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To cite this article: M Sedlářiková *et al* 2022 *J. Phys.: Conf. Ser.* **2382** 012019

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# Corrosion processes of sintered materials based on Fe

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**Abstract.** All currently used metal-based implants have the disadvantage of often requiring secondary surgery to remove the implant. This is why there is a lot of research into biodegradable bone implants these days. Biodegradable iron-based alloys are potential candidates for use as materials for temporary implants. This work deals with the current topic of Fe-based biodegradable sintered materials and their corrosion. These materials are suitable for applications where gradual decomposition is required. Sintered materials based on Fe-Mg are investigated in this work. The manufactured samples were immersed in NaCl solution and simulated body fluid – SBF. Subsequently, changes in corrosion potential and current, pH, conductivity and observations under the microscope were regularly analysed.

## 1. Introduction

Bone injuries such as fractures often result in permanent bone damage such as weakness and structural or volumetric changes in the fused bone. Treatment for such injuries can be long and expensive. Biodegradable materials may offer an improvement to such treatment, as they could provide the necessary short-term fixation and support for the fractured bone to be fused together. Biodegradable bone support will be gradually absorbed by corrosion processes and safely removed from the patient's body. Various compositions of such materials and manufacturing processes are examined in different corrosion environments to evaluate a number of properties such as corrosion rate and corrosion potential. The key parameters for biodegradable materials are mechanical strength, flexibility, tissue compatibility, and fast degradability.

Corrosion is the spontaneous, gradual transformation of metals or non-metallic organic and inorganic materials. It arises as a result of a chemical or electrochemical reaction of the base material with the external environment. Corrosion occurs in liquids, gases, and various chemicals. The results of corrosion can be very different. The appearance of the material may change or it may completely disintegrate. Corrosion is caused by electrochemical processes. The main corrosive agents include the hydroxide group, which is labelled OH. In addition, anions that arise from acids can act as corrosive agents ( $(\text{CO}_3)^{2-}$ ,  $(\text{Cl})^-$ ,  $(\text{NO}_3)^-$ ,  $(\text{SO}_4)^{2-}$ ).



Corrosion can be described by:

- Internal corrosion mechanism
- Type of corrosion environment
- External conditions
- Type of corrosion attack

Electrochemical corrosion is a case of metal corrosion in electrolytes (conductive medium). It consists of two partial reactions – the anode reaction and the cathode reaction. Both the anode and cathode reactions are interrelated and cannot occur without each other unless an external electric current passes through the corroding metal. The anode reaction represents the oxidation of the metal and is therefore its own type of corrosion. The depolarizing (cathode) reaction represents the reduction of oxygen dissolved in the electrolyte or the discharge of a hydrogen ion.

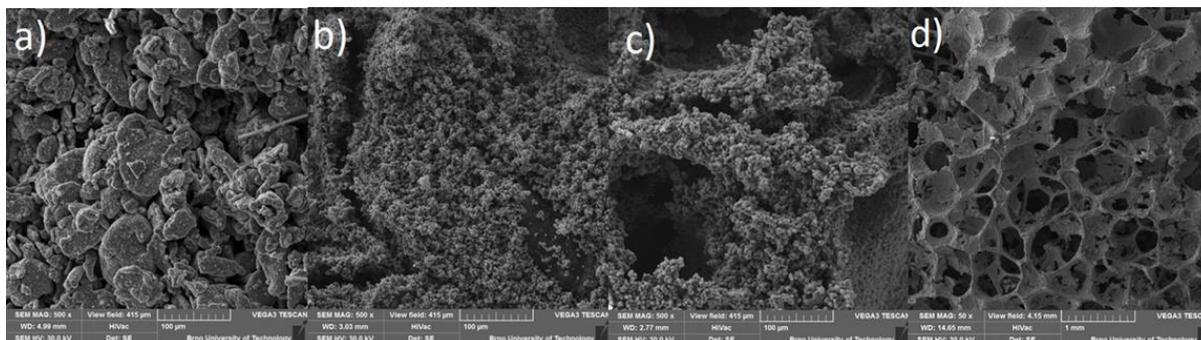
Electrochemical corrosion can be divided into atmospheric corrosion, corrosion in water, corrosion in soils, corrosion in aqueous solutions of acids, bases and salts.

Metals that are more susceptible to corrosion include manganese, iron, aluminium and lead. Metals that are more difficult to corrode include gold, silver and titanium [1].

