University of Southern Queensland

Faculty of Engineering and Surveying

Investigation of A New Generation Degradable Implant Material

A dissertation submitted by

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ABSTRACT

This study investigates a new generation of metallic bio-degradable implant material. Due to the many drawback of permanent metallic implant materials and polymer based bio-degradable material, a metallic biodegradable implant material was needed. A potential material that has the ability to fulfil the required needs is a magnesium alloy AZ31.

Static and dynamic corrosion testing was performed on the magnesium alloy AZ31 under pseudo-physiological condition. If was found that under dynamic conditions, the alloy degraded fast at the beginning before stabilising to a rate of 0.5mm/yr. However, under static conditions, the alloy degraded slowly at the beginning before stabilising to a rate of 0.1mm/yr.

Although the results are not entirely conclusive, the results are similar to testing which has been previously conducted. Future work is needed to continue the research into this very potential material as a bio-degradable implant.

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CHAPTER 1

INTRODUCTION

1.1 Outline of the study

The aim of this study is to develop a new generation of implant material which will be bio-degradable to overcome the drawbacks from the permanent implant materials, and also will be metallic in order to provide sufficient strength.

1.2 Introduction

The development of a new generation of degradable implant material has already begun all around the world. Many scientists and engineers from countries such as China, Germany, the United States of America and Australia, have been exploring the use of alternative materials to the current permanent metallic implants or polymer-based bio-degradable implants in the human body. During their studies, magnesium and magnesium alloys were recognised as possible candidates for this purpose. In particular, magnesium alloy AZ31 was chosen to be further investigated due to its superior mechanical properties.

Materials such as titanium, stainless steels and ceramics have been the most commonly used materials for implants in the human body. Although these materials have been used with great success, research and development is an on-going process. Drawbacks from such permanent implant materials have given rise to other materials being studied which can be bio-degradable after implantation. Tests have been conducted to discover how the magnesium alloy AZ31 will react in the human body. Because the material is highly corrosive, the main focus is to discover how to control its degradation rate

and the release rate of the material elements. There is a genuine need to pursue this study as there is great potential for this material to change the way in which implants are used and how they are perceived by both surgeons and patients alike.

1.3 The Problem

For the applications such as bone devices and bone replacements, the common materials used are titanium, stainless steels and ceramics. The problem with these materials is that in most cases, these materials will permanently remain in the body. The problems that this can cause are irritations, increased stresses on the bones, and causing the metal detectors at such places as airports to alarm when passing through them. Although some of these problems may seem minor, eliminating them will make the implant process that much more desirable for those who require such treatment. Polymer-based bio-degradable materials have already been developed. However, these materials do not have sufficient strength for the purpose at hand. In order for the polymer-based materials to be used in a loaded situation, the size would need to be quite large compared to the titanium and stainless steel implants. These problems will be further discussed in chapter 3. This gives rise to the development of a metallic bio-degradable implant material.

1.4 Research Objectives

This research was designed to further investigate the development of a bio-degradable metallic implant material. Magnesium alloy AZ31 has been discovered as a potential choice for such purpose. The degradation behaviour of this material is the key area that needs to be fully understood before it can be used in the human body.

The aim of this study was firstly to set up a degradation test at the University of Southern Queensland to study the material's degradation behaviour. Secondly, based on previous research, this corrosion testing of the alloy was to be conducted at simulated body conditions. The results found from this testing would then be compared to the findings of the previous study. The difference of the testing conditions between this test and the testing previously conducted is the testing temperature. Previously the temperature used was 25 degrees Celsius. This study will perform the testing at a temperature closer to that of the human body, which is approximately 37 degrees Celsius.

1.5 Summary

This study aims to investigate further the possibility to use magnesium alloy AZ31 as a degradable implant material. A review of the literature available will provide the latest research and progress on the bio-degradable metallic implant materials. The experiment results will show the initial study of the bio-degradable behaviour of the magnesium alloy AZ31 in a simulated bodily solution. The research is expected to result in this material's potential to be compatible with the human body being realised. The outcomes of this project will lead to further research and will provide greater incite into the problems and benefits of this material.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

There have been many papers written associated with the topic of a degradable implant material. It is desirable to see the workings of professionals in this field as it can be very helpful in understanding the many aspects of such a complex subject. Although this project is very limited in what it will achieve, it is important to investigate as many resources as are available. Dube. et al (2003), Estrin. et al (2007), Hartung. et al. (2003) and Shi. et al. (2005) have all written papers on the use of magnesium alloys as an implant material. Shi. et al. (2005) acknowledged the drawbacks associated with metallic implants and investigated Magnesium alloy AZ31 as a possible material. They also investigated ways of slowing down the degradation rate by use of surface coatings. Estrin. et al. (2007) directed their study to encompass fatigue testing of Magnesium alloy AZ31. Hartung. et al. (2003) focussed their studies on the application of stents. Under local regulations by the animal care committee in German animals were used as test subjects for the implantation of stents. While the focus of Dube. et al. (2003) was also on stents, they directed their studies toward pseudo-physiological testing of magnesium alloy AM60B.

2.2 Applications of implant materials

2.2.1 Stents

Stents are the wire frameworks which are inserted into the artery to keep the walls from collapsing. Such an object is very small, yet can be the difference between life and death. Figure 1 below shows a typical stainless steel stent.

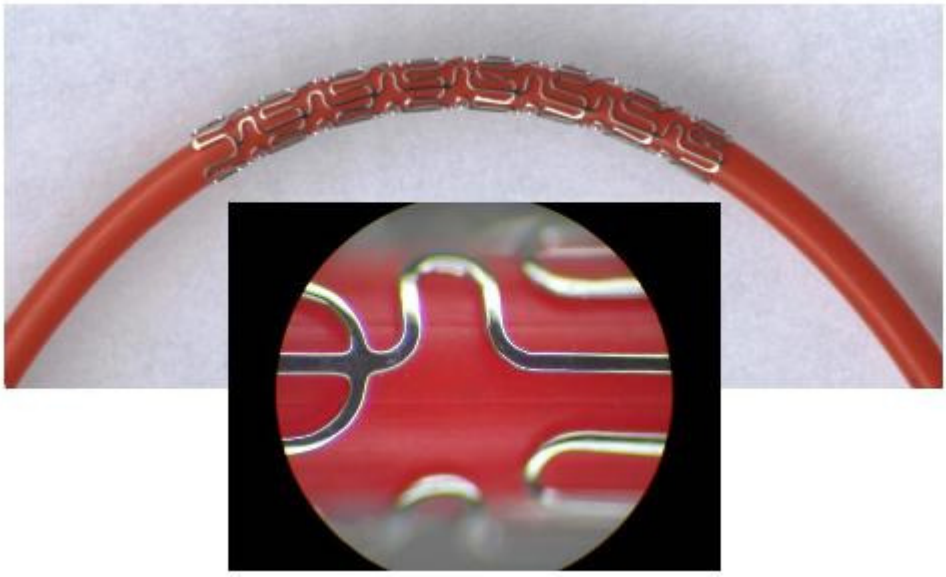

Figure 1: A typical stainless steel stent.

After the stent has been implanted, it will remain in the body indefinitely. The reason it can not be removed again is due to the fact that the tissue in the artery will grow around the stent and totally surround it. Dube et al (2003) highlighted the need for the development of degradable material that was non-toxic to the body. The International Agency for Research on Cancer recognised that stainless steel contained large amounts of nickel, which was potentially carcinogenic (Boffetta, 1993, p. 67). A degradable material that could have been used was that of a synthetic polymer. Although for applications such as stents, the size of the polymer implant would be quite large in order to have sufficient strength for the task. (Lincoff et al, 1996) highlighted the fact that the polymer material induced

exaggerated acute and chronic inflammatory responses during degradation. Thus other materials required investigation.

Magnesium was recognised firstly due to its high corrosion rate. But further study revealed that magnesium is naturally present in large amounts in the body (Durlach and Bara, 2000). It has also been found that deficiency in magnesium is associated with a higher incidence of ischemia heart disease (Seiler and Sigel, 1988). With such properties, it can be seen that magnesium and magnesium alloys are good candidates for the development of stents.

