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Research Paper

Comparative Study of the Release of Corrosion Products from Stainless Steel Immobilization Wire and Arch Bar during Uniform Attack in Bio-fluids

***Omoniyi K. I.[1], Ekwumemgbo A. P.[1] and Yahaya I. A.[2]**
[1]Chemistry Department, Ahmadu Bello University, Zaria, NIGERIA
[2]Science Laboratory Technology Department, Federal Polytechnic, Bida, NIGERIA

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Abstract: *This study compares the amount of released Co, Fe, Mn, Ni and Cr ions from stainless steel immobilization (SSI) wire and arch bar into five pseudo- and actual- bio-fluids of varying pH and chloride ion level, under various incubation time using atomic absorption spectroscopy. Co ion was not released from SSI until at 4 weeks immersion time in WBS (0.019 ± 0.001 µg/ml) and PBS (0.023 ± 0.002 µg/ml, while arch showed resistance till at 6 week of immersion. The total amount of Fe ions released into the bio-fluids by arch bar during the immersion testing was 0.360 ± 0.032 µg/mL compared to 6.462 ± 0.103 µg/mL from the immersed SSI wires (1 day to 6 weeks). However, the leaching rate of SSI wire for Fe ions was only slightly higher than of the arch wire. There is significant difference in the amount of nickel, iron and cobalt ions released from SSI wire due to decrease in pH and increased concentration of chloride ions of the immersion solutions, while the variation of pH and chloride ions of the bio-fluids had a significant effect on the amount of Ni, Mn and Cr ions released from arch bar (P ≤ 0.05). The SSI wire demonstrated a double corrosion resistance profile over that of arch wire for Co leaching, with no significant difference in the amount of Co released by SSI and arch wire for the short term test, but Fe ions released was slightly higher for SSI (P ≤ 0.05).*

Keywords: Bio-fluids, corrosion resistance, leaching, corrosion rate, immersion test.

Introduction

Stainless steel immobilization (SSI) wire is a soft wire used for ligation, to restore a patient's pre-injury dental occlusion by immobilizing the mandibular and maxillary fractures. It is also used to attach fractured bones of the human body. Maxillomandibular fixation, MMF mostly used for treatment of mandible fractures, involves anchoring arch bars to the gums of the maxilla and the mandible, the arch bars are held in place by immobilization wires, which are wrapped around the molars, the device is left for 4 to 6 weeks of the healing process [1].

Despite the advantageous mechanical strength of implanted metallic prostheses, the hostile electrolytic environment lead to its degradation by gnawing away bits of metal from its surface [2]. The driving force that determines how and why implants corrode in biologic fluids is the thermodynamic driving force in the electrochemical reaction, leading to the release of metal ions into the surrounding aqueous electrolyte. This dissolution reaction is coupled with a corresponding reduction reaction of constituents in the aqueous environment to maintain charge neutrality [3].

Kinetic limitation to corrosion of implants by the formation of surface metal-oxide passive film occurs in chromium based steel, aluminium and titanium. It therefore, follows that under optimum circumstances of complete passivation, all implant alloys have a finite, albeit slow, uniform corrosion rate *in vivo*. Damage to this passivating layer occurs due to fretting or wear, and may produce conditions conducive to accelerated focal corrosion and failure [4].

Though, stainless steel (SS) implants have been reckoned with to show corrosion resistance *in vivo*, by the spontaneous passivation and repassivation mechanism in air and under most tissue fluid conditions, release of metal ions from SS implants have been reported, with the major corrosion products being iron, chromium and nickel [5]. These ions have potential for producing allergic, toxic or carcinogenic reactions [6].

Electrochemical constant current linear polarization and atomic absorption spectroscopy (AAS) were used to measure the corrosion rate of coronary stents (made of 316L and 317L stainless steel) immersed in Tyrode's solution at 30°C. The results indicated that the corrosion rate of 316L and 317L stainless steel was 9.8x 10^{-3} μg cm^{-2} $week^{-1}$, 21x10^{-3} μg cm^{-2} $week^{-1}$ respectively. The results from AAS may correctly reflect the quantity of released metal ions in the solution [7].