## 2. Experimental part

### 2.1. Preparation and Description of Samples

Manufacturing of biodegradable bone implants samples can be described in the following steps. The first step was to prepare the material for sintering and the next step was sintering. In the first step, one of the batches was prepared by mixing the powdered metal material with an organic polymer carrier that formed the basic structure. The mixture was poured into a mold; the solvent was evaporated and the samples were dried. The carrier polymer was then removed by annealing. Powders of iron, magnesium and silver were used to prepare two sets of alloys: Fe-0.5Ag-1Mg (sample b) Fe-0.5Ag-3Mg (sample c) (all in wt%). Another batch used polyurethane (PUR) foam that was immersed in a mixture of powdered metals and demineralized water. Sample (e) is composed of pure iron. Another sample was prepared from powdered iron and magnesium Fe-3Mg (sample a) by using Polystyrene (PS). Pure iron powder was also used to make sample d). Other samples were prepared using the PUR method. Drying was used to remove all water and annealing was used to remove the polymer matrix carrier. The second step was sintering using a defined temperature and time. The temperature of 450 degrees Celsius was maintained for 2 hours. The temperature was then raised to 1120 degrees Celsius and held for one hour. This was done in a protective non-corrosive atmosphere of nitrogen or argon. The resulting material from both batches is hard and free of any polymer matrix carrier and is ready for examination and exposure to a corrosive environment. The samples were subjected to two different corrosion solutions. The first solution was sodium chloride and water, the second was simulated body fluid (SBF). Samples number b), c) and e) were soaked in salt solution, and sample a) was exposed to simulated body fluid (SBF). Samples number b) and c) were made by soaking polyurethane foam in a mixture of powdered metal and water. In the case of sample a), the organic polymer matrix carrier method was used. Figure 1 shows the SEM morphology of sintered alloys (a) Fe-3Mg, (b) Fe-1Mg-0.5Ag, (c) Fe-3Mg-0.5Ag, (d) Fe.



**Figure 1.** Environmental scanning electron microscope images of internal structure of samples prepared by a) sample with PS (Fe-3Mg), b) sample with PUR (Fe-1Mg-0.5Ag), c) sample with PUR (Fe-3Mg-0.5Ag), d) sample with PUR (Fe).

## 2.2. Solution preparation

The first solution that was prepared was NaCl. 100ml of distilled water and 0.9 g of NaCl were used. The second solution that was prepared was simulated body fluid (SBF) with ion concentrations almost identical to those of human blood plasma. This solution was approved in 2003 by Technical Committee ISO/TC150 of the International Organization for Standardization. To prepare 1000 ml of SBF, 700 ml of ion-exchanged and distilled water and the reagents listed in Table 1 were used. 1M-HCl was used to lower the pH. [4]

**Table 1.** Reagents used for preparing 1000 ml of SBF [4]

Order	Reagent	Amount	Purity (%)	Formula weight
1	NaCl	8.035 g	99.5	58.44
2	NaHCO <sub>3</sub>	0.355 g	99.5	84.00
3	KCl	0.225 g	99.5	74.55
4	K <sub>2</sub> HPO <sub>4</sub> · 3H <sub>2</sub> O	0.231 g	99.0	228.22
5	MgCl <sub>2</sub> · 6H <sub>2</sub> O	0.311 g	98.0	203.30
6	1.0M-HCl	39 ml	-	-
7	CaCl <sub>2</sub>	0.292 g	95.0	110.98
8	Na <sub>2</sub> SO <sub>4</sub>	0.072 g	99.0	142.04
9	Tris	6.118 g	99.0	121.13

Nominal ion concentrations of SBF in comparison with those in human blood plasma is show in table 2.

**Table 2.** Comparison of SBF with human blood plasma [4]

Ion	Ion concentrations (mmol·l <sup>-1</sup> )							
	Na <sup>+</sup>	K <sup>+</sup>	Mg <sub>2+</sub>	Ca <sub>2+</sub>	Cl <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	PO <sub>34</sub> <sup>-</sup>	SO <sub>24</sub> <sup>-</sup>
Blood plasma	142.0	5.0	1.5	2.5	103.0	27.0	1.0	0.5
SBF	142.0	5.0	1.5	2.5	148.8	4.2	1.0	0.0

The NaCl solution contains only some of the ions found in the human body. In comparison, the SBF solution contains most of the ions represented in the human body and can thus much better simulate the internal environment of the human body. SBF contains both chloride and phosphate ions,

which act differently on the passive layer that forms during corrosion. Phosphate ions support the formation of the passive layer, while chloride ions disrupt it. Depending on the activity of these ions, the value of the corrosion potential shifts to positive or negative values.