2.2.2 Bone devises

Titanium alloys and stainless steels have been used as permanent implants for many years due to their high strength and high corrosion resistance. Due to the research being conducted on stents, alternative materials are being investigated for use in bone devises such as pins and screws. Polymers have been consider, however to achieve the desired strength, the size of the polymer implant would be very large. However, magnesium and magnesium alloys have show great promise for the use in bone devises. The density of magnesium is (0.00174 g/mm^3), which is very similar to that of bone (0.00175 g/mm^3) (Shi. et a, 2005). The Young's modulus of magnesium (45 GPa) is also within the range of bone (40-57 GPa). The Young's modulus of titanium alloys is much higher to that of bone, whereas polymers have a much lower value (Estrin. et al, 2007). The compatibility of the magnesium's mechanical properties to that of bone, make it a desirable material for use as a metallic bio-degradable implant.

2.3 Implant material testing

2.3.1 Pseudo-physiological testing

Pseudo-physiological corrosion testing measures the rate of corrosion of a material in conditions designed to simulate that of the human body. There are two types of test, the static and dynamic. Atrens and Song, (2002) used the static test to simulate uses such as bone devices and the dynamic test to simulate uses such as stents. For such an experiment, specimens of material are required to be tested. Estrin. et al (2007) used static specimens of the size 10mm x 10mm x 2-2.5mm thick, while the size of the static specimens used by Shi. et al (2005) were of the size 20mm x 20mm x 4mm thick.

2.3.2 Animal testing

As stated earlier, Hartung. et al (2003) has undertaken testing on animals such as rats and pigs. While testing on animals is restricted in Australia, local regulations in German allow such testing. The rats were implanted with magnesium alloys to investigate the inflammatory reaction. Once it was found that the rats did not have any adverse effects from the magnesium, further study was undertaken on a number of pigs. These pigs were implanted with a number of stents in their main arteries. All of the animals bar one pig survived the entire testing period without any signs of stent thrombosis or other related events. The pig which did not survive, died after four days of implantation without any apparent reason. It was found from the results gathered that the stents strut cross sectional area would become zero after approximately 90 days. This had to be extrapolated from the data as the testing period was only 56 days, and assumed a linear degradation.

2.3.3 Fatigue testing

Fatigue testing was design to measure a materials ability to withstand cyclic loading. Estrin. et al (2007) tested magnesium alloy AZ31 of three different states, hot rolled (HR), squeeze cast (SC) and equal channel angular pressing (ECAP). Carte. et al, (1999) stated that stents in arteries undergo tens of millions of cycles in their lifetime. This highlights the need for fatigue testing in determining a possible candidate for a metallic bio-degradable implant material. Figure 2 shows the fatigue testing results found by Estrin. et al (2007).

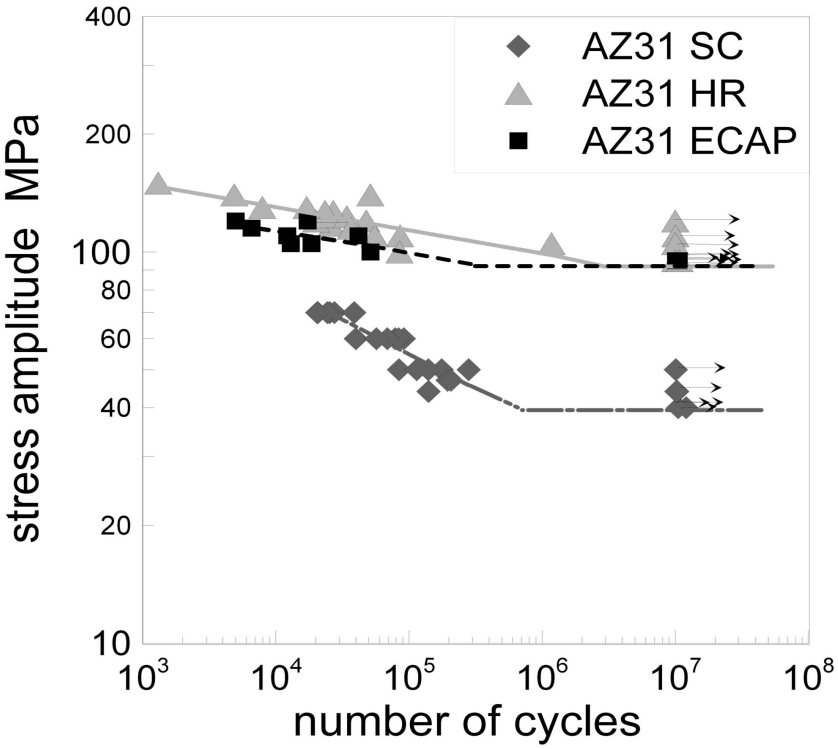

Figure 2: Fatigue properties for the three states of the magnesium alloy AZ31 (Estrin. et al, 2007).

2.4 Degradation rate

Corrosion testing measures the degradation rate of materials. Purity, alloys, surface coating and the state of the material all have influences on the rate of degradation. Estrin. et al (2007) compared the rate of corrosion of the three states of magnesium, HR, SC and ECAP. This revealed that the squeeze cast material degraded at a faster rate (refer Figure 3). Shi. et al (2005) research included the comparison of pure magnesium and magnesium alloy AZ31 (refer Figure 4). The chemical composition of the alloy AZ31 is given in Table 1. Carere. et al (1999) studied the magnesium alloy AM60B. The chemical composition of this alloy is given in Table 2. Carere. et al (1999) found that this material degraded at a rate the was unacceptable for use as stents. Anodised coatings have also been studied by Shi. et al (2005) to reduce the rate of degradation. The coating was of a ceramic-like covering with pores ranging from several micrometers to 10 micrometers in size. This reduced the amount of Hank's solution that was able to come in contact with the specimens, therefore slowing down the corrosion rate.

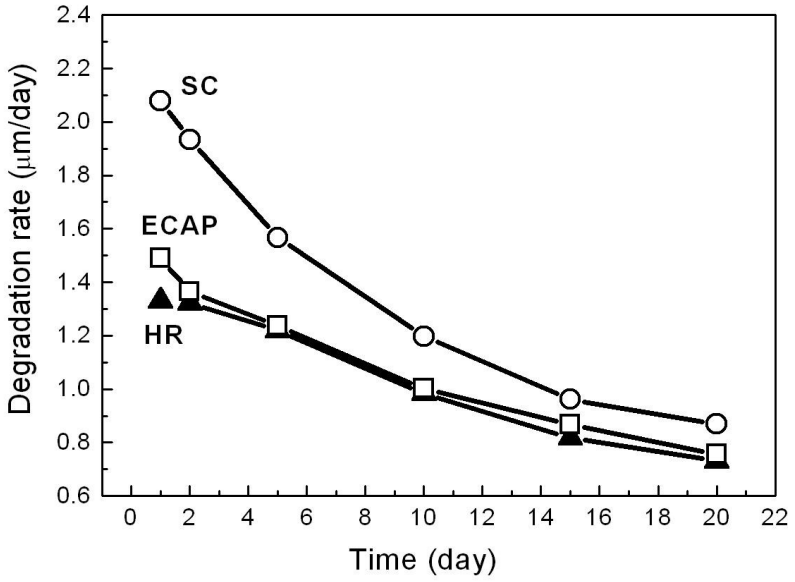

Figure 3: Degradation rate of HR, SC and ECAP samples in Hank's solution under static conditions (Estrin. et al, 2007).

