Incorporating corrosion measurement in hip wear simulators; an added complication or a necessity?

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Abstract

Corrosion is not routinely considered in the assessment of the degradation or the lifetime of total hip replacement bearing surfaces. Biomechanical simulations are becoming ever more complex and are taking into account motion cycles that represent activities beyond a simple walking gait at 1Hz, marking a departure from the standard ISO BS 14242. However, the degradation is still very often referred to as *wear*; even though the material loss occurs due to a combination of tribological and corrosion processes and their interactions. This paper evaluates how, by incorporating real-time corrosion measurements in total hip replacement simulations, pre-clinical evaluations and research studies can both yield much more information and accelerate the process towards improved implants.

Introduction

Total hip replacement is undoubtedly one of the most successful medical interventions with in the order of 200,000 and 80,000 procedures performed annually in the US and UK respectively [1]. Since the pioneering work in the development of total hip replacements, by McKee and Farrar and Sir John Charnley in the 1950-60's [2] there have been many developments and "generations" of designs. First generation polymer/metal combinations were replaced by metal-on-metal replacements after recognition of polymer debris causing osteolysis [3]. First generation metal-on-metal implants had their own limitations linked to manufacturing issues associated with surface finish quality and tolerances. Improvements to metal-on-metal devices were achieved by improving manufacturing and increasing the femoral head size to promote full film lubrication [3]. Recently, there has been controversy around certain metal-on-metal devices due to incidences of pseudo-tumours and their association with high rates of metal debris and ions [4] to the extent that implantation of metal-on-metal implants has declined. Hard-on-hard bearings are still being implanted where either the femoral or acetabular component is ceramic; as such there are still metallic interfaces which can be subjected to tribocorrosion in the bearing surfaces and in other important interfaces.

The history and evolution of total hip replacements is covered more comprehensively elsewhere [3]; this paper focuses on how *in-vitro* simulations can assist in (a) the development of optimum materials and designs (as a research tool) and (b) prediction of *in-vivo* performance (pre-clinical evaluation). Hip joint simulators have developed alongside total hip replacements. An impressive, early development was the Stanmore Hip Joint Simulator, described by Duff-Barclay and Spillman, [5], which provided both wear rates and friction for simulated motion and loading cycles. Values of wear factors and friction coefficients for polymeric materials and rubbers were reported by Walker *et al* [6] from tests on a pin-on-plate apparatus. The same authors reported satisfactory initial results on a Charnley Prosthesis [7] for more representative motion and loading cycles. While the limitations of such simulators were recognized, the ability to compare friction and wear measurements on real implants was of major importance and key aspects remain in today's simulators. The paper by Affatato *et al*. [8] reviews the attributes of current simulators and they conclude that further development is needed to ensure better correlation between *in-vitro* and *in-vivo* results. In the paper the focus is on wear mechanisms "The elements of a wear system include the contact surfaces, lubricant, load, articulating surfaces speed and relative position, motions, surface roughness, and temperature." There is no acknowledgement in the paper that even a proportion of the material damage in current hip joint constructions may be associated with corrosion.

Affatato *et al*.[8] reported for 10 different wear rate evaluations (by mass loss evaluations) in different laboratories and simulators that there was a difference of nearly one order of magnitude; the inconsistency of the data being attributed to laboratories not completely following the ISO standard. In addition, there are internal protocols for surface cleaning and bacterial management which involve removing tribofilms from surfaces during the test and addition of biocidal chemicals; these will undoubtedly influence the surface chemical interactions and the mass loss. In [8] and in the ISO standard [9] it is acknowledged that it is currently still a major challenge to predict the *in-vivo* performance from *in-vitro* data. This will remain the case if simulations are not adequately capturing the realistic conditions that exist *in-vivo*.

Across the field of tribology there are numerous instances where complex systems have to be simulated in the laboratory to inform subsequent field trials. Across industrial sectors including automotive internal combustion engines, aero gas turbines and others there are instances where laboratory simulations have to be simplified enough to enable meaningful parametric testing but still ensure that the real processes that occur in operation can be represented. Ensuring the simulations are "realistic" is in most cases a challenge and the simulation of hip joints is no exception. There are multiple factors that will affect how the hip joint would perform *in-vivo* and understanding the importance of each of these and their interactions is crucial if the goal of the simulation is to be able to predict *in-vivo* performance. Table 1 summarises some of the key factors that are important in hip joint simulations and the authors' assessment of whether

these are adequately covered routinely in the current ISO and British Standards for hip joint testing and/or are covered in bespoke testing in some specialised laboratories.

Lubricant factors	Current standards	Loading factors	Current standards	Mechanisms of degradation	Current standards
Viscosity	*** (specified but does not accurately mimic synovial fluid)	Walking biomechanics	***	Wear	***
Conductivity	*** (as above)	"Every day" motion cycles	*	Production of debris	**
Pressure-viscosity characteristics	*	Intermittent motion/rest	*	Corrosion	*
pH	*			Tribofilm formation	*
Temperature	*** (control is insufficient in some laboratories)				
Protein/organic composition	*** (specified but differs to synovial fluid)				

Table 1. Factors in hip joint simulation that are important and the adequacy of current standards (***included in ISO/British standard (BS ISO 14242-1:2014), ** considered in most laboratory tests but not included in standards, * considered in bespoke specialised tests, - not normally considered)