In vitro corrosion tests of a standard orthodontic appliance consisting of bands, brackets and either stainless steel or nickel-titanium arch wires were carried out by Robert *et al.* (1993). The appliances were immersed for 4 weeks in a prepared artificial saliva medium at 37°C. Five sets were ligated to stainless steel arch wires and the other five sets were ligated to nickel-titanium arch wires. Flameless atomic absorption spectrophotometry results indicate that orthodontic appliances release measurable amounts of nickel and chromium when placed in an artificial saliva medium. For both arch wire types, the release for nickel averaged 37 times greater than that for chromium [8].

Lori *et al.* (2009) carried out the immersion of new and reused arch bar in Hank's solutions of different hydrogen and chloride ions concentrations, whole blood serum and phosphate buffered saline (PBS) *in vitro*, over a six-week immersion time at 37°C. The amount of cobalt, iron, manganese, nickel and chromium ions released using atomic absorption spectroscopy, indicated that the reused wires released more ions than new ones at all time points. The variation of pH and chloride ions of the bio-fluids had a significant effect on the amount of Ni, Mn and Cr ions released [10].

This study is aimed at analysing and comparing the variation of pH and chloride ion concentration of the immersion environment on the released corrosion products of SSI wire into Hank's solution, and to evaluate the rate of metal ions released compared to blood serum (WBS) and phosphate bovine saline (PBS) over a 20 week time interval, and to compare these results with the short-term corrosion test using SS arch bar. This is to better understand the biocompatibility profile of arch bar/SSI wire in various bio-fluids of contact when used for orthodontic restoration. This will further enrich the scientific data needed in appraising the corrosion resistance of arch bar/SSI wire.

Material and Methods

Collection of whole blood serum: Fresh bovine blood was collected into boiling tubes from healthy male cows at the Zango abbatoir, Zaria, Nigeria. The tubes were left in slanting position for 3 hours. The blood serum (WBS) obtained by decanting had a pH of 7.68.

Preparation of Hank's solution: Hank's solution (HS) - to simulate body fluid - was prepared according to Table 1 below. The solution was adjusted to pH 4.0 and 7.0 respectively with 0.5M Na_2HPO_4, 0.5M NaH_2PO_4 buffer solutions and drops of 1% HCl solution. The concentration of HS with high chloride ion (HSCl) was obtained by making the concentration of chloride ion in HS to be 1.63 x10^{-1} $molL^{-1}$.

New and 'as received' Colboloy SSI wire (G & H, Greenwood, USA) of cross sectional area 1.5106 cm^2, using 2πr (h + r) and a nominal length of 12 cm were used for the experiment and a total of 75 Erich arch bars (Unitek, Monrovia, California, USA) cut into standard-sized pieces (6 cm length of average weight 750.5 ± 8.0 mg, surface area 0.60 cm^2) were used as the other test material.

In vitro corrosion study : A 6 cm length of new arch bar was immersed into each polyethylene bottle containing 20 mL of Hank's solution at pH 4.0 (HSpH4), pH 7.0 (HSpH7) or HS with high chloride ion (HSCl), closed and placed in an incubator at 37°C at the end of incubation times of 1 day, 1, 2, 4, 6 weeks, 10 mL of the immersion solution were extracted from the bottle for acid digestion with 10 mL of concentrated HNO_3 and 3 mL of concentrated HCl on a hot plate. The digest was then made up to 20 mL with doubly distilled water. The corrosion experiment was also carried out for WBS and phosphate buffered saline, PBS (Nissui pharmaceutical Co. Ltd, Tokyo, Japan) having a pH of 7.45 [9]. The procedure was repeated for SSI wire, immersing eight of the test material in the bio-fluids with the immersion time extended beyond, to 8, 12 and 20 weeks for investigation of its long-term corrosion profile.

