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Quantifying the influence of calcium ion concentration on the corrosion of high-purity magnesium, AZ91, WE43 in modified Hanks’ solutions

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Abstract

The corrosion rate in a modified Hanks’ solution (containing no Ca2+ ions) was higher than in Hanks’ solution. The increase was by a factor of ~12 for HP Mg and AZ91, and a factor of ~6 for WE43. This quantitatively highlights the critical role of Ca2+ ions for Mg corrosion in synthetic body fluids. The Ca2+ ion containing solutions produced a dense corrosion-product layer of hydroxyapatite, \( \text{Ca}_3(\text{PO}_4)_2 \cdot (\text{CaOH})_2 \), a greater fraction of which stayed on the corroding surface (~0.2–0.3) compared with the Ca2+ ion free solutions which produced magnesium phosphate, \( \text{Mg}_3(\text{PO}_4)_2 \).

1. Introduction

Magnesium (Mg) alloys are promising emerging biomaterials, due to their biocompatibility and good mechanical properties [1, 2]. Mg alloys do not release toxic products when corroding, cause little inflammation in the body, and their physical properties are closer to that of bone reducing the risk of stress shielding effects [1, 3]. Consequently, Mg alloys have many potential applications in medicine, including osteosynthesis devices and implants [4–9], cardiovascular stents [10, 11], and wire based applications [12–14]. However, a key limitation and point of study for Mg alloys are their degradation rates, which may be somewhat too high for an intended application, and also may produce hydrogen gas pockets [15–17]. As a consequence, there has been considerable research dedicated to understanding Mg corrosion in medical environments, i.e. biocorrosion [2, 15, 16, 18–25].

The corrosion mechanisms of Mg have been elucidated by studies aimed at the use of magnesium for automobile and aerospace applications. These same corrosion mechanisms are applicable to Mg biocorrosion [15, 18, 25–34]. In particular, Mg alloys have corrosion rates higher than that of high purity Mg because the second phases cause micro-galvanic corrosion acceleration of the alpha-Mg matrix [31–33]. Impurity elements are a particular issue when their concentrations are above their (composition-dependent) impurity limits, which can be ~1 ppm for a wrought alloy [31]. Shi and Atrens [35] and Cao et al [28] found that not all the corrosion products stayed on the surface of the corroding specimen. Appendix A provides more details.

This understanding of Mg corrosion has provided the foundation for the understanding of Mg biocorrosion. Witte [3] was the first to use laboratory corrosion studies to understand the factors of importance to Mg biocorrosion. He showed that a simple chloride solution does not reproduce biocorrosion. There has been subsequently much research to understand the factors of importance to the biocorrosion of Mg alloys [2, 16, 25, 36–42]. Zainal Abidin et al [43–45] showed that a match to biocorrosion was reproduced by immersion tests of Mg alloys in Nor’s solution (Hanks’ solution with pH buffered by the bubbling of CO2 through the solution). Taltavull et al [46] showed that (i) increasing chloride ion concentration in the synthetic body fluid (SBF) increased the corrosion rate of Mg alloys mainly by facilitating the micro-galvanic acceleration by the second phases in the microstructure, and (ii) the phosphate present in the SBF decreases the corrosion rate by the formation of a more protective surface film of corrosion products.

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These laboratory studies have been complemented by in vivo studies of the corrosion behaviour of Mg in animal models such as a rat or a Guinea pig, whose biology is similar to that of humans [5, 7]. The in vivo studies have identified the corrosion products of Mg biocorrosion. Witte et al [7] showed that the Mg corrosion product layer mainly contained calcium (Ca) and phosphorous (P). Zainal Abidin [45] found that the corrosion layer consisted of Mg, O, P, C and Ca. Marco et al [47] indicated that the corrosion products contained (Mg, Ca)CO₃, (Mg, Ca)PO₄ and Mg(OH)₂.

The laboratory studies (i.e. the in vitro studies) have used solutions whose chemical composition is close to that of human body fluids [16, 25, 38, 43, 48, 49]. Hanks’ solution is such a simulated body fluid (SBF), containing approximately the same concentration of each inorganic compound of blood plasma, and uses the same buffer as blood to maintain appropriate pH [45, 50].

Thus, the factors that influence Mg biocorrosion have largely been elucidated [16, 36, 51]. However, Atrens et al [36] and, Johnston et al [16] have highlighted that there is uncertainty concerning (i) the role of the local environment on the corrosion of Mg in vivo, and (ii) the role of the cations during Mg corrosion, particularly the role of Ca²⁺. The presence of Ca²⁺ in the SBF tends to retard the corrosion rate of Mg alloys [16, 32], however, this analysis has been qualitative. To date quantitative data analysing effect of Ca²⁺ on Mg corrosion in SBF has been absent.

The present study aims at quantitatively elucidating the influence of Ca²⁺ ions on the corrosion of Mg alloys. The influence of the Ca²⁺ ion concentration was studied by immersion testing HP Mg and the two Mg alloys WE43 and AZ91 in solutions which were based on Hanks’ solution and had systematically varied Ca concentrations.

2. Experimental methods

2.1. Magnesium specimens

The chemical compositions of the HP Mg, AZ91, and WE43 are presented in table 1 as measured by atomic emission spectroscopy (ICP-AES) by Spectrometer Services Pty Ltd, Coberg, Vic. Fishing line specimens were used [35]. HP Mg is expected to show predominately uniform corrosion, whereas AZ91 as a two-phase alloy consisting of the alpha-Mg matrix and the beta-phase, is expected to show localised corrosion of the alpha-Mg matrix because of the micro-galvanic acceleration by the second phase, the beta-phase. AZ91 serves as a reference Mg alloy that has been widely studied; however, the Al content of this alloy may make it unlikely that AZ91 is used in vivo. WE43 is however suitable for use as an implant in the human body [6].

