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MICROELECTRODES ON METALLIC IMPLANTS DEGRADATION, ELECTRODEPOSITION AND SURFACE TREATMENT STUDIES ¶

J.P. Sousa
INEB - Instituto de Engenharia Biomédica
Faculdade de Engenharia da Universidade do Porto
Praça do Coronel Pacheco, 1
4050 Porto
PORTUGAL

Abstract

Despite the high success rate with the use of stainless steel and titanium materials in orthopaedic and dentistry for hard tissue replacement, repair and augmentation procedures, it became apparent that biodegradation of these implants did occur. In order to investigate the systemic effects of corrosion products released from these metallic implants, *in vitro* and *in vivo* studies were undertaken. The results of these studies revels that significant levels of metal species are released into the biological tissues. The properties and advantages of microelectrodes makes them useful tools for quantification and characterisation of released metal species either by performing *in vitro* or *in vivo* studies. Microelectrodes are also used to evaluate the surface modification and mineralization processes that occurs at the implants surface. The goal of these studies is to develop a selective microelectrode which should be able to monitor the species involved in the biodegradation and mineralization processes.

Introduction

Metals have been extensively used in orthopaedic and dental applications as biomedical implant materials for a variety of external support an augmentation procedures. Their use in human and veterinary surgery as hard tissue replacement materials enjoys a long and successful history and has becoming a worldwide routine procedure. Actually, at least two thirds of the population of the developed countries are or were portable of permanent or temporary implants. For instance, just in the

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United States each year approximately 150,000 total hip and 100,000 total knee replacements are performed. The indicators are that these numbers will increase in the near future, due to the ageing of population and also to the fact that a younger population is being subject quite often to replacements in bone and teeth [1].

Despite the efforts done in the materials science area for developing new materials such as polymers, bioceramics, composites, membranes, etc., the implant industry is almost exclusively limited to the mechanical and corrosion resistant metals [2]. However, some apatites are finding increasing application in dentistry as tooth filling materials [3]. Also the use of synthetic materials (e.g. PMMA, PVC, PANI, etc.) for applications as surgical implants have raised additional questions related to the systemic effects provoked by the release of materials debris, mechanical properties and life-time.

Surgical materials in common use for implants today include stainless steels (Fe-Ni-Cr-Mo), cobalt alloys (Co-Cr-Mo), titanium alloys (Ti-6Al-4V), and pure titanium (Ti) [2,4-6]. In Table 1 it is represented the chemical composition of these alloys in terms of element weight percentage. For the dental field, a variety of metals and alloys have been combined for intraoral crown and bridge prostheses (e.g. Au and Au-Cu-Sn, Pd and Pd-Pt-Ag, Ag-Cu-Sn, Ag-Cu-Sn-Hg, Ni-Cr and Ni-Cr-Be, and Cu-Zn) [7] but their use is rather limited.

Table 1 - Chemical composition of surgical metal alloys (weight %)

Element (%) / Alloy	Fe	Cr	Ni	Mo	Mn	Co	Si	Ti	Al	C	V
SS 3164	62	18	14	3	2		0.41			0.03	
Co-Cr-Mo	0.75	28.5	1	6	1	60	1			0.35	
Ti-6Al-4V	0.25							89	6		4
Ti							99.99				

The survival of some of the more successful implants is greater than

90% at 10 years. However, no prosthesis can be expected to last indefinitely without some adverse effects on the host. Therefore the choice of materials to be used in any medical device has proven to be a crucial factor for its success or failure. The objectivity criteria for choosing a biomaterial are: i) mechanical properties; ii) biosafety; iii) biocompatibility; iv) biofunctionality. Thus any biomaterial to be implanted in the human body must be safe for the patient, i.e. it must be compatible with tissues [8-9]. As a consequence, those biomaterials aimed for prolonged contact with the body fluids, have to be evaluated with respect to their biological safety and biocompatibility. To perform this evaluation a wide variety of *in vitro* and *in vivo* procedures have been used, with varying degrees of success and acceptability [10-13]. A recent review on requirements of materials for medical devices was written by Sousa [14], where the fundamental features of the functioning, evaluation and implications of any device were addressed.