The focus of the current paper is *corrosion*; the term describes the degradation of a material through interaction with its environment. In the context of hip joints, corrosion is an electrochemical process in which the metal (either the hip joint or the debris it produces), because of being immersed in an electrolytic solution at elevated temperature has the propensity to dissolve. Dissolution sees the metal (as a solid) become metal ions (in solution). In hip joints the term *tribo*corrosion is often used; the *tribo* prefix is extremely important as it changes the kinetics and mechanisms of dissolution. Tribological factors represent the motion between surfaces in hip joint components and the potential for the rubbing surfaces to degrade. The corrosion processes that occur at hip joint surfaces are incredibly slow if the passive film on the CoCrMo alloys remains intact. Passivity of CoCrMo alloys occurs in the same way that stainless steels are referred to as "stainless" [10]. The passive film comprises Cr_2O_3 but it is a complex mix of oxides/hydroxides of predominantly Cr but also Fe. This layer (even though <10nm thick in biological solutions) offers unparalleled resistance to charge transfer [11]. Tribological contact can continuously remove the passive film leaving no physical barrier to charge transfer and a significantly higher corrosion rate ensues. Hence the term tribocorrosion (and sometimes wear-corrosion) refers to that interaction between tribology and corrosion.

It is worth looking in more detail at tribocorrosion; a degradation term that has applicability across various industrial as well as medical components. In the previous paragraph we describe how the rubbing of surfaces can enhance corrosion but it is important to realise that there are further physical interactions between wear and corrosion that lead to the tribocorrosion damage in engineering systems being more than would be predicted by an independent assessment of corrosion and wear.

In a tribocorrosion system, the total surface degradation (T) can be attributed to three main mechanisms. These are: degradation due to pure corrosion reactions (C), degradation due to pure mechanical wear (W), and the change in the level of degradation caused by the synergism (S) between corrosive damage and mechanical damage. The synergism term can further be divided into two sub-categories: the change in corrosion rate as a result of mechanical wear (C_w), and the change in mechanical wear rate as a result of corrosion (W_c). This is demonstrated in Equations 1 and 2.

$$T = C + W + S \tag{1}$$

$$S = C_w + W_c \tag{2}$$

Modelling tribocorrosion in this way has been implemented with reasonable success in both erosion-corrosion and sliding contact systems. Electrochemical testing in the absence of wear gives C. For passive alloys C is always extremely small. Measurement of the corrosion rate by conventional electrochemical techniques in a triblogical system, (such as a pin-on-reciprocating plate tribometer) [12] enables the corrosion rate in-situ to be measured which is essentially $C + C_w$. To obtain the level of pure mechanical wear, a cathodic potential is usually applied to the sample during testing or tests can be done in a fluid that is non-corrosive; in some tests diesel or other solvents have been used. For tribology it is important that the rheology of the fluid is comparable. If the anodic dissolution of the alloy is adequately suppressed, material degradation is exclusively caused by mechanical interactions (W). By subtraction of C, C_w and W from the total degradation under normal conditions, the contribution from W_c and C_w can be obtained.

Amongst the research community in academia and in the research laboratories of the major joint manufacturers there have been varying focus areas over the last 2-3 decades: new materials [13], new geometries [14], new surface finishes and manufacturing tolerances [15], changes in modularity and effects of surgical procedures that affect implantation angle [16]. Without doubt one of the key areas which has been neglected in simulation studies is the effect of corrosion. In this paper the powerful information which can be gleaned from instrumentation of simulators to extract real-time corrosion information is described.

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That tribocorrosion is important in hip joints is generally accepted by the clinical and engineering community. Undoubtedly it has become more prominent in the last 5 years as discussions on fretting/crevice corrosion at modular taper junctions has come to the fore. It would appear that engineers and the clinical community are much less convinced that corrosion is, or potentially could be, an important factor at bearing surfaces. Figure 1 summarises some of the areas in a total hip replacement that can be affected by corrosion and tribocorrosion. It is clear from the literature spanning the last 2-3 decades that there have been numerous studies of the bearing surfaces in a variety of laboratory based simulations and in the vast majority of these the damage is measured gravimetrically and is referred to as a "wear" process [8]. Reducing wear rates in the running-in and steady state phases of hip joint life has become a major focus of much current research work.

The international definition of corrosive wear [17], published by the Organisation for Economic Co-operation and Development (OECD) in 1969, was simply *…"A wear process in which chemical or electrochemical reaction with the environment predominates"* . Additional notes indicated that it was usually*…." a mild form of wear, but it may become very serious, especially at high temperatures or in moist environments".* Furthermore, in some cases…*"chemical reactions take place first, followed by the removal of corrosion products by mechanical action"* or *"by the formation of very small debris which subsequently is chemically transformed; the phenomena may be mutually enhancing".*

The clinical and well simulated laboratory environments are clearly consistent with these situations.