Each Mg alloy specimen was ground with four different grit SiC papers [35] at 5 cm distance from its neighbours. The temperature was maintained by the water bath between 36 and 37 °C, as this is the body temperature. The pH-value was controlled using the CO₂—bicarbonate buffer, by bubbling CO₂ through the solution. Hanks’ solution with pH control by CO₂ is known as Nor’s solution and mimics blood plasma [45]. With this buffer, the pH was maintained between 7.35 and 7.45. Mild solution flow was produced via a pump to ensure that the temperature and pH were homogeneous throughout the tank.

A schematic of the experimental apparatus is presented in figure 1. Each specimen was immersed in the solution as a fishing line specimen [35] at 5 cm distance from its neighbours. The temperature was maintained by the water bath between 36 and 37 °C, as this is the body temperature. The pH-value was controlled using the CO₂—bicarbonate buffer, by bubbling CO₂ through the solution. Hanks’ solution with pH control by CO₂ is known as Nor’s solution and mimics blood plasma [45]. With this buffer, the pH was maintained between 7.35 and 7.45. Mild solution flow was produced via a pump to ensure that the temperature and pH were homogeneous throughout the tank.

Following Shi and Atrens [35] and Cao et al [28] (see appendix A for further details), measurements were made to determine if all the corrosion products remained on the surface during the immersion tests. A measure of the apparent specific corrosion-product weight on the specimen surface after the immersion test, $W_{acpo}$ [mg cm⁻²] was evaluated, as described by Shi and Atrens [35], using:
Table 1. Chemical composition (wt%) of the Mg alloys used for this study.

| Alloy   | Al   | Mn   | Y     | Gd    | Ce    | Zn    | Zr    | Si    | Fe    | La    | Nd    | Pr    | Ca    | Ni    | Cu    |
|---------|------|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| HP Mg   | 0.019| 0.008| <0.002| <0.002| <0.002| 0.003 | <0.005| 0.01  | <0.002| <0.002| <0.002| <0.002| 0.018 | <0.002| <0.002|
| AZ91    | 9.01 | 0.23 | <0.002| <0.002| <0.002| 0.8   | <0.005| 0.02  | <0.002| <0.002| <0.002| <0.002| <0.002| <0.002| <0.002|
| WE43    | 0.029| 0.012| 3.75  | 0.42  | 0.35  | 0.009 | 0.48  | 0.01  | 0.002 | 0.002 | 2.16  | 0.004 | 0.021 | 0.005 | 0.005 |
where \( W_{acp} \) is the specific specimen weight after the immersion test with the corrosion products still on the surface (i.e. the measured mass divided by the surface area of the specimen, \( A\ [\text{cm}^2] \)), and \( W_b \) is the specific weight of the specimen before the immersion test. This formulation was used [35] to test the applicability of using \( W_{awcp} \) to monitor the corrosion rate of the specimen during the immersion test. The actual specific mass of corrosion products remaining on the specimen surface after the immersion test, \( W_{cp} \), was evaluated using:

\[
W_{cp} = W_{acp} - W_b
\]

(1)

where \( W_{acp} \) is the specific specimen mass after the immersion test with the corrosion products still on the surface (i.e. the measured mass divided by the surface area of the specimen, \( A\ [\text{cm}^2] \)), and \( W_b \) is the specific weight of the specimen before the immersion test. This formulation was used [35] to test the applicability of using \( W_{awcp} \) to monitor the corrosion rate of the specimen during the immersion test. The actual specific mass of corrosion products remaining on the specimen surface after the immersion test, \( W_{cp} \), was evaluated using:

\[
W_{cp} = W_{acp} - W_b
\]

(2)

where \( W_b \) is the specific specimen mass after the immersion test after removal of all the corrosion products. The expected mass of the corrosion product, \( W_{ecpw} \), was evaluated using:

\[
W_{ecpw} = F \Delta Wt
\]

(3)

where \( F = 3.60 \) for \( \text{Mg}_3(\text{PO}_4)_2 \) corrosion products, and \( F = 3.96 \) for \( \text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca(OH)}_2 \), as explained in appendix A.

2.3. Corrosion rate

Mg corrosion has the following overall reaction [36]:

\[
\text{Mg} + 2\text{H}_2\text{O} = \text{Mg}^{2+} + 2\text{OH}^- + \text{H}_2
\]

Consequently, 1 mol of Mg corrosion evolves 1 mol of hydrogen gas (\( \text{H}_2 \)). Thus, the corrosion rate can be evaluated from the weight loss of Mg metal, or the volume of evolved hydrogen [53]. However, the corrosion rate measured from the evolved hydrogen becomes inaccurate for low corrosion rates [36, 53], less than 1 mm.y\(^{-1} \). Therefore, the corrosion rate was evaluated in this research as the weight loss rate \( P_w \) (mm y\(^{-1} \)) determined by

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**Table 2.** Concentration of ions in the immersion solutions compared to that of human blood plasma (mmol l\(^{-1} \)).

| Ion       | \([\text{Ca}^{2+}] = 0\) | \([\text{Ca}^{2+}] = 0.5\ [\text{Ca}^{2+}]_H\) | \([\text{Ca}^{2+}] = [\text{Ca}^{2+}]_H\) | \([\text{Ca}^{2+}] = 2[\text{Ca}^{2+}]_H\) | Blood plasma [34] |
|-----------|---------------------------|--------------------------------------------|----------------------------------------------|-----------------------------------------------|------------------|
| \(\text{Na}^{+}\) | 144                       | 143                                       | 142                                          | 139                                          | 142              |
| \(\text{K}^{+}\) | 5.81                      | 5.81                                      | 5.81                                         | 5.81                                         | 3.6–5.5          |
| \(\text{Mg}^{2+}\) | 0.81                      | 0.81                                      | 0.81                                         | 0.81                                         | 1                |
| \(\text{Ca}^{2+}\) | 0                         | 0.63                                      | 1.26                                         | 2.52                                         | 2.1–2.6          |
| \(\text{Cl}^{-}\) | 145                       | 145                                       | 145                                          | 145                                          | 95–107           |
| \(\text{HCO}_3^-\) | 4.20                      | 4.20                                      | 4.20                                         | 4.20                                         | 27               |
| \(\text{H}_2\text{PO}_4\) | 0.44                      | 0.44                                      | 0.44                                         | 0.44                                         |                  |
| \(\text{HPO}_4^{2-}\) | 0.34                      | 0.34                                      | 0.34                                         | 0.34                                         | 0.7–1.5          |
| \(\text{SO}_4^{2-}\) | 0.81                      | 0.81                                      | 0.81                                         | 0.81                                         | 1                |

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**Figure 1.** Schematic of immersion testing apparatus.