In this paper, special attention will be focused in the use of microelectrodes either as qualitative or quantitative tools in the biomaterials field. Their application in this area took place at our laboratory almost four years ago and since then several papers were published in the literature or presented at International Scientific Conferences. Some fundamental applications of microelectrodes will be reported and discussed which emphasises their potential use in biodegradation studies, metallic electrodeposition and surface treatment of biomaterials.

2. Biodegradation of metallic biomaterials

The release of some metal ions from implanted metallic devices into the electrolyte of the human body environment is thermodynamically inevitable. After some accumulation of the released species at, near or farther of the surface of the metal or alloys occured, however, continuation and the rate of release depend on complex thermodynamic, kinetic and mechanistic factors. The biodegradation process is shown in Fig. 1. In 1970, Fontana [15] has already stated that corrosion of metallic materials comprehends 8 distinct forms being the most relevant crevice corrosion, pitting, erosion and fretting, and finally stress corrosion and corrosion enhanced fatigue.

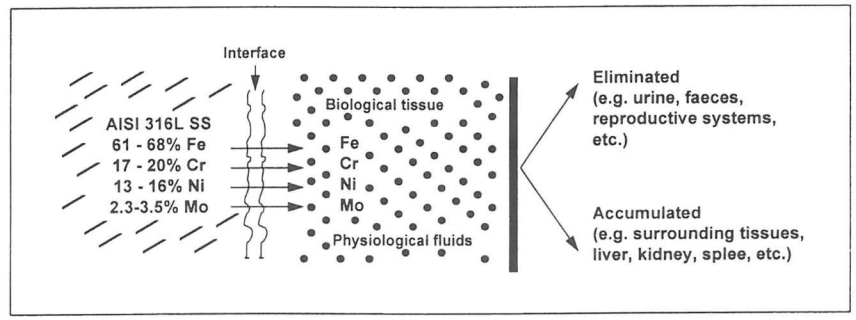
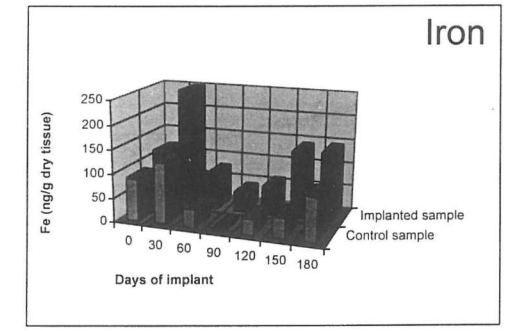


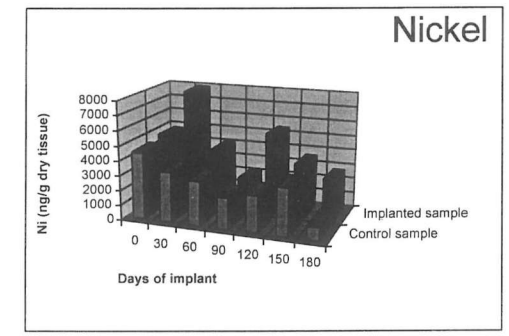
Figure 1 - Schematic representation of the AISI 316L stainless steel biodegradation process.

The corrosion of modern metallic biomaterials is so small that a material loss is almost non-visible nor it can be weighted. However, microscopic analysis of retrieved implants have shown that surface corrosion, indeed, occurs [2,16]. Furthermore the ingestion of species of metal compounds with nutrition which enters the bloodstream, i.e. being metabolised or stored in organs and tissues contributes for a rather incompletely known distribution of the released species on the body. Although the answer to the question "what are the normal metal concentration in tissue?" depends of several functional factors as well as from person to person, mean values for iron (Fe), nickel (Ni), chromium (Cr), cobalt (Co), etc., in biological samples have been reported in the literature [16-17].