The concentration of cobalt , nickel, iron, manganese and chromium ions in the various bio-fluids by immersion of the two test materials was measured using graphite atomic absorption spectrophotometry (TAS990, Intec Co. Ltd., Rome). Three independent samples were prepared for each experimental time group. The concentration of the ions in the immersion solutions alone were taken as control.

Elemental composition of the arch bar carried out indicated this to: 60.05 % Fe, 18.35 % Cr, 18.62 % Ni, 2.94 % Mn and 0.03 % Co.

Results and Discussion

Comparison of the mean concentrations of released metal ions in the various bio-fluids based on the incubation time and immersion solution was carried out using two-way analysis of variance. The Student-Newman-Keul's test was used to compare the level of released metal ion with pH as the discriminating variable, with the statistical significance set at 95 per cent. A comparative analysis for the amount of released metal ions from each of the standard-sized SS test materials investigated was carried out using linear regression and Pearson correlation analysis. The quality assurance for the analyses was conducted through the spiking method, and mean % recovery for the analyses span from 79.94 ± 0.19 to 93.4 ±

0.28.

Release of cobaltions: The corrosion test result indicated that the SSI wire immersed showed no detectable level of Co ion until at 4 weeks immersion time in WBS and PBS respectively. The concentrations of Co ion released into HSCl ranged from 0.000 µg/mL (week 4) to 0.031 ± 0.001 µg/mL (week 20), while the amount released into WBS ranged from 0.019 ± 0.001 µg/ml (week 4) to 0.029 ± 0.001 µg/mL (week 20). As presented in Figure 1, the released amount of Co ions increased with immersion time for all the bio-fluids. The variation of the pH of HS and chloride ions concentration showed a significant effect on the amount of Co ions released ($P < 0.05$). No cobalt ion was detected in the bio-fluids until at incubation time of 6 weeks for the arch wire depicting a better resistance to Co leaching than SSI wire. The highest level of 0.006 ± 0.001 mg/L was recorded for the arch wire immersed in HSCl (Figure 6). Incubation time has no significant effect on the amount of Co released from the two test materials. Cobalt had the least rate of release with the range 0.000 to 0.006 ± 0.001 µg/mL/week for SSI wire and 0.000 to 0.001 ± 0.0003 µg/mL/week for the arch wire, Apart from reasons, such as the difference in the surface morphology and geometry of the test materials, the surface area of the SSI wires used was about 15 times larger than that of the arch bar. Considering the release rate from a per centimetre square surface area, the SSI wire demonstrated a doubly resistance profile over that of arch wire. There is no significant difference in the amount of Co released by SSI and arch wire for the short term test ($P < 0.05$).

Release of iron ions: As presented in Figure 2, the released amount of Fe ions from the SSI wire increased for all the immersion solutions from the one day time pointas as does the arch wire. HSCl had the highest amount of released Fe ions with a range of 0.260 ± 0.010 µg/mL (day 1) to 0.431 ± 0.001 µg/mL (week 20). There was a statistically significant difference between the amounts of Fe ions released into HSpH4 and HSpH7 at incubation times beyond 4 weeks. DMRT showed a significant difference in the amount of Fe ions released into HSpH4 compared to the other media, but increased incubation time did not result to significant release of Fe ions from the new arch bar into the bio-fluids.

On the other hand, the arch bar had Fe ions released from its surface from the 1 day immersion time into HSCl and HSpH4, the released amounts increased in all the immersion solutions with time, the highest value of 0.036 ± 0.002 µg/mL was recorded at the 6 weeks time point in HSCl (Figure 7). The total amount of Fe ions released into the bio-fluids by arch bar was during the immersion testing was 0.360 ± 0.032 µg/mL compared to 6.462 ± 0.103 µg mL from the immersed SSI wires (1 day to 6 weeks). By putting into consideration the fifteen-fold difference in the surface area of the test materials, the leaching rate of SSI wire for Fe ions was only slightly higher than of the arch wire.

As shown in Table 2, the rate of release of Fe ions into the test solutions ranged from 0.0146 ± 0.002 to 0.3580 ± 0.003 µg mL/week using SSI wire and ranged from 0.0094 ± 0.0012 to 0.0113 ± 0.003 µg mL/week considering arch wire.