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Data from immersion tests in the solution without calcium ions ([Ca] = 0) during 5 days (t = 5 days); ΔW is the specific mass loss rate [mg cm\(^{-2}\) \(\cdot\) d\(^{-1}\)], \(W_p\) is the actual specific mass of corrosion products on the specimen surface after the immersion test evaluated using equation (3), \(\Delta W_{acpw}\) is the apparent specific mass of corrosion products on the surface as evaluated by Shi and Atrens [48] evaluated using equation (1), and \(W_{ecpw}\) is the expected specific mass of the corrosion products based on the assumption that the corrosion products are \(Mg_3(PO_4)_2\) and evaluated using equation (3).

### Table 3

| Specimen designation | Time, t (day) | \(\Delta W\) mg cm\(^{-2}\) d\(^{-1}\) | \(W_{acpw}\) mg cm\(^{-2}\) | \(W_p\) mg cm\(^{-2}\) | \(W_{ecpw}\) mg cm\(^{-2}\) | \(W_{cp}/W_{ecpw}\) |
|----------------------|---------------|---------------------------------|-----------------|-----------------|-----------------|-----------------|
| HPMg 1               | 5             | 4.77                            | 22.90           | 0.93            | 86              | 0.011           |
| HP Mg 2              | 5             | 5.91                            | 28.87           | 0.66            | 106             | 0.006           |
| HP Mg 3              | 5             | 5.49                            | 26.61           | 0.86            | 99              | 0.009           |
| AZ91 1               | 5             | 1.85                            | 10.47           | 5.16            | 33              | 0.155           |
| AZ91 2               | 5             | 1.96                            | 4.67            | 5.11            | 35              | 0.145           |
| AZ91 3               | 5             | 1.72                            | 3.88            | 4.70            | 31              | 0.152           |
| WE43 1               | 5             | 2.66                            | 9.98            | 3.33            | 48              | 0.069           |
| WE43 2               | 5             | 2.95                            | 10.86           | 3.87            | 53              | 0.073           |
| WE43 3               | 5             | 2.40                            | 9.20            | 2.80            | 43              | 0.065           |

Data from immersion tests in Hanks’ solution ([Ca] = [Ca]_{Hb}) for 5 days (t = 5 days); ΔW is the specific mass loss rate [mg cm\(^{-2}\) \(\cdot\) d\(^{-1}\)], \(W_p\) is the actual specific mass of corrosion products on the specimen surface after the immersion test evaluated using equation (3), \(\Delta W_{acpw}\) is the apparent specific mass of corrosion products on the surface as evaluated by Shi and Atrens [48] evaluated using equation (1), and \(W_{ecpw}\) is the expected specific mass of the corrosion products based on the assumption that the corrosion products are \(Ca_3(PO_4)_2\) - \(Ca(OH)_2\) and evaluated using equation (3).

### Table 4

| Specimen designation | Time, t (day) | \(\Delta W\) mg cm\(^{-2}\) d\(^{-1}\) | \(W_{acpw}\) mg cm\(^{-2}\) | \(W_p\) mg cm\(^{-2}\) | \(W_{ecpw}\) mg cm\(^{-2}\) | \(W_{cp}/W_{ecpw}\) |
|----------------------|---------------|---------------------------------|-----------------|-----------------|-----------------|-----------------|
| HPMg 1               | 5             | 0.40                            | 0.12            | 1.90            | 7.99            | 0.238           |
| HP Mg 2              | 5             | 0.42                            | 0.10            | 2.02            | 8.41            | 0.240           |
| HP Mg 3              | 5             | 0.51                            | 0.15            | 2.39            | 10.06           | 0.238           |
| AZ91 1               | 5             | 0.17                            | 0.02            | 0.81            | 3.30            | 0.246           |
| AZ91 2               | 5             | 0.15                            | 0.01            | 0.75            | 3.00            | 0.249           |
| AZ91 3               | 5             | 0.16                            | 0.04            | 0.78            | 3.22            | 0.241           |
| WE43 1               | 5             | 0.38                            | 0.29            | 2.17            | 7.45            | 0.291           |
| WE43 2               | 5             | 0.41                            | 0.60            | 2.63            | 8.02            | 0.327           |
| WE43 3               | 5             | 0.47                            | 0.36            | 2.71            | 9.27            | 0.292           |

Means of [16, 36]:

\[
P_w = 2.10 \frac{\Delta W}{At}
\]  

(5)

where \(\Delta W\) (mg) is the weight loss over the immersion period, \(t\) (in days) is the duration of the immersion, and \(A\) (cm\(^2\)) is the surface area of the specimen.

Each specimen, after removal from the solution, was dried and the corrosion products were analysed using a scanning electron microscope (SEM) and Energy Dispersive X-ray Spectroscopy (EDX). The specimen was cleaned by immersion in the standard chromic acid solution [28, 33–35] to remove the corrosion products, dried and weighed to measure the weight loss. The specimen was returned to the SEM and the surface corrosion morphology was analysed.