Histological studies performed on biological tissues surrounding the metallic implants either in humans or test animals have demonstrated the occurrence of proliferation of pathological cells and tissue vascularization [18-19]. Quantification of metal species in these surrounding tissues by atomic absorption spectrometry (AAS) clearly indicates that they preferentially accumulate in this region. In Figs. 2 and 3 it is shown this pattern of behaviour for biological samples of piglets having implanted in one rear ear either AISI 316L stainless steel or pure titanium implants, respectively. The biomaterials were implanted in the back right ear whereas the control samples were taken from the same region of the left ear. From these figures one cannot say that the amount of metal ions

released into the biological tissues increases with time, but that they are higher near the implant, i.e. there must be a biomaterial/tissue reaction.





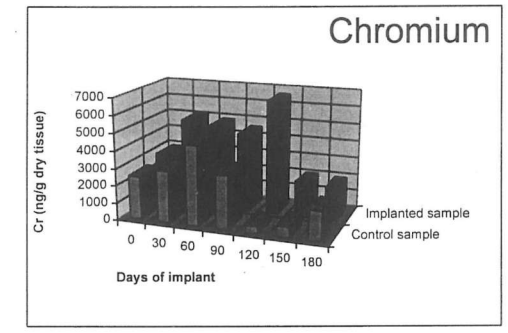


Figure 2 - Atomic absorption spectrometry analysis of biological tissues surrounding an AISI 316L stainless steel implant and control samples: (A) iron levels; (B) nickel levels; (C) chromium levels.

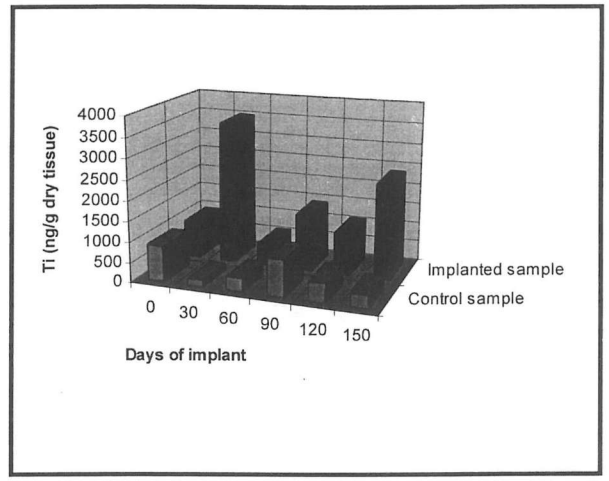


Figure 3 - Results of Ti analysis obtained by atomic absorption spectrometry in biological tissues surrounding a titanium implant and control samples.

Baes et al. [20] have suggested that the metals released from metallic implants initially forms hydroxides, hydrous oxides, and oxides, i.e. sparingly soluble salts, and occasionally complexes, e.g. halides. The cases of nickel, chromium and titanium serve to illustrate this behaviour and is represented in Fig. 4. At physiological pH values, the favoured species are $Ni(OH)_{(aq.)}$, $Cr(OH)^{+}$ and $Ti(OH)_{(aq.)}$.

3. Microelectrodes in biodegradation studies

The properties, advantages and applications of microelectrodes have been reported in the literature [21-24]. They have been used both in fundamental and applied electrochemistry studies and their popularity has increased because they improve greatly the quality of experimental data, allows to access novel data on conventional systems, and facilitate a range of new experiments.

The challenge of developing reliable implantable electrochemical sensors is, however, considerably greater than designing sensors for discrete *in vitro* test instrumentation. Microelectrodes type devices are the