Release of manganese ions: Detectable amount of Mn ion was recorded at 4 weeks immersion time, except for HSpH4 with concentration range from 0.020 µg mL ± 0.001 (day 1) to 0.139 µg mL ± 0.002 (week 20). The order at which the test solutions cause leaching of Mn ions was HSCl > HSpH4> WBS > PBS > HSpH7 (Figure 3). However, the ranking from mild to aggressive corrosion media for the arch wire was PBS < HSpH7 < HSpH4 < HSCl < WBS. Students' t-test depicted no significant difference in the amount of Mn ion released as pH of HS changes. For the arch wire, there is a slight significant difference in the amount of Mn ions released into the media by an increase in chloride ion concentration, while increasing the hydrogen ion concentration of the media resulted to a highly significant difference. For both test materials, at all the time points considered, the level of Mn ions released into the five bio-fluids showed no significant difference. The rate of release of Mn ions was relatively steady at the 4 to 8 weeks time points for SSI wire Figure 3. From Figure 8, the release of Mn ions was not detectable until after 2 weeks of incubation of the arch wire. There was significant difference between the Mn ions released by the SSI wire and arch wire beyond 3 week immersion times, with a Pearson correlation coefficient of $r = 0.611$.

Release of nickel ions: The release of Ni ions into test solution by SSI wire was detected from 4 weeks of incubation, except for PBS. For HSCl, a sharp increase was observed between week 4, with the value (0.099 ± 0.001 µg mL) and week 6 with the value (0.575 ± 0.005 µg mL). As shown in Figure 4, the concentration of the released Ni ions increased with immersion time, with the highest values being obtained for all time points in HSCl. As presented in Figure 6, the arch wire released Ni ions from the 1 week time point. After 6 weeks of incubation, the highest level of Ni ions released was in HSCl closely followed by WBS and HSpH4. The concentration of Ni ions in HSCl after 6 weeks of incubation was 0.029 ± 0.004 mg/L. Students' t-test showed that the effect of pH and chloride ions variations led to marked statistical significance in the amount of Ni ions released into the media by the two test materials, while increased incubation time did not result to significant release of Ni ions from the 4 weeks time point into the bio-fluids (Figure 4 and 9). However, for the SSI wire, beyond the 4 to 20 weeks incubation time, the immersion media did not significantly increase the levels of the Ni released by contact corrosion.

$$Y = 0.12^* X + 0.78 \quad (R= 0.48) \qquad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

Where Y: represents the level of Ni ion released from arch bar.

X: represents the level of Ni ion released from SSI wire.

The linear regression expressed in equation 1indicates that there is an expectation that ligation of SSI wire onto arch wire for prosthetic application would contribute to the released amount of Ni ion from the surface of arch wire by about 12% of that released by SSI wire. This could be resulting from stress corrosion by the SSI/arch composite implants. An independent constant value of 0.78 results from some other multi-factorial situations that come to place in the in vivo setting.

The rate of release of Ni ion from the per unit surface area perspective, indicates that the SSI wire has a release rate that doubles that of arch wire.

Release of chromium ions: Chromium ions were released from the SSI wires from the one day immersion time, just like the arch wire, the amount increasing sharply with incubation time for the five bio-fluids (Figure 5 and 10). For the SSI wire, a statistically significant difference in the Cr ions released results from the variation in pH at immersion time beyond week 2. The concentration of Cr ions released from SSI wire into the immersion solutions constituted about 90% of the total metal ions released from the SSI wires at the various incubation times, whereas, for the arch wire, the chromium ions constitute about half the total concentration of metal ions released into the bio-fluids. The highest amount of Cr ions released by arch bar was recorded as 0.060 ± 0.001 µg/mL for the ach wire incubated in HSCl after 6 weeks. These findings would not be unconnected with the fact that chromium oxide is used for passivation of the SS materials against corrosion, and possibly due to its composition of 18.35% in the arch bar being studied.

