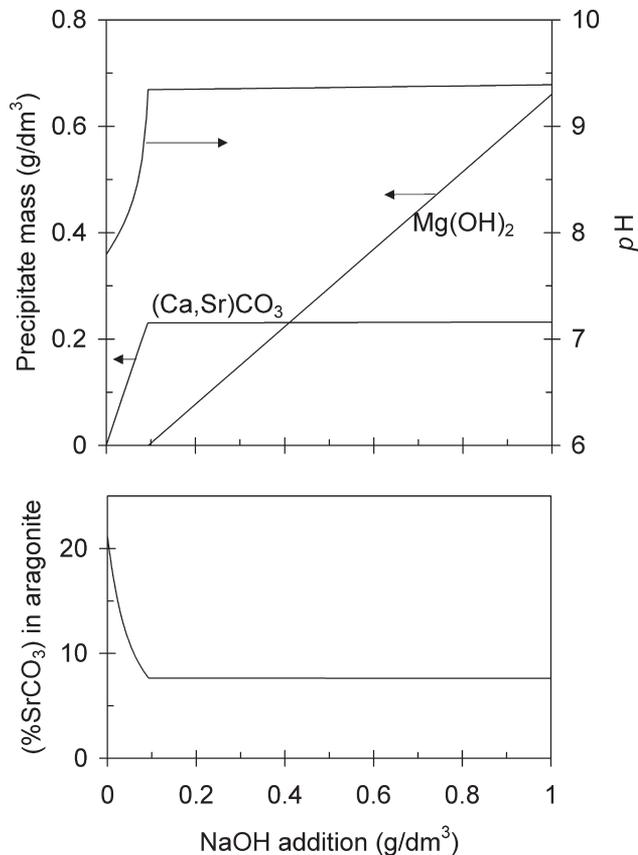


Figure 9—Calculated changes in amounts of solid precipitates and pH, for different levels of addition of NaOH to solution 3 (containing Sr<sup>2+</sup>), considering an ideal solution CaCO<sub>3</sub>-SrCO<sub>3</sub> as a possible phase; the lower graph shows the predicted composition of this solid solution

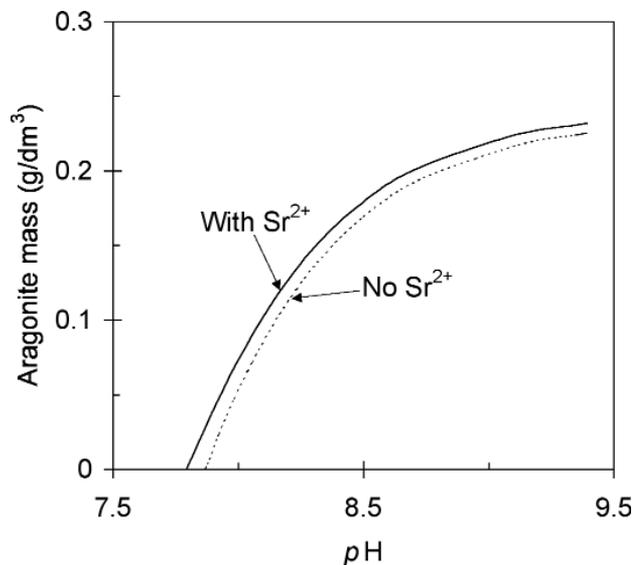


Figure 10—Calculated amounts of aragonite precipitate (pure CaCO<sub>3</sub> for solution 2, and CaCO<sub>3</sub>-SrCO<sub>3</sub> ideal solid solution for solution 3) as function of pH (replotted results of Figures 8 and 9)

- It seems as if strontium only substitutes for calcium in aragonite, which presumably decreases its solubility.
- The growth rate of aragonite crystals is known to be decreased significantly in solutions containing Sr<sup>2+</sup>.

Table VI

**Corrosion rates and current densities obtained for the corrosion of SAE 1006 steel based on weight loss after immersion for 21 days**

	Solution 1	Solution 2	Solution 3
$i_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )	14.4	15.1	12.9
Rate (mm/y)	0.17	0.18	0.15

- The combination of higher nucleation rate (lower solubility) and lower growth rate of aragonite crystals in Sr<sup>2+</sup>-containing solutions results in the formation of finer calcareous precipitates.
- The calcareous layer that is obtained in the Sr<sup>2+</sup>-containing artificial seawater solution (solution 3) is more representative (in terms of composition and morphology) of what is found when steel is immersed in natural seawater. Strontium is therefore a necessary constituent in any artificial seawater when calcareous deposition on steel is studied.
- The corrosion rates of the low carbon steel immersed in the various artificial seawater solutions were not influenced significantly by the differences in calcium carbonate morphologies in this study.