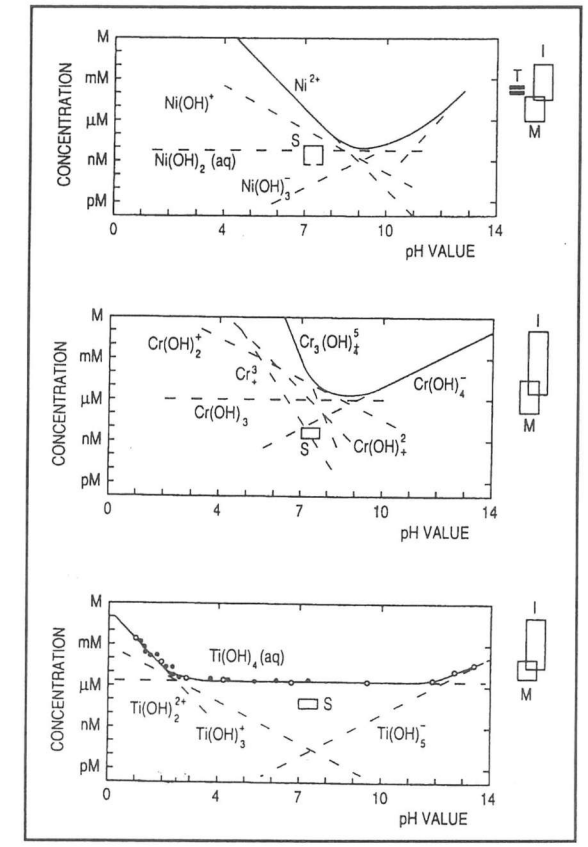


Figure 4 - Distribution of released products as shown by Baes and Mesmer [20] in physiological serum.

preferred approach. Indeed, these devices can be used either *in vitro* or *in vivo* without causing disturbance in the environment and at the same time yielding reliable results. The goal is to design and develop probes that are small enough to slide down in the intended media so as to be in contact with the implanted biomaterials. In addition, since it is desirable to provide multiparameter measurements, ideally the sensors need to be miniaturised and must be capable of measuring the parameter of interest within a dynamic range compatible with the expected physiological variability of

those species in the body [26]. The response time of each sensor should be rapid (< 1 min.). Other requirements include the ability to sterilise, biocompatibility, non-invasive, absence of sharp edges, and the ability to retain calibration stabilities during prolonged exposure in the biological environments.

Thus, bearing in mind the above statements and requirements of electrochemical sensors, metallic microelectrodes have been developed at our group especially designed for monitoring metallic species released from metallic implants [27]. So far, only quantitative and electrochemical characterisation of few metallic species (e.g. Fe^{3+}, Fe^{2+}, Ni^{2+}, and Ti^{4+}) have been carried out either by performing *in vitro* or *in vivo* studies in physiological solution (HBSS which simulates the composition of the body extracellular fluids) and mice organs (e.g. liver, kidney and spleen) as reported elsewhere [28-34]. The attained results strongly encourages the idea of using microelectrodes as a quantitative technique to monitor further metal ions released from implanted materials. For instance, Au microelectrodes were used to quantify iron levels in mice organs previously treated (subcutaneous injection) with a metallic slurry which simulates the composition of the AISI 316L SS biomaterial corrosion species. The obtained cyclic voltammogram for total iron in a spleen sample after acidic digestion on a microwave oven is represented in Fig. 5.

Figure 5 - Steady-state voltammogram of iron in a mouse spleen sample using a Au microelectrode (d = 25 μm) at ν = 500 mV/s.

From the amplitude of the limiting current and making use of the Cottrell equation, using a diffusion coefficient of 6.36 x 10^{-5} cm^2/s [28,33], a concentration of 2.050 ppm was achieved. Similar studies performed for liver and kidney samples have also allowed to quantify iron levels in these samples. In order to verify whether these results were reliable or not, quantification of iron levels in the same samples were performed by a well established spectrometric technique, i.e. atomic absorption spectrometry (AAS) [33-34]. The results obtained by both techniques are represented in Table 2. From this table it is clear that, indeed, microelectrodes is a very suitable and promising quantitative technique.

Table 2 - Quantification of iron levels in mice organs (e.g. liver, kidney and spleen) by AAS and Au microelectrodes.

Organs	EAA (ppm)	VC (ppm)
Liver	8.105	8.337
Kidney	1.117	0.899
Spleen	2.138	2.050

The electrochemical characterisation of iron species in physiological media using Pt microelectrodes show that they have a quasi-reversible behaviour and that the process is diffusion controlled [28, 30-31]. Also the kinetic parameters such as α, E° and k° were estimated both in physiological media [29,31] and osteoblast-like cell cultures medium [35].