For SSI wire, HSpH4, HSCl and WBS released a statistically significant level of Cr ions compared to HSpH7 and PBS at all immersion times studied. Chromium had the highest rate of release with the range 0.0705 ± 0.002 to 0.7600 ± 0.003 µg/mL/week (Table 2). For arch wire the range was 0.0103 ± 0.0001 to 0.0256 ± 0.002 µg/mL/week. An interpretation of the rate indicates that SSI wire has an average corrosion rate of 0.0371 ± 0.0003 µg/mL/cm^2/week whereas arch wire has 0.00987 ± 0.0001 µg/mL/cm^2/week.

$Y = 0.32^* X + 0.89$ (R= 0.57) …… (2)

Where Y: represents the level of Cr ion released from arch bar.

X: represents the level of Cr ion released from SSI wire.

The linear regression expressed in equation 2 indicates that there is an expectation that ligation of SSI wire onto arch wire for maxillomandibular fixation would contribute to the released amount of Cr ion from the surface of arch wire by about 32% of that released by SSI wire due to fretting corrosion among others.

Plate I: Arch bar implanted in the oral cavity of a patient

Conclusion

The SSI wire from this report showed resistance to corrosion at the short term immersion time, except for Cr and Ni ions. The study indicates that SSI wire of bio-medical application will corrode in an acid, neutral or chloride environment after long term use as does arch wire, with the SSI wire showing less corrosion resistance for most of the metal ions investigated.

Table 2: Ranges of the rates of release of metal ions from SSI wire with immersion time into bio-fluids (µg/mL/week)

Bio-fluid	Co	Fe	Ni	Mn	Cr
pH4	0.0000 to 0.0035 ± 0.0002	0.0201 ± 0.0001 to 0.2170 ± 0.0048	0.0000 to 0.0818 ± 0.0038	0.0070 ± 0.0003 to 0.0200 ± 0.0018	0.0885 ± 0.0003 to 0.7100 ± 0.0028
pH7	0.0000 to 0.0033 ± 0.0005	0.0148 ± 0.0003 to 0.2030 ± 0.0028	0.0000 to 0.0634 ± 0.0018	0.0000 to 0.0100 ± 0.0038	0.0705 ± 0.0016 to 0.5300 ± 0.0022
HSCl	0.0000 to 0.0043 ± 0.0008	0.0216± 0.0021 to 0.2700 ± 0.0024	0.0000 to 0.0958 ± 0.0036	0.0000 to 0.0232 ± 0.0018	0.1055 ± 0.0023 to 0.7600 ± 0.0033
WBS	0.0000 to 0.0045 ± 0.0010	0.0171 ± 0.0031 to 0.3580 ± 0.0026	0.0000 to 0.0953 ± 0.0009	0.0000 to 0.0243 ± 0.0008	0.0915 ± 0.0020 to 0.6700 ± 0.0018
PBS	0.0000 to 0.0055 ± 0.0009	0.0146 ± 0.0021 to 0.2000 ± 0.0028	0.0000 to 0.0653 ± 0.0041	0.0000 to 0.0175 ± 0.0008	0.0735 ± 0.00132 to 0.2950 ± 0.0019