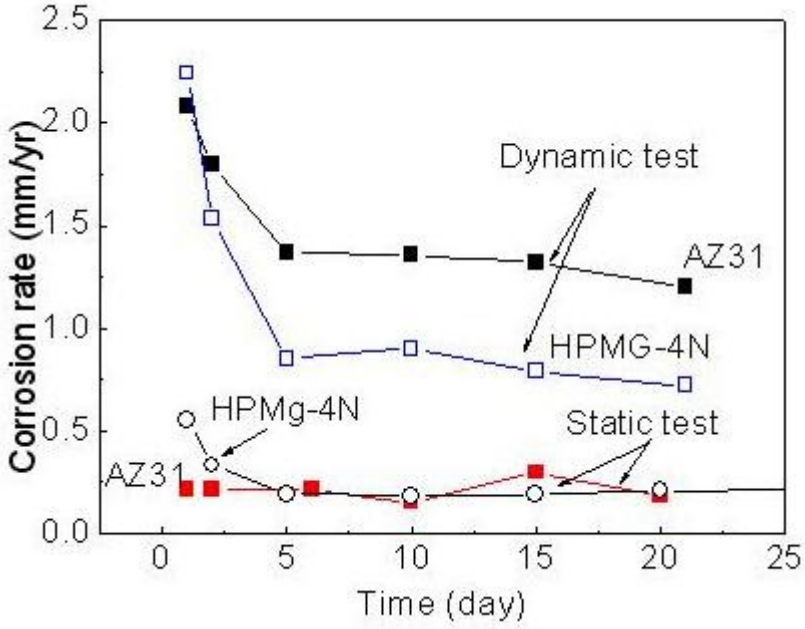

Figure 4: The corrosion rate of AZ31 and Mg(4N) in static and dynamic Hank's balanced salt solution (Shi. et al, 2005)

Table 1: Chemical composition of magnesium alloy AZ31.

Chemical composition of AZ31 [wt %]								
Mg	Al	Mn	Zn	Cu	Fe	Sn	Ni	Be
Bal.	3.24	0.36	1.02	0.002	0.003	<0.002	<0.001	<0.0005

Table 2: Chemical composition of magnesium alloy AM60B.

Chemical composition of AM60B [wt %]								
Mg	Al	Mn	Zn	Si	Cu	Ni	Fe	Be
Bal.	6.0	0.33	0.07	0.006	0.001	<0.001	<0.002	0.0008

2.3 Summary

The studies conducted by the various sources stated, although very different in their approach, had very similar findings. For the course of this project, a similar approach was used to that used by Shi. et al. (2003). Although the exact experiment was not used, it was modified to see if temperature would have a bearing on the corrosion rates of both the static and dynamic specimens.

CHAPTER 3

MATERIAL SELECTION

3.1 Introduction

As stated in section 1.3, there are negative aspects associated with the currently used implant materials. This chapter will review these short comings in detail and highlight the need for the development of alternative materials to minimise these disadvantages. Finally, the advantages of the material magnesium alloy AZ31 will be compared to those of the existing materials to emphasize its superior qualities and show how this material will be used to benefit patients.

3.2 Permanent Implants

The main problems associated with permanent implant materials are, irritations, induced stresses on bones, and the causing of alarms to sound when passing through metals detectors. Common permanent implant materials used are stainless steels, titanium and ceramics.

3.2.1 Irritation

Irritations can come in many different forms. The most common irritations encountered with implants are:

- Uncomfortable feelings
- Protrusions
- Rejection from the body

The most common of all the irritations is that of the implant physically feeling uncomfortable. However, this feeling often disappears with time. At the beginning of the implants life, the patient can notice a difference. Whether this be in the form of a heaviness due to material properties or in the case of a plate, a hardness under the skin in the area affected. Once the patient becomes familiar with the implant, this irritation is often forgotten about.

Protrusions are another form of irritation that is also common. Often when an implant is used, it is impossible to totally conceal the implant. That is, the implant may protrude out of the bone, which can be felt under the skin, or even protrude out of the skin altogether. In the case of certain hand and finger injuries, it is common for stainless steel wires to be inserted into the end to the finger all the way to its base to ensure the finger can not bend. This wire is left to stick out of the finger tip approximately 5-8mm. Once the implant has served its purpose, it is removed by pulling from this protruding part.

If the body chooses to reject an implant, it could prove to be harmful or even fatal for a patient. This is due to the fact that an infection could begin which may or may not be able to be treated. Although many infections can simply be treated by use of antibiotics, some infections can be more serious. Extreme cases of infections have lead to parts of the body being amputated. Modern technology and medical practises have meant that this form of irritation is very rare.

3.2.2 Induced Stresses

By using materials that have different mechanical properties to that of bone, induced stresses can occur in either the bone or the implant itself. The two main factors which influence the amount of stress induced are the hardness and the stiffness or Young's modulus of elasticity of each material. Firstly

let us consider the hardness. The hardness determines the materials wear resistance. For example, consider a hip joint with a ball and socket. If one material is harder than the other, the harder material will wear away at the less hard material causing it to fail more rapidly. However, by having materials of the same hardness, they will both wear away at the same rate therefore reducing the amount of wear and lasting longer. Consider Figure 5 below. The common hip joint of a ball and socket made from titanium and ceramics. It can be seen that the ball and socket are both made from the same ceramic material, while the rod that connects the joint to the bone is made of titanium. This is to reduce the amount of wear in the joint, while providing strength to the connection of the bone via the titanium rod. However, for the purpose of this project, magnesium and its alloys would not be suitable to this application as they would corrode away over time, whereas these joints are more of a permanent fixture.

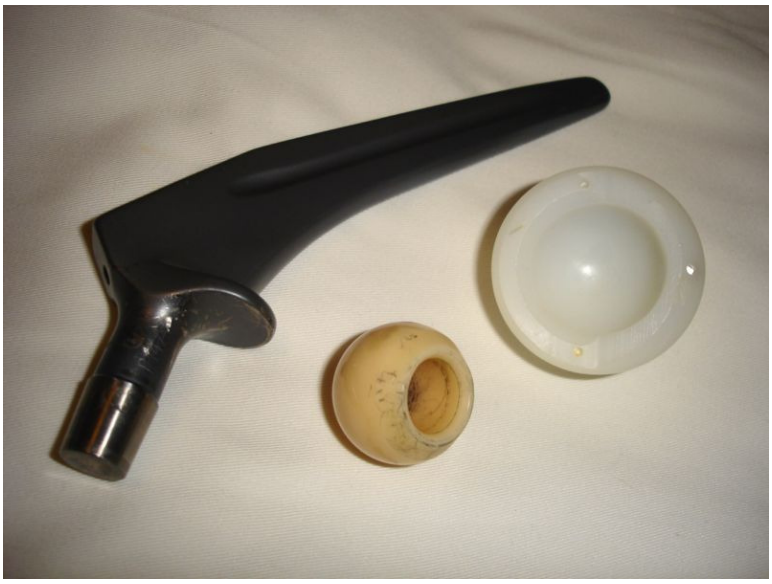

Figure 5: Common ball and socket replacement hip joint.

Let us now consider the Young's modulus of elasticity as a factor in determining the amount of stress induced. The Young's modulus of elasticity can also be called the stiffness of the material. The stiffness of the

material is the materials ability to resist bending. By using materials with different stiffness, an induced stress forms between these materials. This is due to the fact that one material will be forced to bend more than the other as their properties are not the same. Because the stiffness of the titanium is much higher than that of bone, more stress is applied to the bone because the titanium is much stronger. This in turn can cause the bone to break or wear away. This is an undesired result of the implant procedure. However, with materials of similar properties, this problem can be eliminated.

3.2.3. Metallic detection

On a simpler level, implants can be the cause of embarrassment. This is due to the fact that metallic objects will cause metal detectors at such places as airports to sound as they detect a metal object. While this is not a serious issue, it is still worth noting. For implants that are permanent such as hip joints, this occurrence is unavoidable. However, for implants such as pins and screws which have previously been considered permanent, this will change.

3.3 Available degradable implants

Polymer materials are a bio-degradable synthetic implant. The development of these materials was to replace the permanent metallic implants. However, polymers do not have a high level of strength. Nor do they have a high stiffness. For this reason, it has been decided that the bio-degradable implant material should be metallic in order to have the mechanical properties that are sufficient for the task.