Currently, quantification of nickel species in osteoblast-like cell cultures and mouse organs (e.g. liver, kidney and spleen) is being performed using Au microelectrodes at which a mercury film is grown by potentiostatic means [36-37]. The quantification of nickel in these environments by performing square wave voltammetry (SQV) has proven to be a very promising technique and even more reliable than AAS. Further metal ions to be investigated and quantified by microelectrodes are chromium and titanium, since they are also released from metallic implants due to biodegradation processes.

The work ahead in this area consists of modifying the microelectrode tip with a polymeric selective membrane, made of a biocompatible material. The aim is to produce a reliable electrochemical sensor to use *in situ* for monitoring metal ion levels in patients carrying a metallic implant.

4. Electrodeposition studies

Silver is an important alloying element in the production of gold dental alloys. In this group of biomaterials the most widely used are Ag-Au, Ag-Pd, and Au-Ag-Cu. Their composition is represented in Table 3 [38].

Table 3 - Chemical composition of gold dental alloys (weight %)

Alloy \ Element (%)	Au	Ag	Cu	Pd
Au - Ag - Cu	26.0	11.0	63.0	
Ag - Au	20.0	80.0		
Ag - Pd	0.86	74.0	0.14	25.0

Electrodeposition studies are useful for understanding the biodegradation behaviour of alloys over a wide range of potentials. It is thought that the electrodeposition behaviour changes with the overpotential during the biodegradation process. For the alloys containing noble elements, it is known that they rearrange and form an island on the alloy surface [39]. Therefore, the knowledge of the electrodeposition behaviour enables to improve our understanding towards the biodegradation process, namely the steps involved, kinetics and thermodynamic parameters.

Several studies dealing with silver electrodeposition using microelectrodes have been published in the literature [40-45]. The aim of those studies was to characterise the silver centres growth as well as to access kinetic and thermodynamic parameters on the electronucleation process. The authors have found that the growth of silver centres is diffusion controlled at long times whereas at short times (lower than 1 s) is

kinetically controlled. Also the nucleation type, i.e. progressive or instantaneous was assessed.

A more comprehensive study was performed by Sousa et al. [46-48], aiming to investigate the silver electrodeposition process at the molecular level, using carbon microelectrodes (diameter of 5 μm) by potentiostatic means. The typical voltammogram for silver electrodeposition, under the experimental conditions used is shown in Fig. 6. This voltammogram display the characteristic features of nucleation and phase growth, namely the large peak separation and cross-over on the cathodic branch.

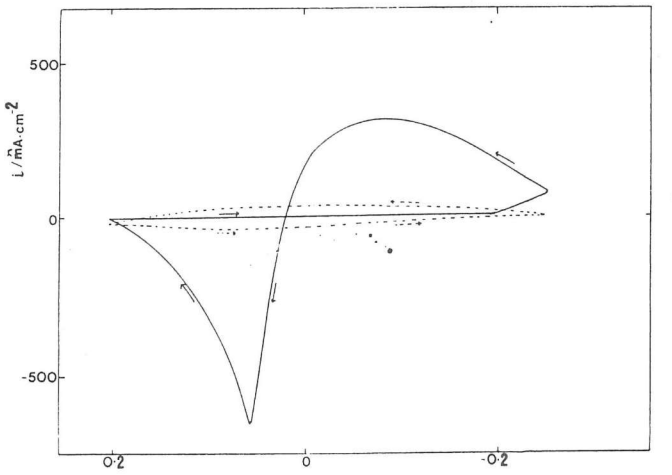


Figure 6 - Cyclic voltammogram for the deposition of silver onto vitreous carbon microelectrode (d = 5 μm) from 5.0 mM $AgNO_3$ in 0.1 M KNO_3 aqueous solution (solid line) and only in 0.1 M KNO_3 (broken line) at ν = 100 mV/s.

Figure 7 shows the current-time transients for the growth of silver at four overpotentials investigated. It is evident that one cannot observe the transition from kinetic to diffusion growth with increasing time as predicted by the theoretical models [47-48] but, nevertheless, one would expect some influence of the transition from kinetic control at very short times to diffusion control at longer times. Indeed, the plot of i *versus* $t^{1/2}$ (Fig. 8) indicates that at long times the crystal growth process is entirely diffusion controlled.