Specimens were immersed again for two weeks in the solution with a calcium concentration twice that of Hanks’ solution ([Ca\(^{2+}\) = 2[Ca\(^{2+}\)]_{Hb}) and in the solution without calcium ions ([Ca\(^{2+}\) = 0], in order to produce sufficient corrosion products on their surface. These specimens were dried and corrosion products were scraped from the surface for X-ray powder diffraction (XRD) analysis.

### 3. Results

#### 3.1. Corrosion product retention

Tables 3 and 4 present the measurements relating to the evaluation of corrosion products analysed using equations (1) – (3), in an effort to determine if all the corrosion products remained on the specimen surface during corrosion. If the corrosion products all remained on the specimen surface, the specimen would gain weight, and the quantity \(W_{acpw}\) would be positive. However, inspection of tables 3 and 4 indicates that \(W_{acpw}\) was negative for most specimens, indicating that not all the corrosion products remained on the specimen surface. This conclusion was further supported by the fact that the quantity \(W_{cp}\) (the measured weight of the corrosion
products remaining on the specimen surface) was in all cases less than the expected mass of the corrosion products, \( W_{\text{cor}} \), based on the amount of Mg metal lost by corrosion.

### 3.2. Weight loss rates

Figure 2 and table 5 present the weight loss rate, \( P_w \), for each Mg alloy in the four solutions with increasing \( \text{Ca}^{2+} \) concentration. The weight loss rate was expected to increase with decreasing calcium ion, \( \text{Ca}^{2+} \), concentration, because \( \text{Ca}^{2+} \) ions enable the development of hydroxyapatite on the Mg surface \[^{[36]}\], which partially protects the Mg specimen from corrosion.

In agreement with these expectations, figure 2 and table 5 show that the weight loss rate increased substantially for all three Mg alloys as the \( \text{Ca}^{2+} \) ion concentration decreased from that of Hanks’ solution \((\text{Ca}^{2+}) = [\text{Ca}^{2+}]_{H}\)) to the solutions with the lower \( \text{Ca}^{2+} \) ion concentrations: \((\text{Ca}^{2+}) = 0.5[\text{Ca}^{2+}]_{H}, [\text{Ca}^{2+}] = [\text{Ca}^{2+}]_{H}, [\text{Ca}^{2+}] = 0.5[\text{Ca}^{2+}]_{H}\).

For HP Mg and AZ91, there was an increase by a factor of approximately 12 between Hanks’ solution \((\text{Ca}^{2+}) = [\text{Ca}^{2+}]_{H}\)) and the solution without \( \text{Ca}^{2+} \) ions \((\text{Ca}^{2+}) = 0\) for HP Mg and AZ91, there was an increase by a factor of approximately 12 between Hanks’ solution \((\text{Ca}^{2+}) = [\text{Ca}^{2+}]_{H}\)) and the solution without \( \text{Ca}^{2+} \) ions \((\text{Ca}^{2+}) = 0\).

In contrast, the corrosion rate was similar for all three Mg alloys in Hanks’ solution \((\text{Ca}^{2+}) = [\text{Ca}^{2+}]_{H}\)) and for the solution containing a calcium ion, \( \text{Ca}^{2+} \), concentration double that of Hanks’ solution \((\text{Ca}^{2+}) = 2[\text{Ca}^{2+}]_{H}\).

### 3.3. Corrosion morphology

Figure 3 presents the typical surface morphology for each alloy after immersion in Hanks’ solution \((\text{Ca}^{2+}) = [\text{Ca}^{2+}]_{H}\)) and in the solution with no \( \text{Ca}^{2+} \) \((\text{Ca}^{2+}) = 0\) and after removal of corrosion products.
HP Mg showed large areas with little corrosion and some areas of localised corrosion including lamellar corrosion. There were more areas of localised corrosion in the solution with no Ca\(^{2+}\) ([Ca\(^{2+}\)] = 0), and the lamellar corrosion was deeper.

AZ91 showed a microstructure of large second-phase particles (beta-phase) of substantial size, and small particles expected to be AlMn intermetallic particles. In Hanks’ solution ([Ca\(^{2+}\)] = [Ca\(^{2+}\)\(_H\)], there was largely uniform corrosion throughout the alpha-Mg matrix with some localized attack next to the second phase particles. In the solution with no Ca\(^{2+}\) ([Ca\(^{2+}\)] = 0) there was much more corrosion of the alpha-Mg matrix, and substantial corrosion around the second phase particles.

In Hanks’ solution ([Ca\(^{2+}\)] = [Ca\(^{2+}\)\(_H\)], WE43 had substantial areas that had suffered little corrosion, between which there was some corrosion, and there was some grain boundary attack. In the solution with no Ca\(^{2+}\) ([Ca\(^{2+}\)] = 0) the corrosion was somewhat deeper, there were few areas with no corrosion, and there was more grain boundary attack. There was also more incidence of localised corrosion attack.

### 3.4. Corrosion product identification

Figure 4 presents the XRD analyses of the corrosion products on WE43 in the modified Hanks’ solution but with a Ca\(^{2+}\) ion concentration [Ca\(^{2+}\)] = 2[Ca\(^{2+}\)\(_H\)] and for AZ91 in the solution with zero Ca\(^{2+}\) concentration, [Ca\(^{2+}\)] = 0. In the solution similar to Hanks’ solution but with a Ca\(^{2+}\) ion concentration [Ca\(^{2+}\)] = 2[Ca\(^{2+}\)\(_H\)], the XRD indicated that the corrosion products were predominately hydroxyapatite. In contrast, in the solution with zero Ca\(^{2+}\) concentration, [Ca\(^{2+}\)] = 0, the corrosion products were predominately magnesium phosphate,
Mg₅(PO₄)₂. The presence of Mg metal peaks in these spectra indicated that the scraping of the corrosion products included some Mg metal, so that the corrosion product layer was quite thin.