2.3. pH measurement

The pH of the solution was one of the measured values. This measurement shows how fast the corrosion processes are over time and how the corrosion rate changes – in some cases the rate is higher at first and then slows down, or it can be linear. From these measurements it is possible to approximately determine how much metal is being degraded and how much remains inside the body. It is also possible to estimate whether the values can be dangerous for the human organism or not.

The first pH measurement was made for a pure solution. The samples were then placed in a solution simulating the environment of the human body, and pH measurements were taken every other month. The changes in pH values are described in Table 3. The pH measurement in Figure 2 shows that the corrosion of sample a) was slower than the other samples.

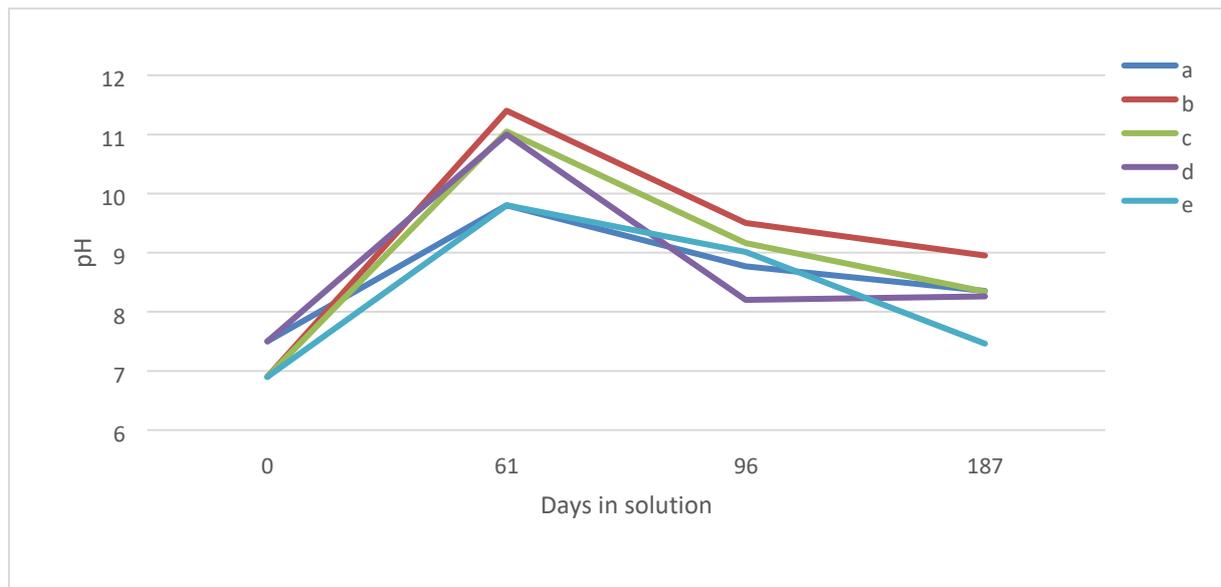


Figure 2. Changes of pH of the samples

Table 3. pH values of solutions and its changes in time

Solution	Sample	pH of solutions			
SBF	a) Fe-3Mg	7.50	9.80	8.77	8.35
NaCl	b) Fe-0.5Ag-1Mg	6.90	11.40	9.50	8.95
NaCl	c) Fe-0.5Ag-3Mg	6.90	11.05	9.16	8.34
SBF	d) Fe	7.50	11.00	8.20	8.26
NaCl	e) Fe	6.90	9.80	9.01	7.46
Number of days		0	32	61	88

Between day one and day 61, the pH was increasing. It was caused by an oxidation reaction in the release of electrons.

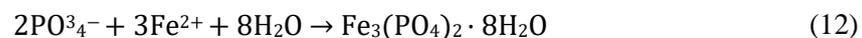
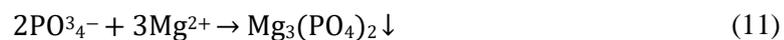
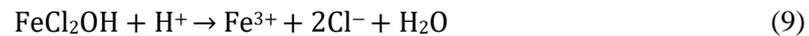
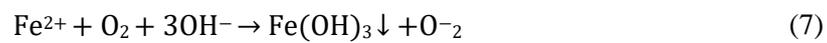
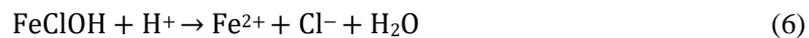
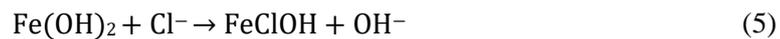


The iron was dissolved in the solution during this reaction. After day 61, the pH began to decrease. It is caused by the reduction reaction of iron.