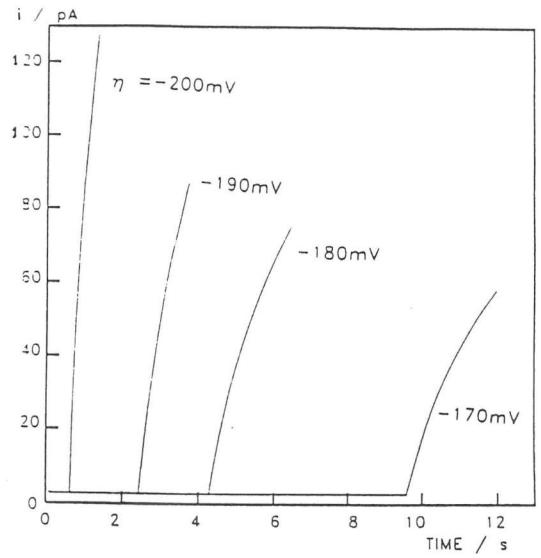


Figure 7 - Current-time transients for the growth of Ag on a vitreous carbon microelectrode (d = 5 μm) from 5.0 mM $AgNO_3$ in 0.1 M KNO_3 aqueous solution at the indicated overpotentials.

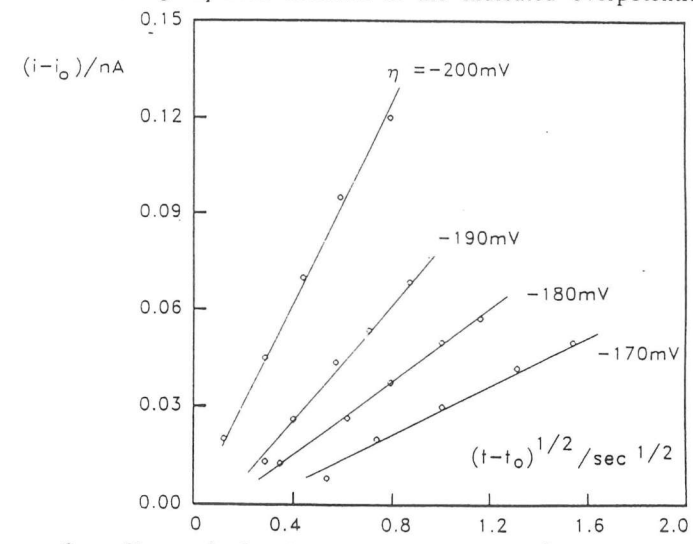


Figure 8 - Test of the kinetics of growth of Ag centers on carbon microelectrodes.

From the induction times and assuming that the formation of centres at the microelectrode surface is a random process (following a Poisson distribution) it was possible to access the formation rates for silver electrodeposition. The attained results [47] clearly indicates that silver once attached to a surface it rather stays and possibly grows than desegregates. Thus the silver usually migrates to the dental alloys surface, forming a resistant layer. Furthermore, SEM analysis have shown that at the surface a passivation film of silver chloride is formed during the implantation time. This passive film may be the responsible for the long duration of dental alloys by avoiding the occurrence of pitting and crevice corrosion.

At the present time, similar studies are being performed for titanium since this material is becoming more and more used for hard tissue replacement. We hope that in the near future, a plausible electrodeposition/dissolution mechanism for titanium will enable to extrapolate the *in vitro* results to *in vivo* behaviour.

5. Microelectrodes role on surface treatment

Metals such as AISI 316L stainless steel, cobalt-base alloys, pure titanium and alloys are currently being used in clinical procedures for hard tissue replacement and augmentation. They possess high strength and fair corrosion resistance but show poor tissue adherence and acceptance. Thus, in the past twenty years several methods to produce unique modification material surfaces were developed. These include utilisation of lasers, ion and electron beams, chemical vapour deposition, physical vapour deposition, plasma sprayed oxide coatings, and ceramic coatings [49].