This analysis is supported by figure 5, which presents SEM images, with EDX elemental maps, of HP Mg specimens immersed in Hanks’ solution with (figure 5(a)) and without Ca²⁺ (figure 5(b)). For the specimen immersed in Hanks’ solution (containing Ca²⁺), the composition of the corrosion products was consistent with hydroxyapatite containing little Mg. The specimen immersed in the modified Hanks’ solution (no Ca²⁺, figure 5(b)), there was no Ca²⁺ on the surface, consistent with the XRD analysis of Mg₅(PO₄)₂.

### 4. Discussion

Figures 4 and 5 indicated that the corrosion product in the solutions containing no Ca²⁺ ions was magnesium phosphate, Mg₅(PO₄)₂, whereas, the solution containing Ca²⁺ ions produced hydroxyapatite, Ca₃(PO₄)₂·Ca(OH)₂, as the corrosion products.

Table 3 indicates that there were measurable corrosion products on the specimen surface for all specimens after immersion in the solution without Ca²⁺ ([Ca²⁺] = 0), i.e. Wcp was positive, and the fraction of corrosion products remaining on the surface, Wcp/Wexp, varied from 0.006 to 0.15. In contrast, table 4 indicates that the fraction of corrosion products remaining on the specimen surface was larger and within a tighter range, 0.24 to 0.33, for immersion in Hanks’ solution ([Ca²⁺] = [Ca²⁺]₀) for 5 days.

The sharp increase in corrosion rate due to the absence of Ca²⁺ in the solution displayed in figure 2 quantitatively highlights the importance of these ions in the SBF. All Mg alloys exhibited higher corrosion rates in the solution containing no Ca²⁺. HP Mg and AZ91 had a corrosion rate of ~12 times greater than in Hanks’ solution ([Ca²⁺] = [Ca²⁺]₀), whereas WE43 showed a lower increase of ~6 times; this was markedly lower than that of the other two alloys. This was consistent with the corrosion morphology, where figures 3(c) and (f) indicate a more similar morphology for the WE43 samples in both solutions, as compared to figures 3(a) and (b) for HP Mg, and (c) and (d) for AZ91, which show an increase in localised corrosion as the Ca²⁺ ion concentration was reduced. Moreover, HP Mg had the highest weight loss rate in the solution with no Ca²⁺. This correlates to the corrosion morphology, especially the greater amount of deep lamellar corrosion when the Ca²⁺ ions concentration was zero. While the presence of Ca²⁺ in the [0.5 Ca²⁺] SBF substantially reduced the corrosion rate, it is worthy of note that these corrosion rates are nevertheless ~2 times greater than in standard Hanks’ solution.

In addition, the sharp increase in corrosion rates can be attributed to the change of the corrosion product layer. The Ca²⁺ ion containing solutions produced a dense corrosion product layer of hydroxyapatite, Ca₃(PO₄)₂·Ca(OH)₂, a greater fraction of which stayed on the corroding surface (~0.2–0.3) compared with the Ca⁺ ion free solutions which produced magnesium phosphate, Mg₅(PO₄)₂, for which the fraction...
remaining on the specimen surface was 0.006 to 0.15. These findings were consistent with the prior research [52, 54–57].

In summary, the modified Hanks’ solution containing no Ca$^{2+}$ ions produced higher corrosion rates than unmodified Hanks’ solution. The increase was substantial. This quantitatively highlights the critical role of Ca$^{2+}$ ions for the corrosion of Mg alloys in synthetic body fluids. The Ca$^{2+}$ ion containing solutions produced a dense corrosion product layer of hydroxyapatite, Ca$_3$(PO$_4$)$_2$·Ca(OH)$_2$, a greater fraction of which stayed on the corroding surface (∼0.2–0.3) compared with the Ca$^{2+}$ ion free solutions which produced magnesium phosphate, Mg$_3$(PO$_4$)$_2$, for which the fraction remaining on the specimen surface was 0.006 to 0.15. The higher corrosion rates are attributed to the corrosion products, magnesium phosphate, Mg$_3$(PO$_4$)$_2$ in the Ca$^{2+}$ ion free solutions being less protective and allowing more localised corrosion for HP Mg and AZ91, whereas the corrosion was more similar for WE43 in both solutions containing and not containing Ca$^{2+}$. Synthetic body fluids which seek to mimic in vivo corrosion should contain a Ca$^{2+}$ ion concentration similar to that in vivo.

5. Conclusions

1. The modified Hanks’ solution containing no Ca$^{2+}$ ions produced higher corrosion rates than unmodified Hanks’ solution. The increase was by a factor of ∼12 for both HP Mg and AZ91, and a factor of ∼6 increase for WE43. This quantitatively highlights the critical role of Ca$^{2+}$ ions for the corrosion of Mg alloys in synthetic body fluids.

2. The Ca$^{2+}$ ion containing solutions produced a dense corrosion product layer of hydroxyapatite, Ca$_3$(PO$_4$)$_2$·Ca(OH)$_2$, a greater fraction of which stayed on the corroding surface (∼0.2–0.3) compared with the Ca$^{2+}$ ion free solutions which produced magnesium phosphate, Mg$_3$(PO$_4$)$_2$, for which the fraction remaining on the specimen surface was 0.006 to 0.15.

3. The higher corrosion rates are attributed to the corrosion products, magnesium phosphate, Mg$_3$(PO$_4$)$_2$ in the Ca$^{2+}$ ion free solutions being less protective and allowing more localised corrosion for HP Mg and AZ91, whereas the corrosion was more similar for WE43 in both solutions containing and not containing Ca$^{2+}$.
4. Synthetic body fluids which seek to mimic in vivo corrosion should contain a Ca$^{2+}$ ion concentration similar to that in vivo.

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Data statement

The data for these findings are contained within this paper and are also available at https://espace.library.uq.edu.au/view/UQ:732817. The data are embargoed until publication of this paper. (The embargo is nominally set to 1-08-2020).