3.4 A new generation bio-degradable implant material

The solution to these problems is a magnesium alloy AZ31. While previously considered undesirable for use in the human body for its high corrosion rate, its potentials are beginning to be realised. This ability to corrode is now being recognized as a benefit instead of a flaw. It is believed that as the magnesium alloy corrodes away, the bone will grow to replace it. Over a period of time when the magnesium has fully dissolved, the one will have fully healed itself. The mechanical properties of this alloy are almost identical to that of bone. The benefit of this is that any stress that may have been induced by material property differences is no longer a problem. However, because the alloy will dissolve, the body will have to accommodate the chemicals released. Magnesium, aluminium and zinc are all elements that the body uses. The key is to release these substances at a controlled rate so as not to poison the body.

3.5 Summary

Material selection is an important part of any engineering procedure. Using materials which compliment each other is one step towards success. Although stainless steels and titanium have been used with great success in the past, magnesium alloy AZ31 offers an outstanding alternative. By being degradable, the magnesium will totally dissolve away until the bone is fully healed. This will inturn eliminate the long term irritations and induced stresses that previous materials have caused.

CHAPTER 4

EXPERIMENT METHOD

4.1 Introduction

The most important criteria for the magnesium alloy AZ31 to meet, is that of an acceptable corrosion rate suitable for the body to handle. The recommended daily intake for magnesium is 300-400mg per day. To investigate the rate at which the alloy AZ31 would degrade, an experiment was devised to simulate the conditions of the human body. As human and animal testing is prohibited in Australia, this experiment was prepared in a laboratory. Two corrosion tests were conducted simultaneously, a dynamic and a static simulation. These tests were to mimic that of the human body to provide theoretical corrosion rate data which could be compared to the allowable corrosion rate. In order to conduct the required experiment, it was essential to have the right equipment as well as multiple specimens. The experiment consisted of multiple specimens of magnesium alloy AZ31 being submersed in a salt based solution that would simulate body fluids.

4.2 Materials and specimen preparation

In order to keep this project experiment and the experiments previously made as similar as possible, it was imperative that the specimens were as close to the original specimens in every way. Size, shape and surface finish being the most crucial aspects to the specimens. The magnesium sample material was part of the same squeeze cast magnesium alloy AZ31 material used in the previous trials. The first step to preparing the specimens was to cut them from the billet of material to the correct size and shape. The size specified for the static specimens was approximately 10mm x 10mm x 2-2.5mm thick. The dynamic specimens were of a different size and shape to

mimic the testing previously conducted. The size of the dynamic specimens was approximately 5mm x 5mm x 10mm long. This was completed by using an angle grinder with a 1mm thick cut off wheel attached.

Figure **6** shows the material of a static specimen after the initial cut has been performed. Notice the coarse cut produced by the grinder. The surface finish required for this experiment was the finish created by #2000 grid sandpaper. To speed up the polishing process, a #500 grid sandpaper was used to remove the main scour marks.

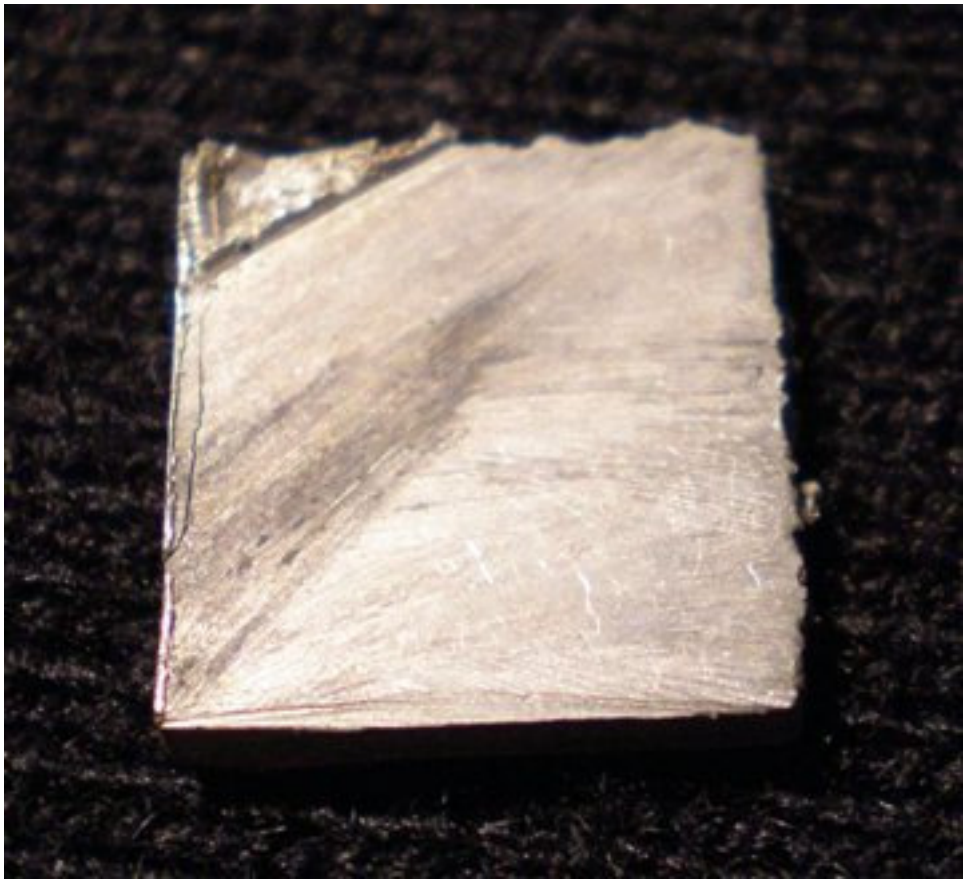

Figure 6: A static test specimen after it has been cut with a cut off wheel from a grinder.

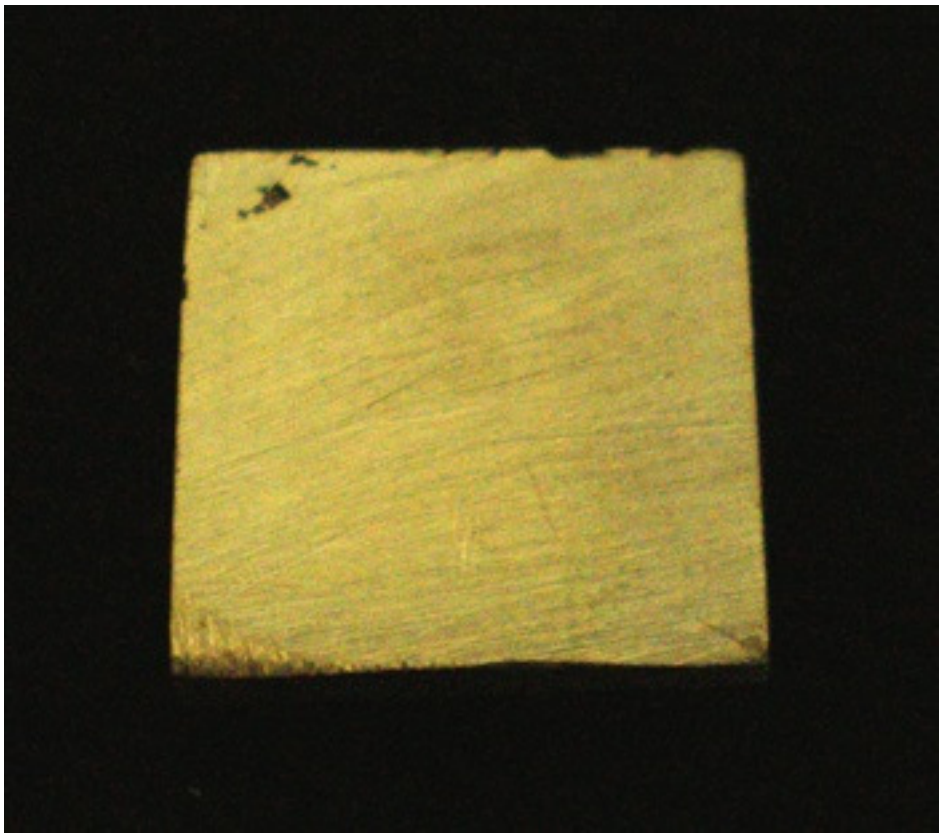

Figure 7: A static test specimen after the initial stage of grinding with the #500 grid sandpaper.