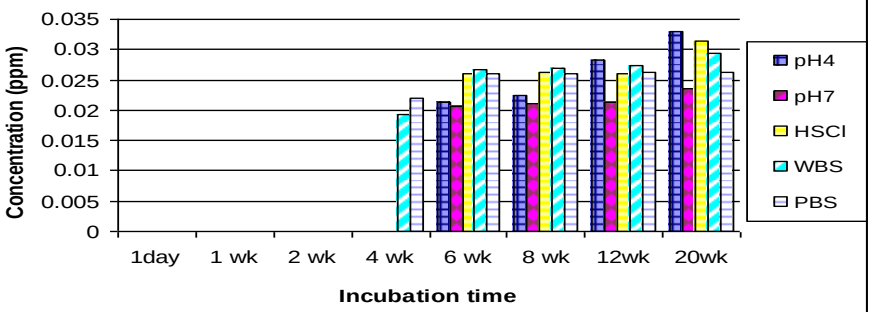

Figure 1:Cobalt ions released by SSI wire into bio-fluids

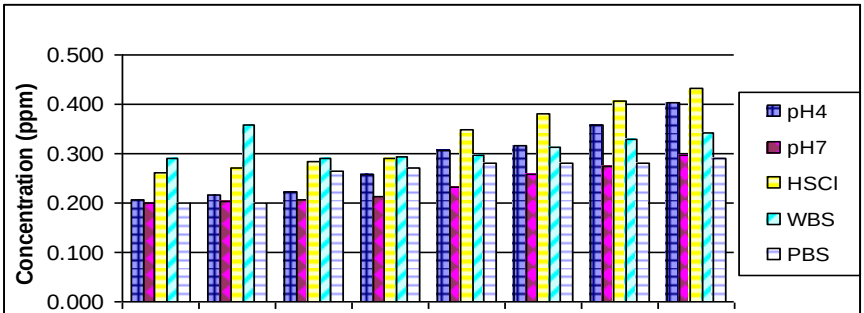

Figure 2:Iron ions released by SSI wire into bio-fluids

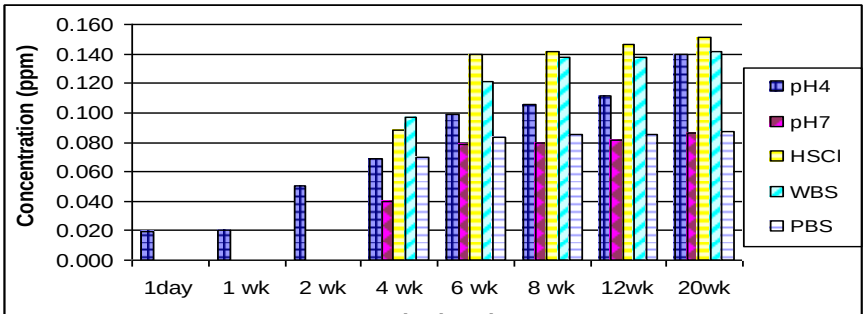

Figure 3: Manganese ions released by SSI wire into bio-fluids

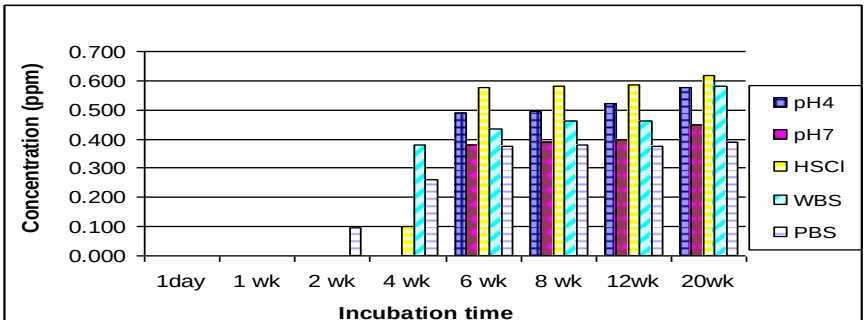

Figure 4: Nickel ions released by SSI wire into bio-fluids

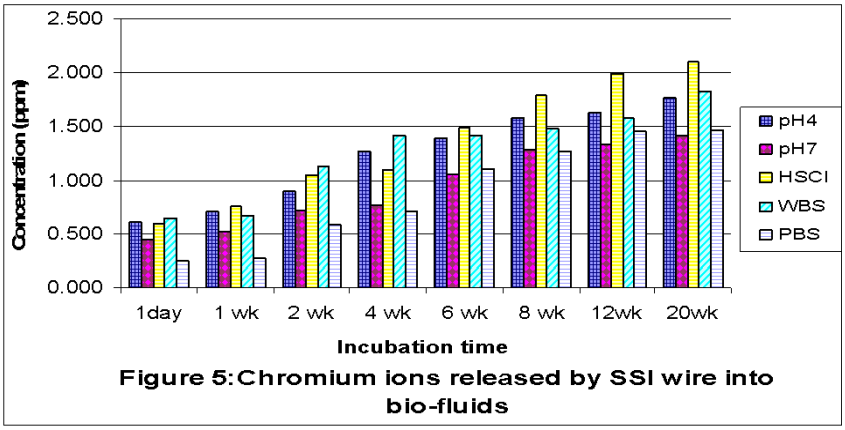

Figure 5:Chromium ions released by SSI wire into bio-fluids

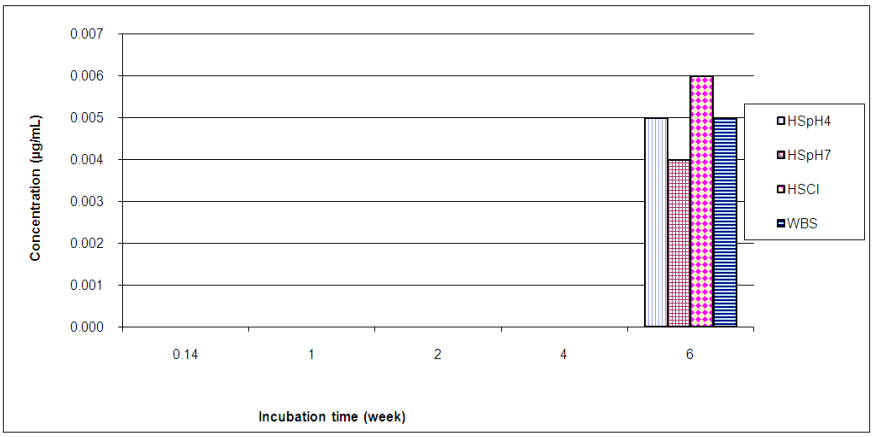

Figure 6: Cobalt ions released by arch bar into bio-fluids

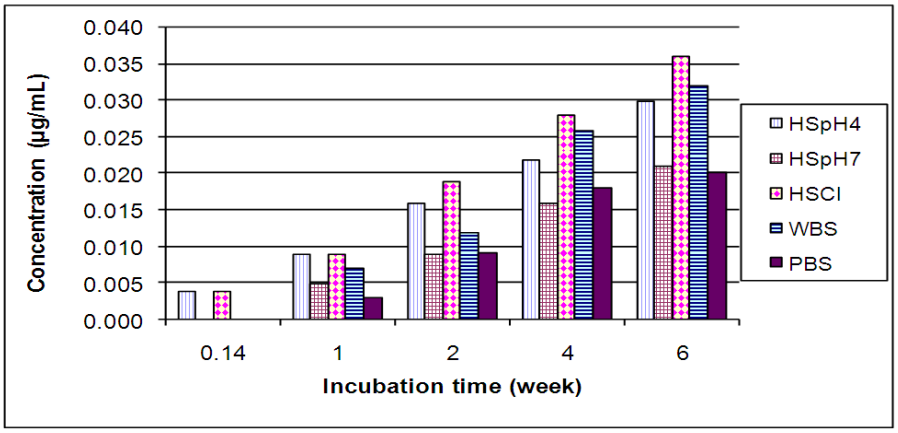

Figure 7: Iron ions released by arch bar into bio-fluids