### References

1. MÖLLER, H., BOSHOFF, E.T., and FRONEMAN, H. The corrosion behaviour of a low carbon steel in natural and synthetic seawaters. *Journal of the South African Institute of Mining and Metallurgy*, vol. 106, 2006. pp. 585–592.
2. *ASM Metals Handbook*, vol. 13: Corrosion, 9th ed. Materials Park, OH, ASM International, 1987. pp. 893–902.
3. JONES, D.A. *Principles and Prevention of Corrosion*. Upper Saddle River, NJ, Prentice Hall, 1996. p. 365.
4. DESLOUIS, C., FESTY, D., GIL, O., RIUS, S., TOUZAIN, S., and TRIBOLLET, B. Characterisation of calcareous deposits in artificial seawater by impedance techniques I. *Electrochimica Acta*, vol. 43, 1998. pp. 1891–1901.
5. BARCHICHE, C., DESLOUIS, C., FESTY, D., GIL, O., REFAIT, P., TOUZAIN, S., and TRIBOLLET, B. Characterisation of calcareous deposits in artificial seawater by impedance techniques III. *Electrochimica Acta*, vol. 48, 2003. pp. 1645–1654.
6. BARCHICHE, C., DESLOUIS, C., GIL, O., REFAIT, P., and TRIBOLLET, B. Characterisation of calcareous deposits by electrochemical methods: role of sulphates, calcium concentration and temperature. *Electrochimica Acta*, vol. 49, 2004. pp. 2833–2839.
7. CHEN, S., HARTT, W.H., and WOLFSON, S. Deep water cathodic protection. *Corrosion*, vol. 59, 2003. pp. 721–732.
8. MÖLLER, H. The influence of Mg<sup>2+</sup> on the formation of calcareous deposits on freely corroding low carbon steel in seawater. *Corrosion Science*, vol. 49, 2007. pp. 1992–2001.
9. MANTEL, K.E., HARTT, W.H., and CHEN, T.-Y. Substrate, surface finish, and flow rate influences on calcareous deposit structure, *Corrosion*, vol. 48, 1992. pp. 489–499.
10. ELBEIK, S., TSEUNG, A.C.C., and MACKAY, A.L. The formation of calcareous deposits during the corrosion of mild steel in seawater. *Corrosion Science*, vol. 26, 1986. pp. 669–680.
11. HARTT, W.H., CULBERSON, C.H., and SMITH, S.W. Calcareous deposits on metal surfaces in seawater—A critical review. *Corrosion*, vol. 40, 1984. pp. 609–618.
12. ASTM D1141. *Standard Practice for the Preparation of Substitute Ocean Water*. West Conshohocken, PA, ASTM International, 1999.
13. LAQUE, F.L. *Marine corrosion*. London, John Wiley and Sons, 1975. p. 104.
14. MELCHERS, R.E. Probabilistic models for corrosion in structural reliability assessment—Part 2. *Journal of offshore mechanics and arctic engineering*, vol. 125, 2003. pp. 272–280.