Figure 7 shows the specimen after it has been sanded with #500 grid sandpaper. Notice how most of the coarse cut marks have now been removed. However, further sanding was required to reach the necessary surface finish. A special grinding machine was used so that the specimens could be fully polished. Figure 8 below shows the sanding machine.

Figure 8: The grinding apparatus used for the sanding the test specimens.

It can be seen that the machine is connected to a tap. This is to allow water to wash the sandpaper free of residue from the specimens as well as keeping the specimen cool while it is being sanded. The friction cause by the sandpaper rubbing on the specimen can make the specimen very hot. To allow the specimen to be handled, the water provides the cooling needed. Figure 9 below shows a specimen being sanded. Once all of the sanding had been completed, the specimens were cleaned using ethanol to remove any oil that may have been left from being handled. Figure 10 and Figure 11 show the finished static and dynamic specimens respectively.

Figure 9: The grinding apparatus in use with a constant flow of water as a cleaning and cooling fluid.

Figure 10: Fully polished static test specimen.

Figure 11: Fully polished dynamic test specimen.

It can be seen that the surface finish of the specimens is very smooth. The two types of specimen are of different shape and size. This is so that the dynamic specimen can fit into the clear flexible hose. The two holes drilled in to the specimen were to allow the fishing line to be attached, linking all of

the dynamic specimens together. These holes were drilled into the specimens with the use of a hand drill with a drill size of 2mm in diameter. The fishing line also held the specimens inside the hose and stopped them from moving. Fishing line was used so that there would not be any other metals inside the solution that may cause a reaction to occur. Thus, eliminate another variable.

4.3 Equipment

Before any experiments could take place, all of the equipment required for the experiments needed to be collected and set up. A laboratory with relatively constant temperature was used at the University of Southern Queensland to hold the experiment so as to eliminate temperature variation as a variable. While the air conditioned laboratory kept the surroundings of the experiment at constant temperature, a temperature regulator was used keep the solution temperature of the experiment at a constant level. Previous experiments on this topic used a temperature of 25^{o}c, whereas the core temperature of the human body is 37^{o}c. Therefore in this project the temperature for which the testing will be completed is 37^{o}c to simulate the body conditions. The results collected were then compared to that of the previous experiments' conducted at 25^{o}c, which can be seen in chapter 5.

A small 6lt tank was used to store the solution and the static and dynamic specimens for the period of the experiment. In the tank a temperature regulator and the submersible pump were placed. The pump was used to keep a constant flow of Hank's balanced salt solution flowing past the dynamic specimens. The pump flow rate was 500ml per minute. Although the fluid was returned to the tank where the static specimens were held, the flow rate was not significant enough to cause movement of the solution in the tank itself. The clear flexible hose had one end connected to the outlet of the pump, while the other end of the hose was placed back into the tank to

circulate the fluid around the specimens. The purpose of this was to simulate the blood flowing past the magnesium in the body.

The solution used to perform the testing in was a Hank's balanced salt based solution. This solution came in powdered form. Each container of powder made up 1lt of Hank's solution fluid. Table 3 shows the components which make up the powder of the solution.

Table 3: The components of the Hank's balanced salt solution powder.

Components	g/L
Calcium Chloride [anhydrous]	0.1396
Magnesium Sulphate [anhydrous]	0.09767
Potassium Chloride	0.4
Potassium Phosphate Monobasic [anhydrous]	0.06
Sodium Chloride	8.0
Sodium Phosphate Dibasic [anhydrous]	0.04788
D-Glucose	1.0

5lts of the solution was mixed and placed into the tank. The temperature regulator was switched on to ensure that when the specimens were placed in the solution, it would be at the testing temperature of 37^{o}c.

4.4 Experimental procedure

Before any specimens could be tested, they each had to be weighed. The initial weight of each specimen was recorded on a label.

Figure **12** shows the label used. On each label the day, specimen number, test type, mass before and mass after testing were recorded. Note the accuracy of the weight measurement. It was important to use scales of a very high degree of accuracy.

Figure **13** shows the scales that were used.

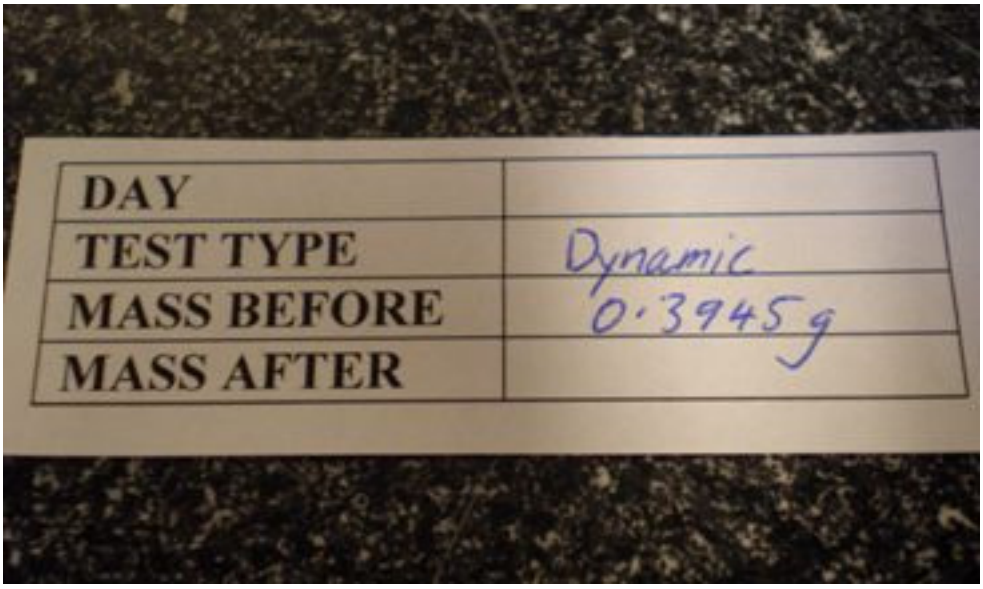

Figure 12: A sample of the labels used to identify each test specimen.

Figure 13: The highly accurate scales used for weighing each test specimen.

These scales measured in grams to an accuracy of four decimal places. For scales to be this precise, any variables that may influence the reading need to be eliminated. For this reason, the special enclosure is used so as not to allow any external forces to act on the specimen. Once every specimen was weighed and labelled, it was place in its own sealed plastic bag to protect the surface finish.

With the Hank's solution at the correct temperature of 37^{o}c, the ph level of the solution had to be adjusted to 7, which is neutral. This was completed with the use of the hydrochloric acid. Only a few drops were required. The ph level was tested with the ph meter. Once the ph reached 7, the specimens were able to be added to the solution. Before this could take place however, for the static specimens to stay submersed in the solution, thin insulated electrical wire was twisted around the specimens. This allowed the specimens to have the maximum surface area exposed to the solution. While the wire kept the specimens off the bottom of the tank, it was also able to hold the specimens away from the side of the tank. The wire was looped over the side of the tank and taped in place to stop any movement. Small labels were attached to each wire showing the day and number of each specimen.
Figure **14** shows the static specimens submersed in the solution and taped to the side of the tank.