Appendix A. Corrosion products

Shi and Atrens [23] considered the fate of corrosion products on the surface of high purity Mg (HP Mg) specimens during corrosion in 3.5% NaCl saturated with Mg(OH)$_2$. No corrosion products were observed beneath the corroding HP Mg specimens, which was consistent with all the corrosion products remaining on the surface of the corroding specimens. However, the evaluated apparent specific mass of corrosion products on the surface of the corroded specimens, $W_{acpw}$, was less than that the expected specific mass of corrosion products, $W_{ecpw}$, so that it was concluded that not all the corrosion products remained on the surface during corrosion. During the current research, this conclusion is revisited.

Shi and Atrens [23] evaluated the apparent specific mass of corrosion products on the specimen surface after the immersion test, $W_{acpw}$ [mg cm$^{-2}$], using:

$$W_{acpw} = W_{acp} - W_b$$  \hspace{1cm} (A1)

where $W_{acp}$ is the specific specimen mass after the immersion test with the corrosion products still on the surface (i.e. the measured mass divided by the surface area of the specimen, $A$ [cm$^2$]), and $W_b$ is the specific mass of the specimen before the immersion test. This approach was used to explore the possibility of monitoring the corrosion behaviour using the increase of the specific specimen mass during corrosion.

However, the actual specific mass of corrosion products on the specimen surface after the immersion test, $W_{cpl}$, is evaluated using:

$$W_{cpl} = W_{cpl} - W_a$$  \hspace{1cm} (A2)

where $W_a$ is the specific specimen mass after the immersion test after removal of all the corrosion products.

The corrosion rate, $\Delta W$, is evaluated as the mass loss rate [mg cm$^{-2}$ d$^{-1}$] using:

$$\Delta W = (W_b - W_a) / t$$  \hspace{1cm} (A3)

where $W_b$ and $W_a$ are in measured in units of [mg cm$^{-2}$], and the duration of the immersion test, $t$, is expressed in units of [day].

The actual specific mass of corrosion products on the specimen surface after the immersion test, $W_{cpl}$, can be evaluated from the apparent specific mass of corrosion products on the specimen surface after the immersion test used by Shi and Atrens [48], $W_{acpw}$, by rearranging equation (A3) and substituting for $W_a$ in equation (A2) to give:

$$W_{cpl} = W_{cpl} - W_b + \Delta W t = W_{acpw} + \Delta W t$$  \hspace{1cm} (A4)

The overall Mg corrosion reaction is usually written as [22, 23]:

$$\text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2$$  \hspace{1cm} (A5)

This indicates that each mol of Mg metal (24.31 g) that corrodes is converted to one mol of Mg(OH)$_2$ corrosion product (58.31 g); or a specific mass loss of $\Delta W t$ [mg cm$^{-2}$] equals $\Delta W t (58.31 / 24.31)$ [mg cm$^{-2}$] of Mg(OH)$_2$ corrosion product. Thus, the expected mass of the corrosion product, $W_{ecpw}$, can be evaluated using

$$W_{ecpw} = \Delta W t M_{\text{Mg(OH)}_2} / M_{\text{Mg}} = \Delta W t 58.31 / 24.31 = 2.40 \Delta W t$$  \hspace{1cm} (A6)

where $M_{\text{Mg(OH)}_2}$ is the molecular weight of Mg(OH)$_2$ (58.31 g) and $M_{\text{Mg}}$ is the molecular weight of Mg (24.31 g). This equation can be generalised to:
Table A1. Data [48] from immersion tests for HP Mg immersed in 3.5% NaCl saturated with Mg(OH)\(_2\) for the stated duration, \(t\), days. \(\Delta W\), is the specific mass loss rate [mg cm\(^{-2}\) s\(^{-1}\)] evaluated using equation (A3), \(W_{\text{cp}}\) is the actual specific mass of corrosion products on the specimen surface after the immersion test evaluated using equation (A2), \(W_{\text{ecpw}}\) is the apparent specific mass of corrosion products on the surface as evaluated by Shi and Atrens [49] evaluated using equation (A1), \(W_{\text{cp}}\) is the expected specific mass of the corrosion products based on the assumption that the corrosion products are Mg(OH)\(_2\) and evaluated using equation (A6), and \(M_{\text{cp}}\) is the molecular weight of the corrosion products evaluated using equation (A7).

| Specimen designation | time, \(t\), day | \(\Delta W\), mg cm\(^{-2}\) d | \(W_{\text{ecpw}}\), mg cm\(^{-2}\) | \(W_{\text{cp}}\), mg cm\(^{-2}\) | \(W_{\text{ecpw}}/\Delta W\) | \(W_{\text{cp}}/W_{\text{ecpw}}\) | \(M_{\text{cp}}, g\) |
|----------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 37                   | 3               | 0.14            | 0.6             | 1.02            | 1.01            | 7.29            | 1.01            | 59             |
| 38                   | 3               | 0.15            | 0.6             | 1.05            | 1.08            | 7.00            | 0.97            | 57             |
| 39                   | 5               | 0.13            | 0.8             | 1.45            | 1.56            | 11.15           | 0.93            | 54             |
| 40                   | 5               | 0.15            | 0.8             | 1.55            | 1.80            | 10.33           | 0.86            | 50             |
| 41                   | 5               | 0.15            | 1.1             | 1.85            | 1.80            | 12.33           | 1.03            | 60             |
| 42                   | 7               | 0.35            | 2.7             | 5.15            | 5.88            | 14.71           | 0.88            | 51             |
| 43                   | 7               | 0.54            | 4.7             | 8.48            | 9.07            | 15.70           | 0.93            | 55             |
| 44                   | 10              | 0.16            | 1.1             | 2.70            | 3.84            | 16.88           | 0.70            | 41             |
| 45                   | 10              | 0.17            | 1.5             | 3.20            | 4.08            | 18.82           | 0.78            | 46             |
| 46                   | 14              | 0.13            | 1.2             | 3.02            | 4.37            | 23.23           | 0.69            | 40             |
| 47                   | 14              | 0.13            | 2.1             | 3.92            | 4.37            | 30.15           | 0.90            | 52             |
| 48                   | 14              | 0.13            | 2.9             | 4.72            | 4.37            | 36.31           | 1.08            | 63             |
| 49                   | 14              | 0.11            | 1.9             | 3.44            | 3.70            | 31.27           | 0.93            | 54             |
| 50                   | 20              | 0.18            | 4.8             | 8.40            | 8.64            | 46.67           | 0.97            | 57             |
| 51                   | 20              | 0.09            | 2.2             | 4.00            | 4.32            | 44.44           | 0.93            | 54             |