To challenge the current convention in reporting hip joint degradation it is important to understand the origins by which metal is lost at functioning bearing surfaces. Although the surfaces of the femoral head and acetabular cup are manufactured to give smooth surfaces (with roughness values of 5-20nm R_a) to try to ensure that for most of the cycle there is an elastohydrodynamic film, there is no doubt that asperity-asperity contact occurs. This contact leads to a local and repeated removal of the passive film which provides an effective barrier to charge transfer in static conditions. As such the corrosion regime is then one of active dissolution at these local points. Dissolution of metal and the associated production of ions is *not a purely mechanical wear process*; wear should be reserved as a description of processes where the removal of material is via mechanical processes such as ploughing of surfaces, work hardening, removal of hardened material, fracture, fatigue etc. Why is this important and is it just semantics? Actually, it is important for two reasons. Firstly, if the goal of measuring damage is to make better and more resilient hip joints then it is absolutely crucial to understand the origins of the damage. Making a hip joint to resist material loss through depassivation and production of metal ions requires a very different solution to one where fracture and removal of local wear particles is the dominant mechanism. Secondly, the end point of in-vitro simulation has to be accurate prediction of damage for pre-clinical

evaluation. If as a community we are fitting *wear* models to a damage mechanism that is actually *tribocorrosion* then it can only ever, at best, be empirical and not capturing the full physics relating to material loss.
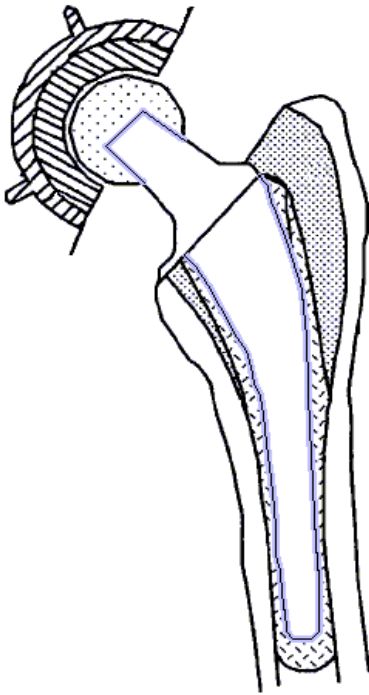

Figure 1. Potential tribocorrosion areas in a total hip joint. Blue dotted lines represent the taper and stem interfaces where a combination of triblogical loading and surfaces in relative motion in an electrolytic solution can lead to a combined wear-corrosion process. Such processes also occur at the bearing surface.

The focus of the rest of this paper is to demonstrate how capturing real-time corrosion measurements in hip joint simulations and, in some cases, using these measurements in conjunction with other analytical techniques post-test can provide very valuable information on the mechanisms of degradation of hip joints. This all contributes to the community then being able to more intelligently develop the next generation of designs and materials with better *tribocorrosion* resistance.

Corrosion: Integration of Real-Time Measurements into Simulators

The hardware and methodologies to instrument modern day hip joint simulators is not covered in much detail here. Figure 2 shows how the electrochemical cell is integrated into the simulator to enable real-time assessment of corrosion at the femoral head/acetabular cup components. Other papers [18] have covered this and have explained how a conventional three-electrode electrochemical cell can be successfully integrated with the biomechanical simulation to provide real-time electrochemical data [19]. This paper covers the details of what can be measured and how this contributes to our understanding of hip joint lubrication, wear and damage.
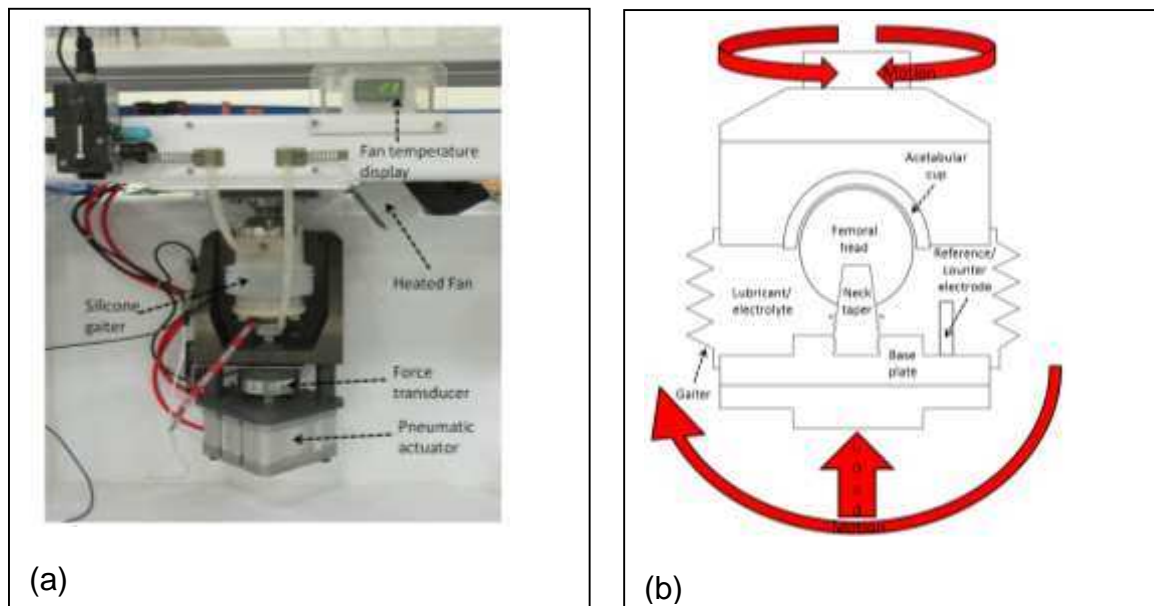
Figure 2. (a) Photo of the single station hip simulator set up (Simsol) (b) Schematic diagram showing the key components of the single station simulator and the loading/motion control [19]

What measurement of electrochemical corrosion parameters can tell us

Real-time corrosion measurements are valuable; they enable information to be accessed relating to the surface and interface processes that hitherto have been largely ignored. In the following discussion five examples of the information that can be gathered and how that complements the gravimetric information routinely collected according to the ISO standards are presented.