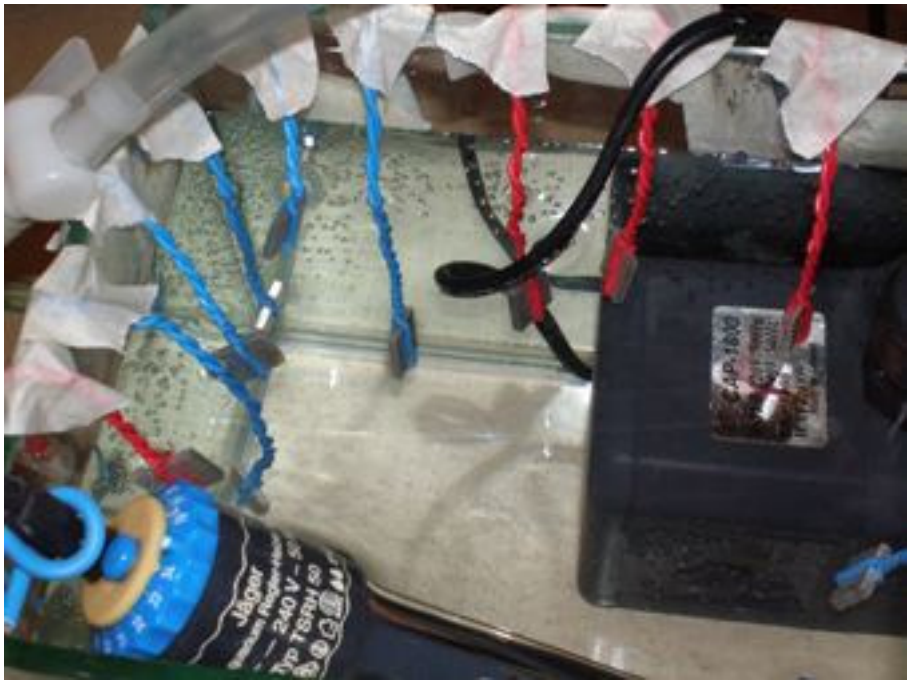

Figure 14: The static specimens submersed in the Hank's solution and taped to the side of the tank. Also the temperature regulator and submersible pump can be seen.

For the dynamic specimens, they were all connected to each other with the use of fishing line. The specimens were then fed through the clear flexible hose. The hose was then connected to the pump and the pump switch on. Figure 15 below shows a schematic view of the dynamic simulation.

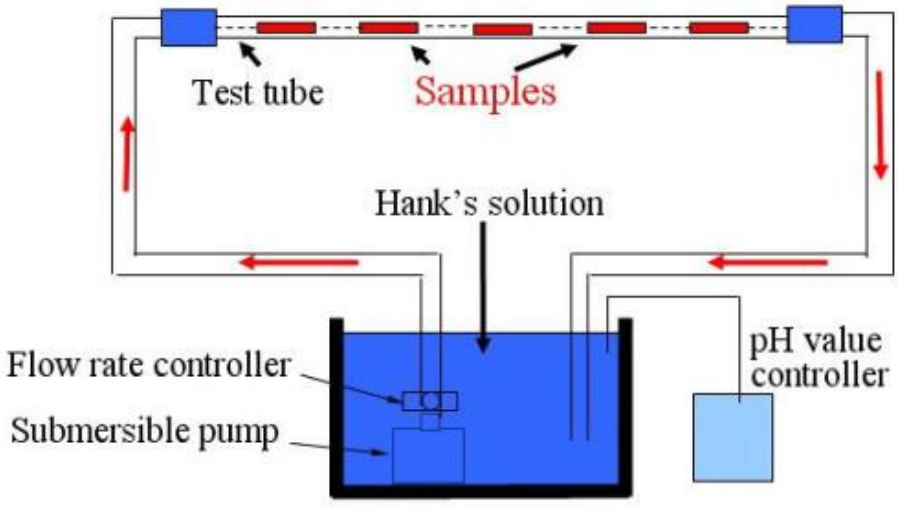

Figure 15: A schematic drawing of the dynamic simulation.

It was important to remove all of the air in the hose so that the specimens in the hose were fully submersed. Once the test had commenced, the ph level of the solution was monitored twice daily to ensure that it stayed at 7. Because of the reaction between the magnesium alloy and the solution, the ph level rose over time. The acid was used to lower the ph level. Any handling of the test and testing equipment was done while wearing the personal protective equipment. This included protective glasses, a laboratory coat, covered footwear and latex gloves. Specimens were then removed from the tank at the required intervals. These intervals were 1, 2, 5, 10, 15 and 20 days. Three specimens of both static and dynamic tests were removed on each of these days. On removal from the solution, each specimen was washed clean using the cleaning solution containing 200g/L CrO_3 and saturated $AgNO_3$, the rinsed with distilled water and dried. When completely dry, the specimens were weighed again and the weight recorded on the corresponding labels. After the twenty day testing period, the equipment was cleaned and packed away.

4.5 Summary

For the testing to take place, it was essential that all of the preparation work had been completed properly. With all of the equipment gathered, the specimens could be cut and shaped to the required size and surface finish for the testing to commence. Constant monitoring was a very important part of the testing process. Careful handling and correct cleaning methods were used to ensure the specimens were removed correctly. With the weight of each specimen collected, the data required compiling.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Introduction

As this study is re-testing the corrosion rate of magnesium alloy AZ31 under pseudo-physiological condition, it is very important to test and collect data in the same manner as was conducted from previous studies so as to be able to accurately compare results. Both static and dynamic corrosion testing was completed on 36 specimens.

5.2 Data collection

As stated in section 4.4, the results found from weighing each specimen were recorded on a label. At the end of the twenty day period, once all the specimens were weighed, the figures on the labels were transferred to computer to show in graphical form the degradation rate of the specimens. Below Table 4 shows the results from the static corrosion testing. From Table 4 and Table 5, in order to convert the weight of the material lost to the corrosion rate shown, a simple calculation was made. By dividing the mass by the density of the magnesium alloy (equation 1), then dividing again by the surface area of each specimen (equation 2), the corrosion rate of millimetres per year was calculated. Below are the simple equations used.

$$volume / year = \frac{mass / year}{density} \quad (1)$$

$$thickness / year = \frac{volume / year}{surfacearea} \quad (2)$$

The density of magnesium alloy AZ31 is 0.00174 g/mm^3, and the surface area of the static and dynamic specimens was 280 mm^2 and 250 mm^2 respectively. By converting the corrosion rate into the form of mm/year, this allows future comparisons of specimens that are of different sizes, while still maintaining the relationship between the thickness of the material and the corrosion rate.

Table 4: The results gathered and calculated from the static corrosion testing of magnesium alloy AZ31.

Static Corrosion Test					
Day	**Specimen No.**	**Initial Mass (g)**	**Final Mass (g)**	**Corrosion Rate (mm/yr)**	**Average**
1	1	0.614	0.6141	-0.0749	-0.0499
	2	0.6688	0.6691	-0.2248	
	3	0.5532	0.553	0.1498	
2	1	0.6167	0.6167	0.0000	-0.0874
	2	0.5985	0.599	-0.1873	
	3	0.6681	0.6683	-0.0749	
5	1	0.814	0.815	-0.1498	-0.1798
	2	0.7248	0.726	-0.1798	
	3	0.5796	0.581	-0.2098	
10	1	0.7309	0.7304	0.0375	0.0100
	2	0.5403	0.5405	-0.0150	
	3	0.679	0.6789	0.0075	
15	1	0.5561	0.5542	0.0949	0.0200
	2	0.5464	0.5445	0.0949	
	3	0.6023	0.6049	-0.1299	
20	1	0.6973	0.6945	0.1049	0.0862
	2	0.6534	0.6532	0.0075	
	3	0.6285	0.6246	0.1461	

This data was then transformed into graphical form.

Figure **16** shows the average static corrosion rate for each day of the experiment.