The SBF solution is a solution containing chlorides, sulfates, and phosphates (Table 2), and the increase in pH value due to corrosion of pure iron promotes the precipitation and deposition of phosphates [5].

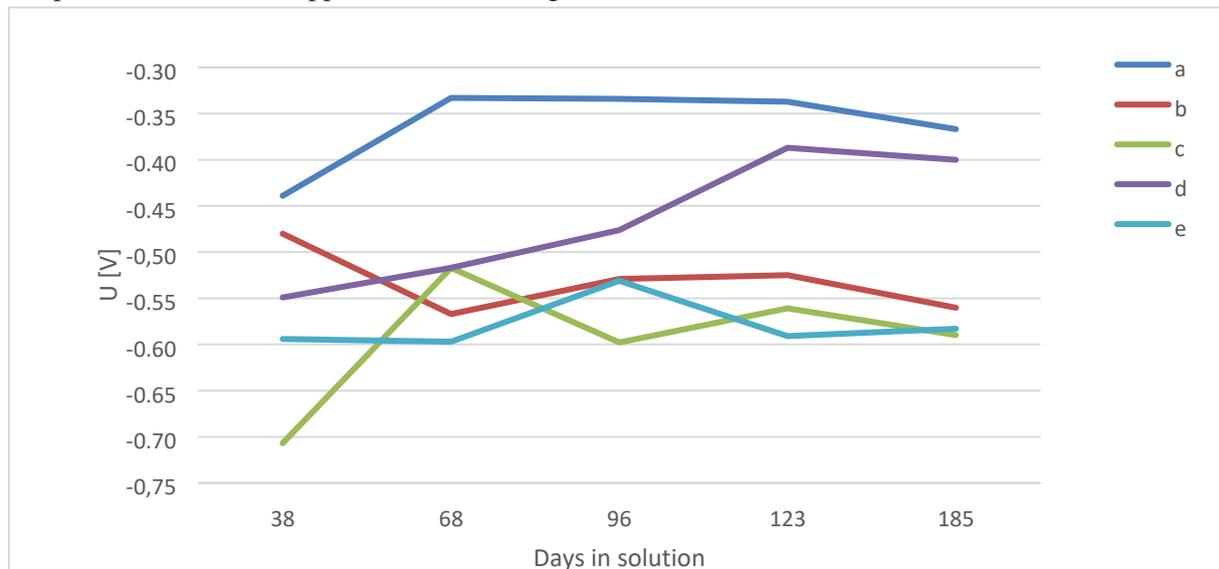
Reaction in SBF:



A serious problem is the alkalizing effect, for example, with biodegradable materials based on magnesium alloys [6]. A study by Song, G. L. mentioned that the corrosion of magnesium implant caused an increase in the pH value of the local body fluid near the magnesium alloy [5], which could adversely affect the balance of pH-dependent physiological reactions and lead to alkaline poisoning effect [7].

Another measurement was made to determine the corrosion potential and current. The measurements were performed on an AUTOLAB TYPE II potentiostat, using a three-electrode arrangement consisting of a working electrode (PIGE), an auxiliary electrode (platinum) and a reference electrode (fully saturated calomel). The measurement was carried out in a 9% NaCl solution

and the potentiodynamic method was chosen, for which a step of 0.001 V and a scan rate of 0.01 V·s<sup>-1</sup> were set. Before the measurement, the samples were properly cleaned using isopropyl alcohol and distilled water, then they were dried for 4 hours, and then a metal powder was obtained from the sample, which was then applied to the working electrode.