(I) *Mechanistic information of the passive state of the bearing materials and the lubrication regime*

CoCrMo alloys, predominantly the alloys used in bearing surfaces (femoral/acetabular) components in hip joints are classified as passive alloys. Passivity, in relation to CoCrMo and other alloys (e.g titanium, stainless steel) has been widely studied across industrial and medical sectors. Passivity from an electrochemical point of view is manifested in very low ($<10^{-7}$-10^{-8}A/cm^2) corrosion currents [10]. Corrosion of such alloys, if it does occur, is normally associated with localised breaches of the passive film and the formation of pits or crevice corrosion. In the case of hip joint bearing surfaces electrochemical monitoring opens up the opportunity to assess whether or not passivity is maintained when motion occurs. If passivity is maintained then it would be a strong sign that no gross contact between the surfaces occurs and that the elastohydrodynamic lubrication regime prevails. Any metal-metal contact would lead to local removal of the passive film and associated increase in the transfer of charge/corrosion rate. In tribometer studies of the tribocorrosion phenomenon it is widely reported that the depassivation of alloys caused by the contact between loaded interfaces leads to a shift

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in the active (negative) direction of the open circuit potential. Figure 3 shows this phenomenon for CoCrMo alloys in contact with an alumina ball in tribometer studies using serum as a lubricant at 37°C [12].
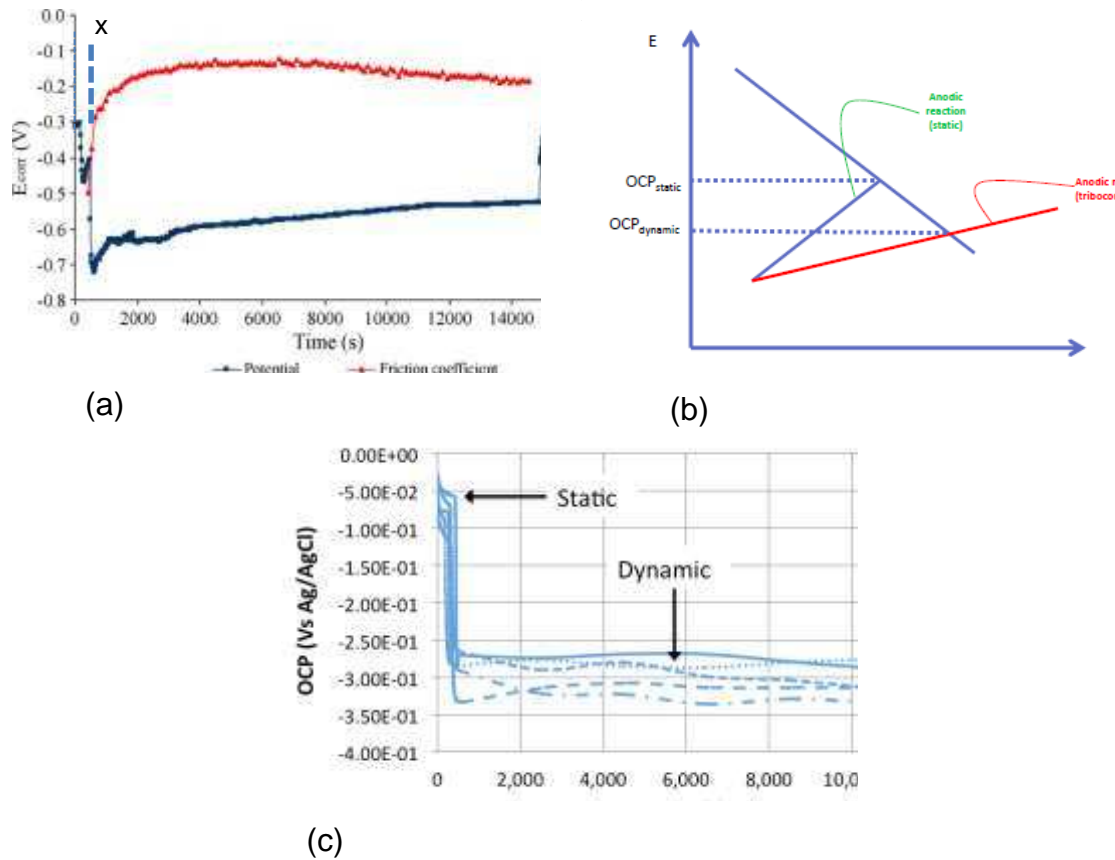

(a)

(b)

(c)

Figure 3. (a) Active shift in open circuit potential (OCP) at the start of sliding (x) for an Al_2O_3 ball loaded against a HC CoCrMo plate in 50% serum (b) Evans' diagram showing how depolarisation of the anodic reaction leads to a shift in potential (c) Active shift of the OCP when motion/loading starts in the instrumented simulator.

The potential shift occurs because of the depolarisation of the anodic reaction (Co-$Co^{2+}+2e^-$) and, as shown in Figure 3b the Evans' diagram clearly indicates why the changed kinetics of the anodic reaction can lead to a negative shift in potential. In the work conducted by Yan *et al* [12] and Yan [20] represented in Figure 3a the sliding motion is from a reciprocating pin-on-plate simulation and the loads (Hertzian contact pressures) were higher than would be expected on a hip joint bearing surface. As such, gross metal-metal contact is expected and electrochemical measurements of the open circuit potential confirm this. Figure 3c shows how, on introducing motion to the femoral head/acetabular cup couple in the instrumented hip simulator, a comparable behaviour was observed albeit with the active shift in potential being slightly smaller. In general terms the ΔOCP in the hip simulator is less than in the tribometer which suggests the extent of contact is less. Modelling of the lubrication regime in the hip joint bearing surface has demonstrated it is in the mixed lubrication regime [21] and the

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measurements of OCP would tend to confirm this; there is metal-metal contact but the change in OCP is less than in systems in the tribometer where Lambda ratio (λ)<<1.