Ion implantation consists in the introduction of one or more atomic species into the surface of a metallic by using a high energy ion beam. This results in modified physical and chemical properties of the near surface region. The other ion surface modification technique is known as ion plating which is a deposition process during which the biomaterial surface is coated with a film deposited from a flux of high energy particles from an activated source and a pre-induced ionised plasma.

Thermal plasma spray is another technique which enables the deposition of a very thin homogeneous film of sintered ceramics or other active materials at the biomaterial surface. This is a very useful technique to improve the biocompatibility of metallic biomaterials. Sintered ceramics have been used as biomaterials for their chemical inertness, anti-corrosion,

biocompatibility and biostability in biological environments [50]. Although ceramics are strong, they are usually brittle and lack toughness which makes difficult to produce thin, wide and special shaped biomaterials, limiting their use as bioactive materials. Thus if a metallic substrate surface is modified with a thin film of an appropriate ceramic material, the interaction with the biological tissues is improved while the tough but less compatible metal substrate acts to provide mechanical support.

The favourite materials for hard tissue replacement or repair are titanium and its alloys [51]. These materials are highly resistant in biological environments, since they present a relatively bioinert behaviour. Therefore, they do not present a favourable response to osteointegration, i.e. surface mineralisation is hardly achieved. The only implant material with which bone carries out a primary bonding is hydroxyapatite ceramic, i.e. an enduring bond is created when ossification starts from the first moment at the implant surface. The properties and biological profile of this calcium phosphate ceramic have been addressed in the literature [52]. Thus the ideal biomaterial should encompass a titanium substrate covered with a bioactive calcium phosphate layer. This has been achieved through an incubation process of calcium phosphate in solutions containing different concentrations of titanium. This titanium enriched calcium phosphate substrate greatly enhances the mineralisation process.

The small dimensions of microelectrodes allows to place them very close to the material surface during *in vitro* mineralisation studies. It enables to monitor the calcium and phosphate profiles at the material/tissue interface, i.e. selective microelectrodes could enhance our knowledge about the mineralisation process in terms of kinetics and bioactive species role. Also they should be able to monitor the release of material debris into adjacent tissues. Due to some problems not yet overcome (e.g. sterilisation, response drift, etc.), our first approach is to perform discrete measurements of calcium and phosphate levels at the interface region. Further work needs to be done in this particular area in what concerns the development and characterisation of miniaturised selective devices to monitor only the parameters and bioactive species of interest.

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ELIMINATION OF CORROSIVITY OF NATURAL WATER BY SIMULTANEOUS REMOVAL OF OXYGEN AND MINERAL SALTS BY ION EXCHANGERS ¶

R. Tosik
Institute of General and Ecological Chemistry
Technical University of Łódź
36 Żwirki Street , 90-924 Łódź , POLAND

ABSTRACT

Corrosivity of natural water controls concentration of soluble oxygen and amount of mineral salts. In order to decrease the corrosivity of water are applied deoxygenation and demineralization methods. This article presents investigations on oxygen and mineral salts removal by ion exchangers. A special kind of a bed which contained two ionic forms : sulphite and hydroxyl was investigated for simultaneous removal of oxygen and anions from water. The natural water from a deep well supplied the bed after its initial decationization on strong acid cation exchanger. The model solutions were used with hydrochloric and sulphuric acids in amounts equal to decationization of water from the well, too.

It was stated that the removal efficiency of oxygen and anions was very high. The bed may be used as a difunctional ionic column for the simultaneos removal of oxygen and anions if demineralization process is designed by ion exchanger's method. The corrosivity of water may be eliminated and technological installation should be simplificied using such a bed.

INTRODUCTION

In oxygenated natural water, its corrosivity depends on electrochemical processes resulted with soluble oxygen and mineral salts. Oxygen causes cathodic reaction which potential is more than 1 volt greater than hydrogen electrode and may be presented as a equilibrium potential which depends on : the concentration of OH^- ions and the partial oxygen pressure pO_2 .

$E' = E^0 - RT / F \ln (OH^-) + RT / 4F \ln pO_2$ [1] :

$$O_2 + 2 H_2O + 4 e^- = 4 OH^- \qquad \text{eq 1}$$

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