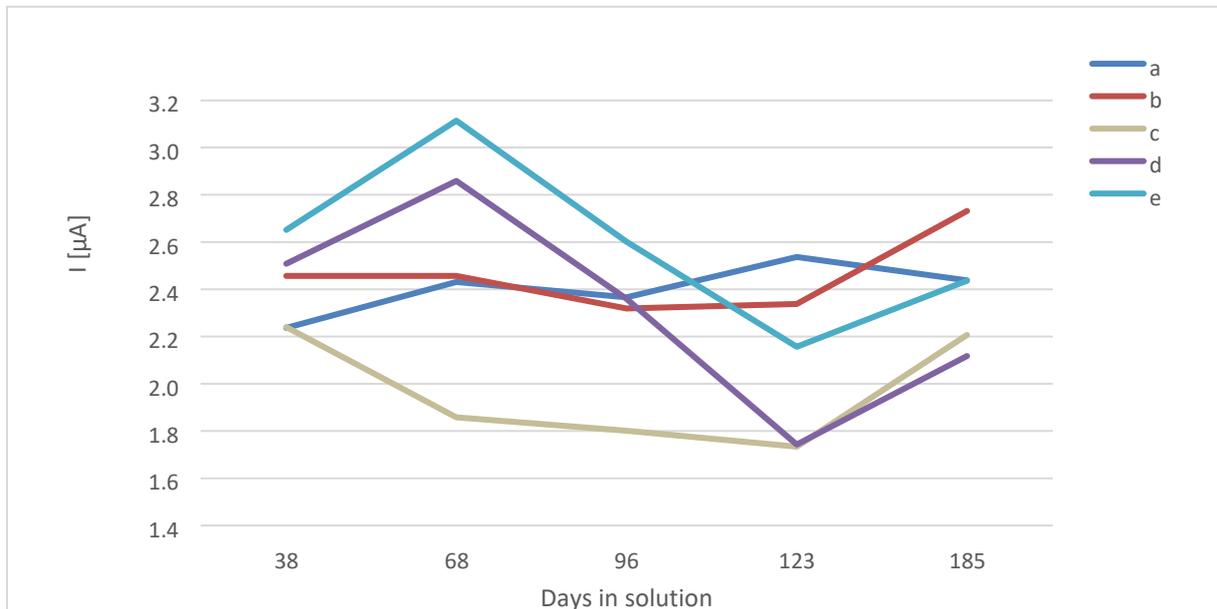
**Figure 3.** Difference in corrosion potential between samples a), b), c), d) and e) versus time (days)

**Table 4.** Changes in corrosion potential of samples in SBF and NaCl solutions as a function of time

Solution	Sample	Corrosion potential (V)				
SBF	a) Fe-3Mg	-0.439	-0.333	-0.334	-0.327	-0.367
NaCl	b) Fe-0.5Ag-1Mg	-0.480	-0.567	-0.529	-0.525	-0.560
NaCl	c) Fe-0.5Ag-3Mg	-0.707	-0.517	-0.598	-0.561	-0.590
SBF	d) Fe	-0.549	-0.517	-0.476	-0.387	-0.400
NaCl	e) Fe	-0.594	-0.597	-0.531	-0.591	-0.583
Number of days		38	68	96	123	185

The increase in corrosion potential in the first days is due to the formation of OH<sup>-</sup> at the beginning of dissolution, then the corrosion potential decreases because the reaction of 2Fe<sup>2+</sup> + OH<sup>-</sup> forms a passivation layer on the surface of the sample. The possibility of the formation of passive layers was also supported by the measured pH (Figure 2), which was alkaline and thus indicated the formation of hydroxyl anions. The reduction in the corrosion potential of sample b is caused by the lower mass of magnesium in this sample compared to samples a and c. This measurement is shown in Figure 3 and the values are shown in Table 4.

The corrosion current is related to how many electrochemical reactions are taking place. If more reactions in the sample take place, the corrosion current is larger. Sample a) was placed in SBF solution. The SBF solution contains many ions that increase the corrosion current. There is a similarity between the current curves of samples b and c. The difference is due to the different concentration of magnesium in the samples. Figure 4 shows the corrosion currents of the samples and the values are shown in Table 5.