OCP is a semi-quantitative measure of the corrosion behaviour of a system; it is a balance between anodic and cathodic reactions and a shift of the kinetics of either one can shift the potential. There is no universal relationship between the OCP and corrosion rate and instead OCP shifts are useful to show changes in the controlling reactions in corrosion as shown in the previous paragraphs. So, whilst OCP is a good and simple measure to assess changes in a system behaviour alternative, and normally more complex, electrochemical measures are needed to fully characterise the corrosion of the system.

To investigate the corrosion kinetics as a function of the loading cycle and the complex combination of internal and external rotation, adduction-abduction and flexion-extension the DC potentiostatic method was chosen. This involves applying a modest anodic overpotential of 100mV to the working electrode (the tribocouple) and the resulting changes in current were measured at 20 points/second. For the first time the tribological cycle can be mapped onto the corrosion cycle. Figure 4 shows some typical current snapshots collected throughout the simulator test.

In some instances there is clear periodicity in the current suggesting there is a link between the loading parameters and the current (perhaps due to the extent of metal-metal contact) (Figure 4a). It is hypothesised that the combination of sliding/contact at the interface depassivates the metallic components at the contact points and the magnitude of the current is determined by a number of factors. The important tribological factors were assumed to be sliding speed, load and the minimum film thickness and from this a "severity factor" was determined. Assessing the correlation between the minimum film thickness, lambda ratio, sliding speed and load as single factors against the potentiostatic current proved that multifactorial effects determine the current. In Figure 4b the severity factor is plotted against the current and in Figure 4c a modified severity factor is plotted which adds to the current decay term a single time constant decay term according to the repassivation kinetics work done by Sun *et al* [22].

$$\textbf{Severity Factor = U W} / \textbf{h}_{min} \qquad \text{-------------- (3)}$$

where U is the linear sliding velocity (m/s), W is the load (N) and h_{min} is the minimum film thickness (m). It is likely that each of the dominant terms in [3] will carry different powers, but this will have to be considered further as more experimental results become available. The minimum film thickness term could also be represented by the lambda ratio (h/R_a), which is known to offer a good indication of the mode of lubrication in highly loaded contacts such as gears and rolling element bearings. Furthermore, the load term (W) has a relatively modest influence on theoretical film

thickness, but is likely to be more influential upon surface damage as far as tribocorrosion is concerned. For the severity factor terms it is possible to see that there is a correlation with the current response suggesting that some of the appropriate physics is captured and progress towards a mechanistic understanding of what causes current transport in tribocorrosion interfaces is being made. Figure 4d shows the modified severity factor plotted against another set of periodic data from another timeframe of the test and it can be seen that three severity peaks and three current peaks are identified. However, achieving a universal model for current from simulator studies is not trivial and it should appreciated that this work is a step forward but that much remains to be done.

In using this new form of Severity Factor, it should be noted that the simple steady-state equation for film thickness was used at each time step considered. This neglects the important squeeze-film action and hence the angular location of the mimimum and maximum film thickness. Furthermore, the highly non-Newtonian characteristics of the serum used as lubricant have not been considered. It appears to be necessary to embrace these features of a complex tribological and tribocorrosion process in future analysis.
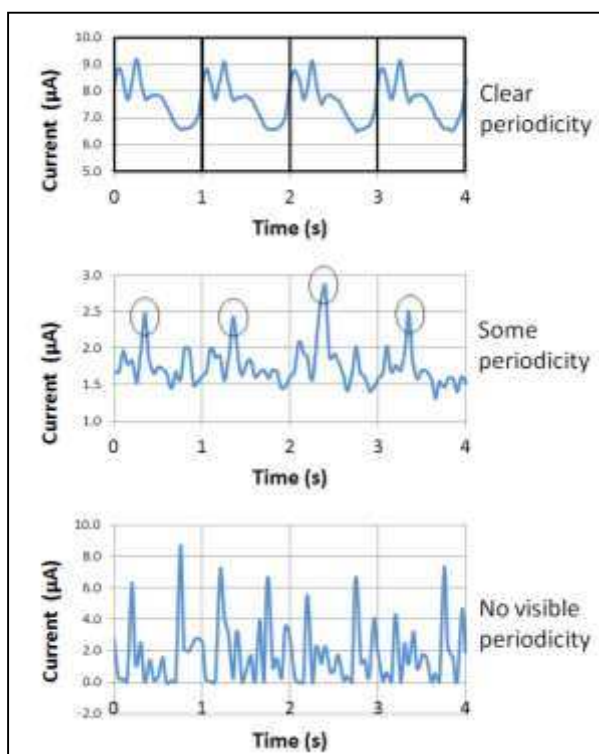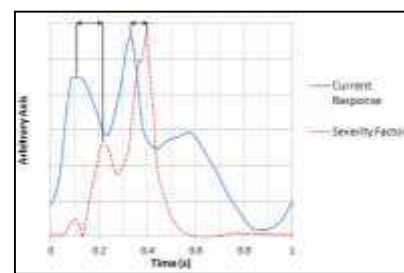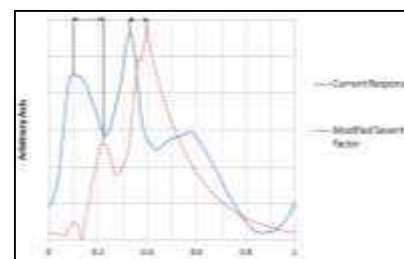
(a)
(b)
(c)
(d)