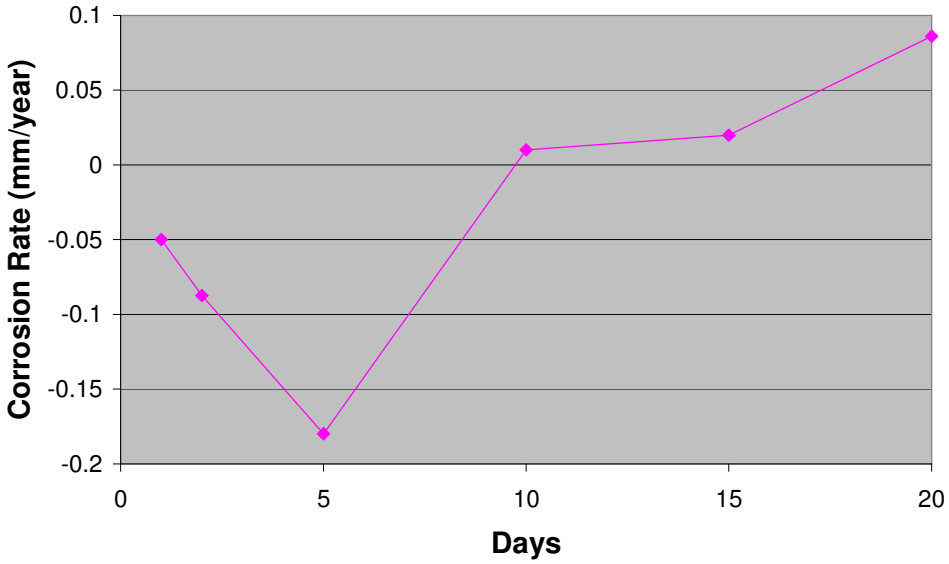

Figure 16: A plot of the corrosion rate of the static test specimens over a 20 day period.

The results gathered from the static testing revealed some very abnormal figures. It can be seen from

Figure 16 that for the first 10 days of the experiment the specimens did not degrade at all. In fact, it seems that they actually gained weight. While this may seem very strange, there are a number of factors which may have influenced these results. Further discussion of these anomalies is in section 5.3. After the tenth day of the experiment, the static specimens began to behave in a manner which was expected, with the exception of the spike towards the twentieth day.

Similarly, the dynamic test results were gathered and calculated in the same way as the static corrosion testing. Table 5 and Figure 17 show the results from the dynamic simulation.

Table 5: The results gathered and calculated from the dynamic corrosion testing of magnesium alloy AZ31.

Dynamic Corrosion Test					
Day	Specimen No.	Initial Mass (g)	Final Mass (g)	Corrosion Rate (mm/yr)	Average
1	1	0.3326	0.3299	2.2655	3.3004
	2	0.4721	0.4682	3.2724	
	3	0.4346	0.4294	4.3632	
2	1	0.3489	0.3477	0.5034	0.5314
	2	0.5023	0.5006	0.7132	
	3	0.5196	0.5187	0.3776	
5	1	0.3817	0.3785	0.5370	0.5090
	2	0.4832	0.48	0.5370	
	3	0.3705	0.3678	0.4531	
10	1	0.4217	0.4132	0.7132	0.6237
	2	0.4398	0.4341	0.4783	
	3	0.4201	0.412	0.6797	
15	1	0.4434	0.4335	0.5538	0.4456
	2	0.4041	0.4011	0.1678	
	3	0.3997	0.3887	0.6153	
20	1	0.3945	0.376	0.7761	0.9356
	2	0.408	0.3862	0.9146	
	3	0.3963	0.3697	1.1160	

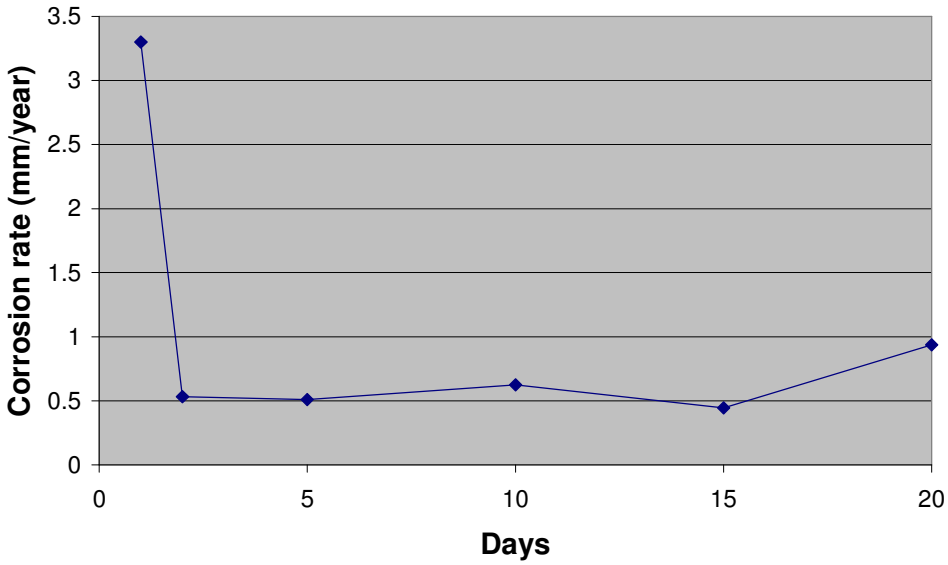

Figure 17: A plot of the corrosion rate of the dynamic test specimens over a 20 day period.

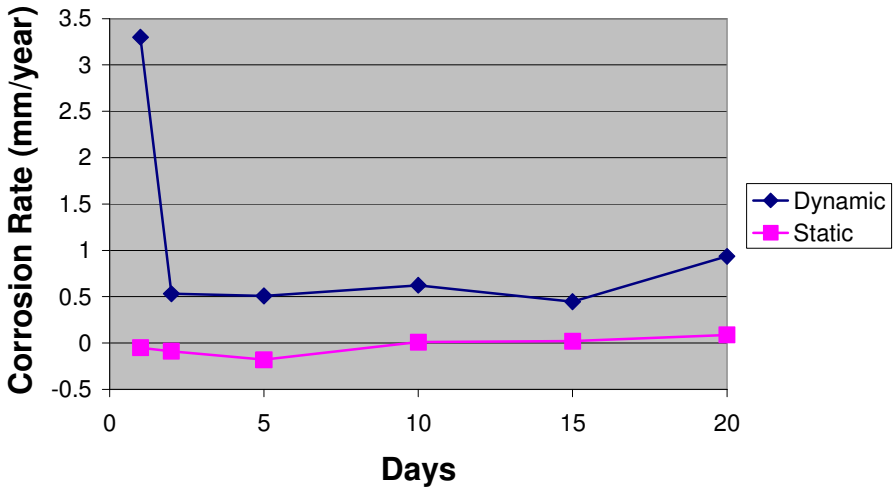

Figure 18: A plot which compares the corrosion rates of both the static and dynamic tests.

Figure 18 shows the corrosion comparison of the static specimens to the dynamic specimens. From this chart it can be seen that the dynamic specimens degraded at a much higher rate than the static specimens. From the works of Shi. et al (2003), this seems to be a common trend for such experiments, as their findings revealed much the same results. That is, the dynamic specimens corroded more quickly at the beginning before levelling out after 5 days, whereas the static specimens corroded at a relatively constant rate.

5.3 Analysis

5.3.1 Results

The irregularity of the static corrosion results raises a lot of questions. There are many reasons for these results, which include:

1. an error in the weighing process
2. mixing up the specimens during the experimental process
3. surface coating forming on the specimen during the experimental period
4. an inconsistency in the Hank's solution

It is important to investigate each factor individually before eliminating it as a problem.

With regard to (1), human error is sometimes unavoidable. However, in the case of this project the specimens were weighed using very accurate scales. All of the specimens were weighed in one sitting. That is, if any of the specimens were measured incorrectly, than all of the specimens weights must be incorrect. But this is not the case. Therefore, it can be assumed that the weighing process was correct.

(2) suggests that a mix up of specimens occurred during the experiment process. This could mean that when the final weighing of the specimens took place that the weight appeared to be larger because the specimen was not the correct one according to its label. However, due to each specimen having a unique weight, the variance of measured weight was consistent with each specimen. Therefore, it can be concluded that the specimens were not disorganized.