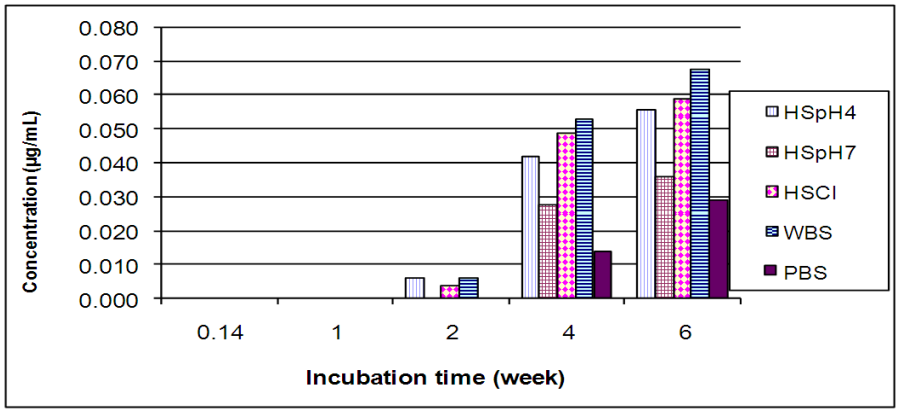

Figure 8: Manganese ions released by arch bar into bio-fluids

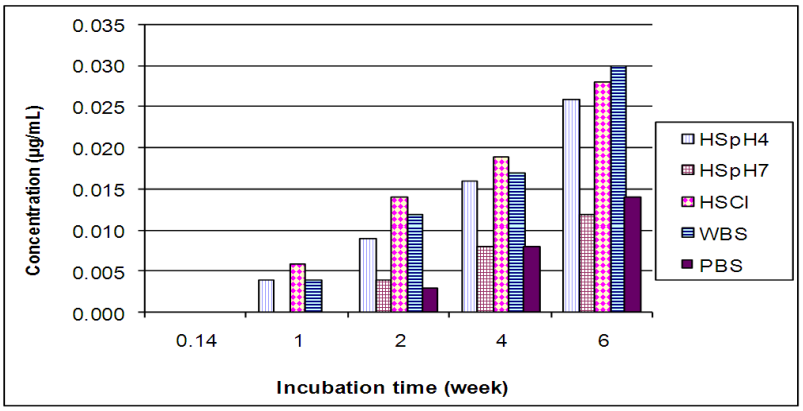

Figure 9: Manganese ions released by arch bar into bio-fluids

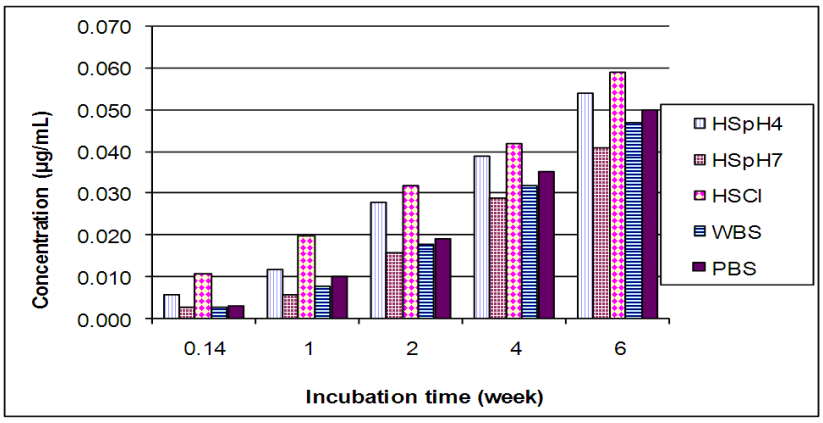

Figure 10: Manganese ions released by arch bar into bio-fluids

Notwithstanding, the low levels of released metal ions by the two test materials into bio-fluids, indicating the tendency of the body mechanism to depurate the low amount of the deleterious materials. The *in vivo* setting being multi-factorial would elevate the leached amounts of the metal ions.

Corrosion test of metallic prostheses is of clinical pertinence, as a result, towards attaining the ever-envisaged bio-friendly metallic implants. The team is investigating the corrosion inhibitory potentials of metallic implants on the test materials. There is need for more long-term investigations of metal ions released from SSI wire into bio-fluids, since the patient hosts the wire throughout life when used to fasten fractured bones.

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Table 1
Ion concentration of Hank's solution [11]

Ion	Concentration ($molL^{-1}$)
Na^{+}	1.42×10^{-1}
K^{+}	5.81×10^{-3}
Mg^{2+}	8.11×10^{-4}
Ca^{2+}	1.26×10^{-3}
Cl^{-}	1.45×10^{-1}
HPO_4^{2-}	7.78×10^{-4}
SO_4^{2-}	8.11×10^{-4}
CO_3^{2-}	4.17×10^{-3}

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