Figure 4 (a) Typical current versus time snapshots from a simulator test with 25% serum at 37°C showing regions of periodicity and no periodicity (b) Current transient mapped against the severity factor (not including repassivation) (c) Current transient mapped against severity factor (including repassivation) (d) Different current transient mapped against the severity factor (including repassivation) [19]
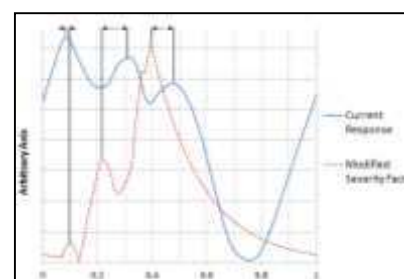
Where there is no periodicity there can be a few reasons for this:

(a) From subsequent contact and protein/nascent metal interactions a tribofilm is formed and that tribofilm is "protective" and prevents metal ion release across the loading cycles in the tribometer.

(b) The metal is not depassivated because the lubrication regime is EHL and no significant metal-metal contact is occurring. This will be discussed later in the paper.

(II)   *Synergies between wear and corrosion*

From tribocorrosion studies of passive materials, performed mainly in relation to engineering applications of materials in corrosive environments it has been shown that wear and corrosion interactions can be significant. In many industries pumps, valves and other slurry handling equipment can be affected by tribocorrosion. In the early 2000s whether corrosion played an important part of the degradation in hip joints was largely unknown *but* appreciation of the tribocorrosion process pointed towards it being significant. Immersing a system of passive metals in a corrosive fluid at 37°C with the potential for fretting contact and/or tribological sliding would suggest that tribocorrosion would be an important degradation mechanism. Simulations of sliding wear of an alumina ball on a CoCrMo plate in work by Yan et al [12, 20] in various biologically relevant solutions showed that corrosion related damage could account for up to 50% of the total material loss. This was the first hint that tribocorrosion should perhaps be given more respect as an important damage mechanism.

Hesketh [19] adapted the tribometer cell with incorporated electrochemical measurements to consider a CoCrMo ball on a CoCrMo plate at more realistic loads. In his study the initial Hertzian contact pressure was of the order of 200MPa and dropped as the wear on the ball occurred to reach values of 20MPa by the end of the test. The lubricant was 25% foetal bovine serum at 37°C. In these less extreme conditions the same depassivation of the tribocouple occurred, shown by an active shift in OCP and calculation of the proportions of wear and the associated interactions with corrosion were comparable to the more severe conditions as shown in Figure 5a. Corrosion accounted for >40% of the total damage occurring in the tribocorrosion contact.

It has been shown previously that in the simulator the OCP shift associated with depassivation was recorded but the change in OCP was less than in the tribometer pointing to the fact that the loads and the extent of depassivation may be less [19]. Figure 5b shows the proportions of damage associated with corrosion and wear for the

simulator for a simple walking cycle at 1Hz run for a million cycles. This data hides changes in these proportions which may occur at different points in the test (i.e. in running-in and steady-state) but still illustrates that 20% of damage can be associated with corrosion. Later in the paper the importance of deviations from this simple cycle are shown and how departures from the ISO loading cycle can lead to large changes in the current measured at the tribocorrosion interface.
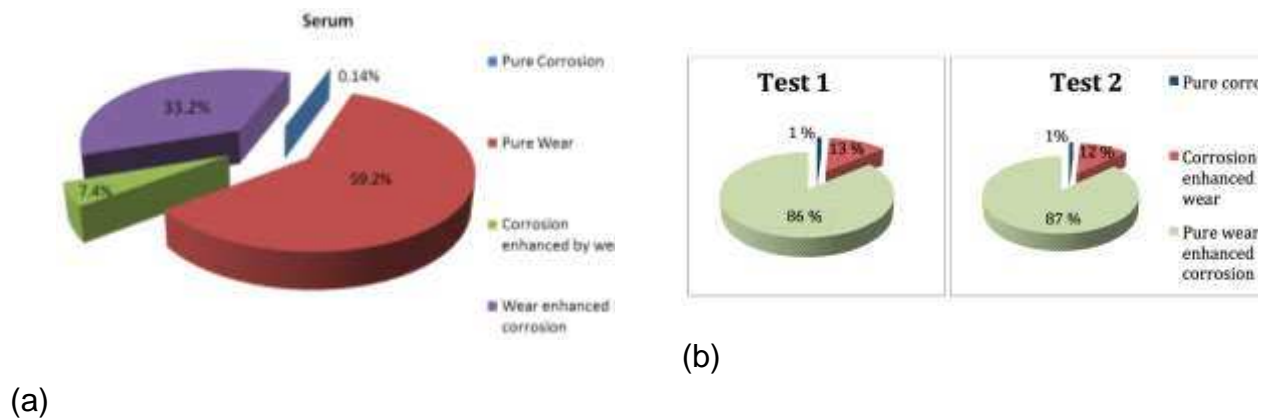

(b)

(a)

Figure 5 (a) Proportions of damage in the pin-on-reciprocating plate tribometer in 25% serum at 37°C with maximum Hertzian pressure of 200MPa (b) Proportions in the simulator with a walking cycle with a swing phase load of 2800N and at 1Hz for 1 million cycles [19].