\[
W_{\text{ecpw}} = F \Delta W t
\]  
\[
W_{\text{cp}} = M_{\text{cp}} \left( \frac{W_{\text{cp}}}{\Delta W t} \right)
\]

where the factor \(F = 262.87/(24.31 \times 3) = 3.60\) if it is assumed that the corrosion products are largely Mg\(_2\)(PO\(_4\))\(_2\) and it is assumed that 1/3 of a molecule of Mg\(_2\)(PO\(_4\))\(_2\) is formed for each Mg atom dissolved. A similar estimation can be made with \(F = 384.26/(24.31 \times 4) = 3.96\) if the corrosion product composition is largely Ca\(_3\)(PO\(_4\))\(_2\) \cdot Ca(OH)\(_2\), and it is assumed that 1/4 of a molecule of Ca\(_3\)(PO\(_4\))\(_2\) \cdot Ca(OH)\(_2\) is formed for each Mg atom dissolved.

Equation (A6) can be rearranged to give the molecular weight of the corrosion products, \(M_{\text{cp}}\) as:

\[
M_{\text{cp}} = M_{\text{Mg}} \left( \frac{W_{\text{cp}}}{\Delta W t} \right)
\]

Table A1 provides data [23] from immersion tests for fish specimens of HP Mg immersed in 3.5% NaCl saturated with Mg(OH)\(_2\) for the stated duration, \(t\), days. The actual specific mass of corrosion products on the specimen surface after the immersion test, \(W_{\text{cp}}\), was in each case essentially as the same as the expected specific mass of the corrosion product, \(W_{\text{ecpw}}\), based on the assumption that the corrosion products were composed of Mg(OH)\(_2\). This was consistent with all the corrosion products remaining on the specimen surface.

The specific mass of the corrosion products, normalised by the corrosion rate, namely the quantity \(W_{\text{cp}}/\Delta W\), increased with immersion duration, with similar values of this ratio for each immersion duration. This is consistent with the amount of corrosion products increasing with the amount of corrosion.

The quantity \(W_{\text{cp}}/W_{\text{ecpw}}\) is the actual specific mass of corrosion products on the specimen surface after the immersion test, \(W_{\text{cp}}\), normalised by the expected specific mass of the corrosion product, \(W_{\text{ecpw}}\). This quantity was essentially constant for these tests with an average value of 0.9 ± 0.1. The fact that this quantity was essentially constant and essentially equal to 1.0 was consistent with the corrosion products remaining on the specimen surface. Furthermore, the calculated molecular weight of the corrosion products, \(M_{\text{cp}}\), consistent with the data is 53 ± 6 g, was consistent with the value of 58.31 g for Mg(OH)\(_2\). These deductions are consistent with the observations that there were no corrosion products on the bottom of the beaker during the corrosion experiments indicating that all the corrosion products remained on the surface of the specimens.

However, Mg(OH)\(_2\) does absorb water, up to 10 mol of water of hydration per mol of Mg(OH)\(_2\) [56, 57], and the secondary ion mass spectroscopy (SIMS) data of Unocic et al [58] are consistent with the relative degree of hydration decreasing from the specimen surface for the corrosion product film (Mg(OH)\(_2\)) on ultra-high-purity Mg exposed for 24 h to distilled water.

If the corrosion products after drying in the above experiments [23] did retain some water of hydration so that the actual chemical formula was Mg(OH)\(_2\) \cdot x\(H_2\)\(\text{O}\), then the molecular weight of the corrosion products would be larger than 58.31 g, and the data in table A1 would indicate that not all the corrosion products remain on the surface of the corroding HP Mg specimens.
This is consistent with the research of Cao et al [16] who studied the corrosion of ultra-high-purity Mg in 3.5% NaCl solution saturated with Mg(OH)₂. Cao et al [16] found that the specific weight of the specimens after immersion tests lasting 14 days containing the corrosion products still on the specimen surface, Wacpw, was less than the specific weight of the specimens before the immersion tests, W0, for both plug in specimens and for fishing line specimens. This indicated that some corrosion products were lost from the specimen surface in these tests.

This analysis indicates that (i) some corrosion products may be lost from the surface of corroding Mg specimens, and (ii) there is some evidence indicating that the Mg(OH)₂ corrosion products contain some water of hydration, so that the appropriate chemical formula is probably Mg(OH)₂ · xH₂O.