(3) refers to a surface coating forming on the specimens during the experiment period. When the magnesium alloy AZ31 is placed in the Hank's solution, the two chemicals cause a reaction. Equation (3) shows the chemical reaction which takes place (Veldman, 2000).

$$Mg + 2H_2O \rightarrow Mg^{2+} + 2OH^- + H_2 \quad (3)$$

As this reaction takes place, there is the potential for sediment to be left on the surface of the specimens. Magnesium hydroxide, other phosphates and carbonates were the products which formed a layer on the surface of the sample (Estrin. et al, 2007). This could possibly be the reason why only the static specimens were affected. As the fluid passed by the dynamic specimens, the residue was unable to form on the surface, whereas the static specimens were in a static medium allowing the deposits to form. This layer of coating provided a form of corrosion resistance similar to that of the anodised coatings in Chapter 2. However, the rate at which the coating grew must have been faster than that of the corrosion. To be sure that this was a significant factor, tests would have to be made in order to calculate the amount of residue on the specimens. Therefore, the formation of a surface layer due to magnesium hydroxide, other phosphates and carbonates is a contributing factor to the corrosion resistance found in the static specimens.

With regard to (4), there can not be an inconsistence in the Hank's solution. This could only take place if the testing was completed in two separate containers, one for the static test and one for the dynamic test. This study used the same testing container for this very reason, so that the solution would be exactly the same for both static and dynamic testing. Therefore it can be concluded that the consistency of the Hank's solution was constant for both testing procedures. The main area of interest in regard to the weight gain of the static specimens is the surface coating caused by the chemical reaction.

5.3.2 Test specimens

It was imperative that there was more than one specimen for each day of the trial. The significants of this being that in the event of a fault with one or two of the specimens for a given day, they would be able to be discarded yet there would still be a specimen for which data could be recorded. For this reason it was chosen that three specimens would be used for each day of the trial per test type, static and dynamic.

By analysing these specimens, information could be gathered that was not available from merely weighing the specimens alone. Figure 19 and Figure 20 below show one specimen for each day of the trial from both the static and dynamic testing.

Figure 19: The static test specimens after 1, 2, 5, 10, 15, 20 days from left to right.

Figure 20: The dynamic test specimens after 1, 2, 5, 10, 15, 20 days from left to right.

It is clear to see on the first three static specimens the line where the insulated electrical wire was rapped around them. Although this is not a serious issue, there is still some corrosion resistance caused by the wire because the does not allow the solution to come into contact with the whole specimen. However, this does not seem to be an influence towards the end of the testing. The last three static specimens show no sign of the wire being any restriction.

Another feature that can be seen on both types of test specimen is the areas which were more affected by the corrosion. This is particularly clear on the fourth static specimen. Notice how the area in the middle of the specimen is much more corroded. This shows that certain areas of the specimens were more susceptible to corrosion. It is unclear why this is the case. However, this may be explained by the method used to cut the specimens. An angle grinder with a 1mm thick cut off wheel was used. Due to the fact that cooling fluid is unavailable when using a grinder, the grain structure of the surface of the specimens may have been changed. Some areas may have cooled faster than others, which in turn would change the grain structure of certain areas of the specimens. Although this is not certain, by studying the specimens under an electron microscope, this would be made clear.

Figure 16 and Figure 17 show an increase in the corrosion rates of both the static and dynamic specimens between days 15 and 20 of the trial. The reason for this is that as the corrosion takes place, there is not an even layer that is removed. In fact with the inconsistency in the surface grain structure, it was uncertain how or in which area the corrosion would begin. So as the corrosion continued, small pieces of magnesium alloy AZ31 would actually be removed. This can particularly be seen from the last dynamic specimen in Figure 20. As the fluid passed by the specimens, it would force the pieces to fall off. This is the cause of the increase in the corrosion rate of both the static and dynamic specimens.

5.4 Summary

It can be seen that although the data collected from the dynamic simulation was as expected, the reliability of the data is questionable. Certain variables caused irregularities to arise, leading to some errors. Although these errors were found, further study is needed to be fully certain of the reasons behind them. Only by critically analysing the data and the specimens could any irregularities be found. Therefore, it is important to be critical when it comes to the analysis of data.

CHAPTER 6

CONCLUSION AND RECOMMENDATION

6.1 Conclusions

Magnesium alloy AZ31 has a great potential to change the way implants are used in the human body. Although this study was inconclusive, it has highlighted key areas of interest for further study. By studying the results found by this experiment, certain behaviours in the magnesium alloy have been found. With more time and resources, it would be possible to yield very convincing results.

It was seen that through the course of this research, various restrictions increased the error in the results found. Limited time and resources meant that the experiments could not be recreated. However, the results did show that there were many variables which influenced the outcome of the experiments.

Comparing the results from these experiments to those found from previous research on this topic, revealed similar trends in the corrosion rate of magnesium alloy AZ31 under pseudo-physiological conditions. From the experiments of Shi. et al (2005) and Estrin. et al (2007) it can be seen that by increasing the temperature of the corrosion testing, there was not a significant difference in the test result.

6.2 Future work

There is a clear sign that from this project, further research is needed to be fully conclusive that magnesium alloy AZ31 could in fact be used as a degradable implant material. By understanding the errors that were found from this project and eliminating them from further experiments, more usable data could be collected.

The preparation of these specimens should be done with the utmost care. Using a cut off wheel on an angle grinder is not recommended. An alternative would be to use programmable machines to cut and polish the specimens to the require finish. This would eliminate the human error and the test pieces would all be made to a known tolerance. Retesting after using this cutting method would help reveal whether or not the grain structure of the material was altered. Alternatively, untested specimens from this experiment could be studied under an electron microscope to see if any changes to the grain structure occurred during the cutting process.

The way in which the specimens were held in the tank produced another variable. The insulated electrical wire caused some corrosion resistance because a small section of the specimen was covered by the wire. An alternative to this method could be to adopt the fishing line approached used by the dynamic testing. By drilling a hole in the top of the specimen, similar to that of the dynamic specimens, fishing line could be attached to the static specimens. This would reduce the amount of area that was covered, and reduce the amount of corrosion resistance the covering caused.

Further study into the reaction caused between the magnesium alloy AZ31 and the Hank's solution should be undertaken. This research should focus on any residue left behind on the specimens that may cause a coating to form which in turn increases the corrosion resistance of the magnesium alloy.

Similarly, any residue that may form as a result of the solution being static should be studied.

The size of the experimental parameters is another issue that requires further investigation. That is the ratio of magnesium alloy AZ31 to the amount of Hank's solution. By using the same fluid to conduct both static and dynamic simulations, may have caused the Hank's solution to become diluted. To simulate the human body better, a larger tank or reservoir could have been used. Retesting under these conditions may produce different results.

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APPENDIX A

University of Southern Queensland

FACULTY OF ENGINEERING AND SURVEYING

ENG4111/4112 Research Project
PROJECT SPECIFICATION

FOR:	**ADRIAN GUSTAFSON**
TOPIC:	INVESTIGATION INTO A NEW GENERATION OF IMPLANT MATERIAL
SUPERVISOR:	Dr. Hao Wang
SPONSORHSIP:	USQ
PROJECT AIM:	In this project we aim to develop magnesium-based biodegradable implant materials, study the bio-corrosion behaviour of magnesium and magnesium alloys in pseudo-physiological condition and determine the effect of static and dynamic conditions on the degradation process.

PROGRAMME: **Issue A, 26 March 2007**

1. Research the background information already gathered so far into the development of magnesium-based biodegradable implant materials.
2. Undertake static bio-corrosion behaviour tests on samples of magnesium and magnesium alloys for a second time to substantiate results.
3. Undertake dynamic bio-corrosion behaviour tests on samples of magnesium and magnesium alloys.
4. Analyse the corrosion data for both tests, static and dynamic, for all samples.

As time permits

5. From the data collect above, undertake tensile tests of specimens of varying sizes and shapes.
6. Critically analyse whether or not this material could be viable for various practical applications in the human body.

AGREED:_____ (student) _____(supervisor)

Date: / / 2007 Date: / / 2007

Co-examiner:_____