(III)   *Debris and ions; material balance*

There has been much controversy and discussion around the production of metallic debris and ions; their links to the formation of pseudotumours, acute lymphocyte-dominant vasculitis-associated lesion (ALVAL) have been confirmed in many cases. Adverse Reaction to Metal Debris (ARMD) [23] captures the many different problematic instances that have arisen due to implantation of metal-containing implants. Discussion of the link between the rate of debris/ion production and the patient symptoms and clinical outcomes is beyond the scope of this paper but the discussion here relates to how *in-situ*, real-time electrochemical measurements can be used, in conjunction with other analysis (e.g ICP, AES) to establish the origins of metallic ions and their rate of production.

Figure 6 shows a schematic representation of the pathway for the production of wear debris and metallic ions from the bearing surface couple in the hip joint. Only the bearing surface is considered in Figure 6 but analogous processes occur at the stem/cement and taper junction interfaces.
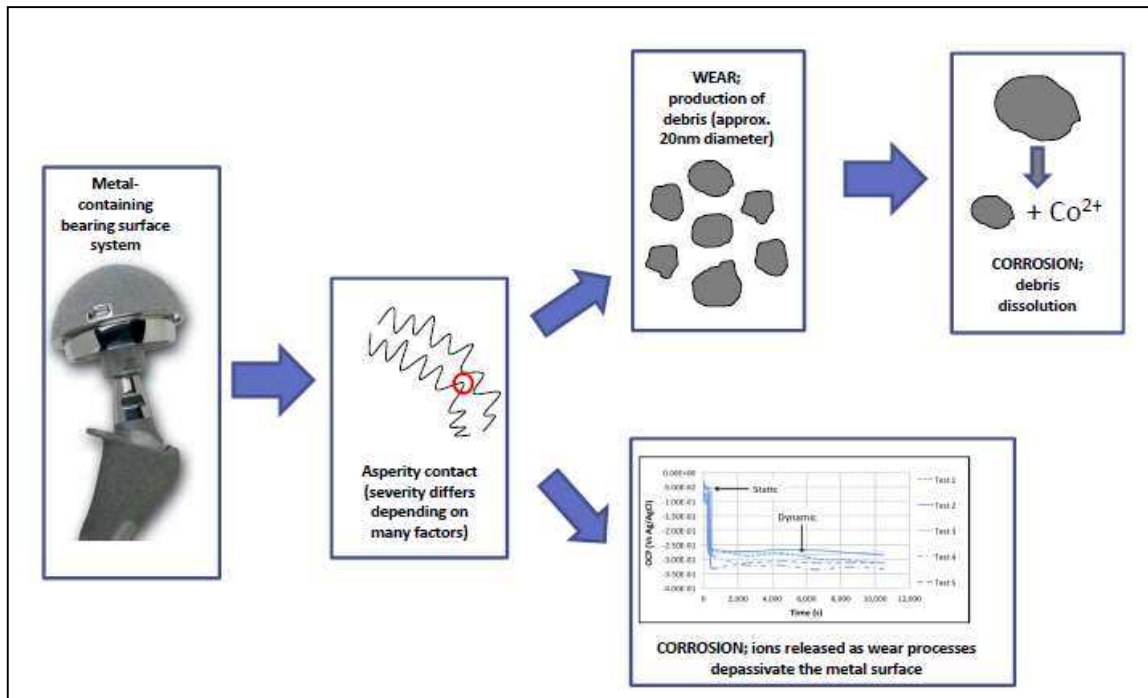
Figure 6. Pathway for debris and ion production at the bearing surface showing how asperity contact can produce debris *or* ions from wear-enhanced corrosion. Debris can either reside as solid particles or can dissolve and further enhance the ion content.

An important aspect of Figure 6 is the demonstration that ions that are released into the fluid in the joint capsule can come from two major sources; from dissolution of preformed debris from mechanical wear processes and from metal dissolution enhanced by the removal of the passive film at the surface. Incorporating electrochemical measurements with measurements of ions (by ICP) enables these ratios to be determined. Also, the balance of alloying elements as dissolved ions can be calculated.