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**References**

[1] Staiger M P, Pietak A M, Huadmai J and Dias G 2006 Magnesium and its alloys as orthopedic biomaterials: a review Biomaterials 27 1728–34
[2] Zheng Y, Gu X and Witte F 2014 Biodegradable metals Materials Science and Engineering: R: Reports 77 1–34
[3] Gu X-N and Zheng Y-F 2010 A review on magnesium alloys as biodegradable materials Front. Mater. Sci. Chin. 4 111–5
[4] Salunke P, Shanov V and Witte F 2011 High purity biodegradable magnesium coating for implant application Materials Science and Engineering: B 176 1711–7
[5] Witte F, Fischer J, Nellesen J, Crotstock H-A, Kaese V, Pisch A, Beckmann F and Windhagen H 2006 In vitro and in vivo corrosion measurements of magnesium alloys Biomaterials 27 1013–8
[6] Witte F, Hegt N, Vogt C, Cohan S, Kainer K U, Willumeit R and Feyerabend F 2008 Degradeable biomaterials based on magnesium corrosion Corr. Opin. Solid State Mater. Sci. 12 63–72
[7] Witte F, Kaese V, Haferkamp H, Switzer E, Meyer-Lindenberg A, Wirth C and Windhagen H 2005 In vivo corrosion of four magnesium alloys and the associated bone response Biomaterials 26 3557–63
[8] Seitz J-M, Lucas A and Kirschner M 2016 Magnesium-based compression screws: a novelty in the clinical use of implants JOM 68 1–6
[9] Chen X 2017 Magnesium-based implants: beyond fixators Journal of Orthopaedic Translation 10 1–4
[10] Haude M, Incé H, Abizaid A, Towg R, Lemos P A, von Birgelen C, Christiansen E H, Wijns W, Neumann F-J and Kaiser C 2016 Safety and performance of the second-generation drug-eluting absorbable metal scaffold in patients with de-novo coronary artery lesions (BIOSOLVE-II): 6 month results of a prospective, multicentre, non-randomised, first-in–man trial The Lancet 387 31–9
[11] Bowen P K, Drellich A, Drellich J and Goldman J 2015 Rates of in vivo (arterial) and in vitro biocorrosion for pure magnesium Journal of Magnesium and Biomedical Materials Research Part A 103 341–9
[12] Seitz J-M, Durisin M, Goldman J and Drellich J W 2015 Recent advances in biodegradable metals for medical suture: a critical review Adv. Healthcare Mater. 4 1915–36
[13] Johnston S, Lau C, Dargusch M S and Atrens A 2019 Absorbable Mg surgical tack: proof of concept & in situ fixation strength J. Mech. Behav. Biomed. Mater. 97 321–9
[14] Ieko N, Nakamura R, Naka K, Hashimoto T, Yoshida T, Urade T, Fukushima H, Yabuuchi H, Fukumoto T and Ku Y 2016 Fabrication of a magnesium alloy with excellent ductility for biodegradable clips Acta Biomater. 29 468–76
[15] Atrens A, Song G L, Liu M, Shi Z, Cao F and Dargusch M S 2015 Review of recent developments in the field of magnesium corrosion Adv. Eng. Mater. 17 400–53
[16] Johnston S, Dargusch M and Atrens A 2018 Building towards a standardised approach to biocorrosion studies: a review of factors influencing Mg corrosion in vivo pertinent to in vivo corrosion Science China Materials 61 475–500
[17] Frankel G, Samaniego A and Birbilis L 2013 Evolution of hydrogen at dissolving magnesium surfaces Corros. Sci. 70 104–11
[18] Jiang B, Xiang Q, Atrens A, Song G and Pan F 2017 Influence of crystallographic texture and grain size on the corrosion behaviour of as-extruded Mg alloy AZ31 sheets Corros. Sci. 126 374–80
[19] Cao J, Laws K, Birbilis N and Ferry M 2012 Potentiodynamic polarisation study of bulk metallic glasses based on the Mg–Zn–Ca ternary system Corrosion Engineering, 47 329–34
[20] Zhao D, Brown A, Wang T, Yoshizawa S, Seifer C and Heinerman W R 2018 In vivo quantification of hydrogen gas concentration in bone marrow surrounding magnesium fracture fixation hardware using an electrochemical hydrogen gas sensor Acta Biomater. 73 539–66
[21] Zhao D, Witte F, Li F, Wang J, Li J and Qin L 2017 Current status on clinical applications of magnesium-based orthopedic implants: a review from clinical translational perspective Biomaterials 112 287–302
[22] Cao Y, Wang L, Li L, Gu X, Zhang K, Xia J and Fan Y 2019 Effect of stress on corrosion of high-purity magnesium in vivo and in vitro Acta Biomater. 83 477–86
[23] Zhao D, Wang T, Nahon K, Guo X, Zhang Z, Dong Z, Chen S, Chou D-T, Hong D and Kumta P N 2017 In vivo characterization of magnesium alloy biodegradation using electrochemical H2 monitoring, ICP-MS, and XPS Acta Biomater. 50 556–65
[24] Brandt-Wunderlich C, Ruppehl P, Zumstein P, Schmidt W, Arbeiter D, Schmitz K P and Grabow N 2019 Mechanical behaviour of in vivo degraded second generation resorbable magnesium scaffolds (RMS) J. Mech. Behav. Biomed. Mater. 91 171–81
[25] Mei D, Lamaka S V, Lu X and Zheludkevich M L 2020 Selecting medium for corrosion testing of bioabsorbable magnesium and other metals—a critical review Corros. Sci. 171 108722
[26] Atrens A D, Gentle I and Atrens A 2015 Possible dissolution pathways participating in the Mg corrosion reaction Corros. Sci. 92 173–81
[27] Schlüter K, Shi Z, Zapponi C, Cao F, Quandt E and Atrens A 2014 Corrosion performance and mechanical properties of sputter-deposited MgY and MgGd alloys Corros. Sci. 78 43–54
[28] Cao F, Shi Z, Hofstetter J, Uggowitzer P I, Song G, Liu M and Atrens A 2013 Corrosion of ultra-high-purity Mg in 3.5% NaCl solution saturated with Mg(OH)₂ Corros. Sci. 75 78–99
[29] Atrens A, Song G L, Cao F, Shi Z and Bowen P K 2013 Advances in Mg corrosion and research suggestions Journal of Magnesium and Alloys 1 177–200
Atrens A, Song G, Shi Z, Soltan A, Johnston S and Dargusch M 2017 Understanding the corrosion of Mg and Mg alloys

Abidin N I Z, Martin D and Atrens A 2011 Corrosion of high purity Mg, AZ91, ZE41 and Mg2Zn0.2Mn in Hank

Zhao M-C, Liu M, Song G and Atrens A 2008 In...

Song G and Atrens A 2003 Understanding magnesium corrosion—...