## The influence of Sr<sup>2+</sup> on the formation of calcareous deposits

15. LIN, S.H. and DEXTER, S.C. Effects of temperature and magnesium ions on calcareous deposition. *Corrosion*, vol. 44, 1988. pp. 615–622.
16. BUSENBERG, E., and PLUMMER, L.N. The solubility of strontianite in CO<sub>2</sub>-H<sub>2</sub>O solutions between 2 and 91°C, the association constants of SrHCO<sub>3</sub><sup>+</sup>(aq) and SrCO<sub>3</sub>(aq) between 5 and 80°C, and an evaluation of the thermodynamic properties of Sr<sup>2+</sup>(aq) and SrCO<sub>3</sub>(cr) at 25°C and 1 atm total pressure. *Geochimica et Cosmochimica Acta*, vol. 48, 1984. pp. 2021–2035.
17. GAL, J.Y., BOLLINGER, J.C., TOLOSA, H., and GACHE, N. Calcium carbonate solubility: a reappraisal of scale formation and inhibition. *Talanta*, vol. 43, 1996. pp. 1497–1509.
18. KINSMAN, D.J.J. and HOLLAND, H.D. The co-precipitation of cations with CaCO<sub>3</sub>—IV. The co-precipitation of Sr<sup>2+</sup> with aragonite between 16° and 96°C. *Geochimica et Cosmochimica Acta*, vol. 33, 1969. pp. 1–17.
19. SCHROEDER, J.H. Experimental dissolution of calcium, magnesium and strontium from recent biogenic carbonates: a model of diagenesis. *Journal of sedimentary petrology*, vol. 39, 1969. pp. 1057–1073.
20. PLUMMER, L.N. and BUSENBERG, E. Thermodynamics of aragonite-strontianite solid solutions: Results from stoichiometric solubility at 25 and 76°C. *Geochimica et Cosmochimica Acta*, vol. 51, 1987. pp. 1393–1411.
21. LUCAS-GIROT, A., HERNANDEZ, O., and OUDADESSE, H. Re-examination of the structural properties of solid solutions Sr<sub>x</sub>Ca<sub>1-x</sub>CO<sub>3</sub>. *Materials Research Bulletin*, Article in Press, 2006. doi:10.1016/j.materresbull.2006.09.016.
22. FALLON, S.J., McCULLOCH, M.T., and ALIBERT, C. Examining water temperature proxies in Porites corals from the Great Barrier Reef: a cross-shelf comparison. *Coral Reefs*, vol. 22, 2003. pp. 389–404.
23. GUTJAHR, A., DABRINGHAUS, H., and LACMANN, R. Studies of the growth and dissolution kinetics of the CaCO<sub>3</sub> polymorphs calcite and aragonite II. The influence of divalent cation additives on the growth and dissolution rates. *Journal of Crystal Growth*, vol. 158, 1996. pp. 310–315.
24. WRANGLER, G. *An Introduction to Corrosion and Protection of Metals*. New York, Chapman and Hall, 1985. p. 236.
25. BERNSTEIN, R.E., BYRNE, R.H., BETZER, P.R., and GERCO, A.M. Morphologies and transformations of celestite in seawater: the role of acantharians in strontium and barium geochemistry. *Geochimica et Cosmochimica Acta*, vol. 65, 1992. pp. 3273–3279.
26. RUSHDI, A.I., McMANUS, J., and COLLIER, R.W. Marine barite and celestite saturation in seawater. *Marine Chemistry*, vol. 69, 2000. pp. 19–31.
27. FINCH, A.A. and ALLISON, N. Strontium in coral aragonite: Sr coordination and the long-term stability of coral environmental records. *Geochimica et Cosmochimica Acta*, vol. 67, 2003. pp. 4519–4527.
28. GREGOR, R.B., PINGITORE, N.E., and LYTLE, F.W. Strontianite in coral skeletal aragonite. *Science*, vol. 275, 1997. pp. 1452–1454.
29. FINCH, A.A., ALLISON, N., SUTTON, S.R., and NEWVILLE, M. Strontium in coral aragonite: Characterisation of Sr coordination by EXAFS. *Geochimica et Cosmochimica Acta*, vol. 67, 2003. pp. 1189–1194.
30. ALLISON, N., FINCH, A.A., NEWVILLE, M., and SUTTON, S.R. Strontium in coral aragonite: Sr coordination and geochemistry in relation to skeletal architecture. *Geochimica et Cosmochimica Acta*, vol. 69, 2005. pp. 3801–3811.
31. BALE, C.W., CHARTRAND, P., DEGTEROV, S.A., ERIKSSON, G., HACK, K., MAHFOUD, R.B., MELANCON, J., PELTON, A.D., and PETERSEN, S. FactSage thermochemical software and databases. *Calphad*, vol. 26, 2002. pp. 189–228. ◆

PUTTING OUR **PASSION** INTO PRACTICE

TEL +27 11 236 4900    WWW.LEPPANBEECH.CO.ZA

**LEPPAN BEECH INC.**  
ATTORNEYS

**Our specialisations include:**

- Compliance auditing
- Applications for new rights
- ISO/OHSAS implementation assistance
- All aspects relating to environmental compliance
- Conversion applications from old order rights to new order rights
- Mining specific services
- Representation at enquiries
- Compliance/risk registers
- Statutory appointment structuring
- Health and safety training and advice
- Litigation (criminal, civil and administrative)