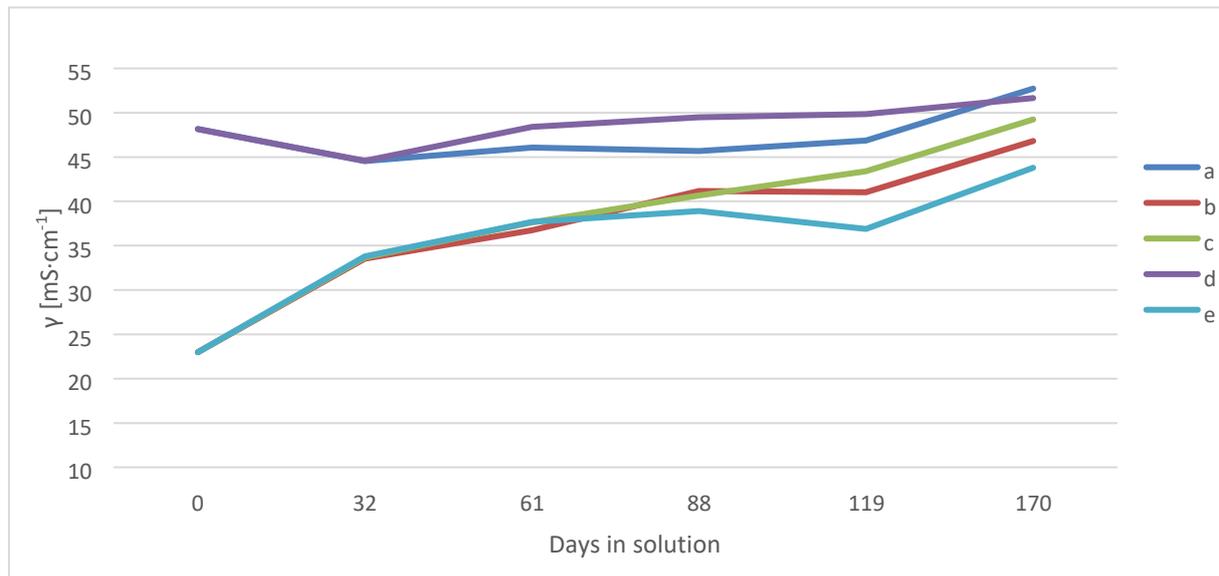


**Figure 4.** Difference in corrosion current between samples a), b), c), d) and e).

**Table 5.** Changes of corrosion current of the samples a), b), c), d) and e).

Solution	Sample	Corrosion current [µA]				
SBF	a) Fe-3Mg	2.240	1.858	1.802	1.734	2.207
NaCl	b) Fe-0.5Ag-1Mg	2.457	2.457	2.319	2.338	2.732
NaCl	c) Fe-0.5Ag-3Mg	2.237	2.431	2.367	2.537	2.438
SBF	d) Fe	2.508	2.859	2.359	1.743	2.118
NaCl	e) Fe	2.652	3.114	2.602	2.157	2.437
Number of days		38	68	96	123	185

The process of precipitation of ions in the solution caused a significant decrease in conductivity in sample a). On the other hand, for samples b) and c) there was a slower decrease in the conductivity value. After 123 days, the value increases because the chloride ions disrupt the passivation layer on the surface of the samples.



**Figure 5.** Difference in corrosion solution conductivity between samples a), b), c), d), e) depending on time (days).

**Table 6.** Changes of corrosion solution conductivity of the samples a), b) c), d) and e)

Solution	Sample	Corrosion solution conductivity [ $\text{mS}\cdot\text{cm}^{-1}$ ]					
SBF	a) Fe-3Mg	48.165	44.535	46.080	45.683	46.863	52.723
NaCl	b) Fe-0.5Ag-1Mg	22.976	33.532	36.725	41.174	41.011	46.807
NaCl	c) Fe-0.5Ag-3Mg	22.976	33.687	37.624	40.647	43.401	49.244
SBF	d) Fe	48.165	44.573	48.404	49.479	49.850	51.658
NaCl	e) Fe	22.976	33.771	37.678	38.889	36.898	43.785
<b>Number of days</b>		<b>0</b>	<b>32</b>	61	88	119	170

### 3. Conclusion

Experiments have shown that corrosion occurs and changes its behaviour over time according to the amount of corrosion products that are generated in different samples. Corrosion of the samples occurs when they are submerged in approximately 15 millilitres of the solution. But human blood flows throughout the whole body and is purified in the kidneys. It is likely that the corrosion of the implant would not be slowed as much by the corrosion products in solution when implanted in the human body. Observations under the microscope (Figure 1) showed the structure of the samples and allowed a better observations of the porosity. These observations clearly showed that the porosity of the samples was highly dependent on the type of foam used and not dependent on the combination of metals used. Multiple reactions occur simultaneously in the sample during the degradation process. During the dissolution of metals - oxidation, metal cations are formed, which in combination with chloride anions can form metal chlorides. Hydroxyl ions are also produced. Hydrolysis breaks down metal chlorides, forming metal hydroxides, and increases the concentration of hydrogen ions, which can counteract the hydroxyl ions and lower the pH, making the solution more acidic.

### Acknowledgments

This work was supported by the project of specific research at Brno University of Technology: Materials and Technologies for Electrical Engineering IV, reg. no. FEKT-S-20-6206.

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