In Figure 7a the balance of ions recorded in the simulator in a 1million cycle test is presented for three time periods and three repeat tests. There is no major difference in the ratios apart from the noticeable smaller amount of Mo at the end of the test. Also, the total amount of ions decreases as time progresses (as shown later). There is a strong Co-enrichment which is in agreement with the alloy content but at odds with the reported Cr-enrichment in particles detected as reported by many authors and discussed here in section V. Figure 7b shows how the balance of ions coming from depassivation of the surface and the dissolution of debris changes for the test for 330,000, 660,000 and 1 million cycles. The ions released from depassivation of the surface are calculated from in-situ corrosion measurements and assuming all of the current measured goes into producing $Co^{2+}/Cr^{3+}/Mo^{3+}$ ions in solution around the joint space. Interestingly the proportion of ions coming from the surface increases even though, as shown in Figure 7c the corrosion mass loss reaches a plateau at around 660,000 cycles.
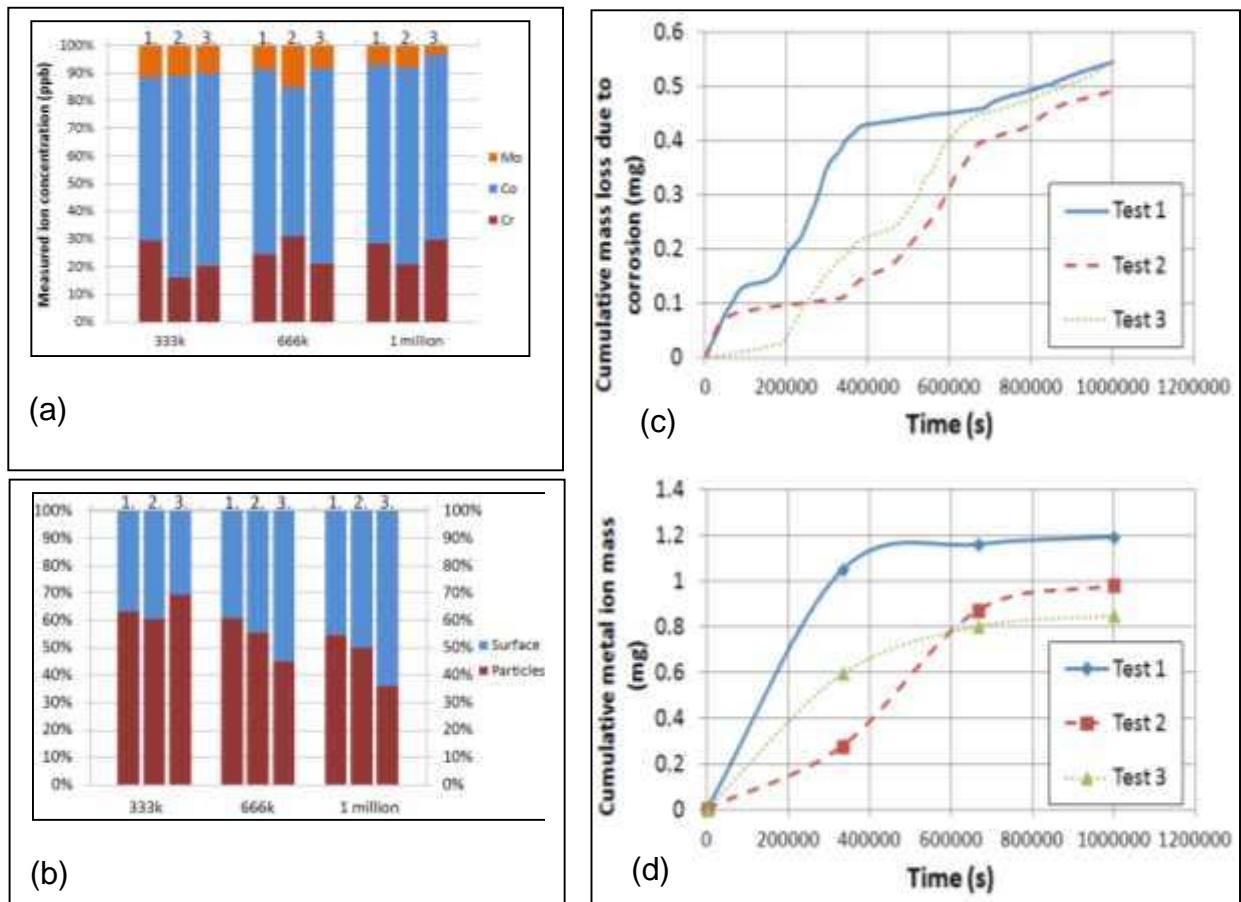
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Figure 7. (a) Ion release (Mo/Cr/Co) from a simulator test on the bearing surface at 330,000, 666,000 and 1 million cycles (b) proportion of ions released from the surface (wear-enhanced corrosion) and from the dissolution of debris particles (c) cumulative mass loss due to corrosion calculated from electrochemical measurements (d) cumulative ions measured from ICP [19]

(IV)   Effects of misalignment and real-life cycles

The importance of surgical technique has been discussed in detail, especially in relation to the inclination angle of the acetabular cup and the potential for microseparation to occur. Micro-separation describes the process whereby the acetabular cup and femoral head physically separate during abduction-adduction leg lift manoeuvres and during normal gait. Fluoroscopy studies have reported the extent to which this occurs [24] and simulator studies including effects of separation and the resulting impingement of the head and cup when they come together have replicated wear patterns seen in retrievals where a high inclination angle was observed. In the normal hip joint, the femoral head is retained within the acetabulum by numerous supporting structures, including the fibrous capsule; the acetabulum labrum; the ligament of the head of the femur; and the iliofemoral, ischiofemoral, pubofemoral, and transverse acetabular ligaments [25]. During hip joint replacement, the ligament of the head of the femur

commonly is found to be disrupted or degenerative and is removed surgically. A portion of the remaining supportive structures is transected and resected to facilitate surgical exposure. This means that separation is common and should be considered in simulator studies.

Williams *et al.*[26] reported a non-statistically significant increase in wear rate from 2.03 (±2.60) to 2.70 (±2.20) mm^3/Mcycle for 28 mm bearings subjected to microseparation over the first million cycles. Beyond the bedding-in phase however, overall wear volume after five million cycles was shown to increase from approximately 3 to 8 mm^3. Leslie *et al.*[16] reported on the combination of a high cup inclination angle (55°) and microseparation for a 39 mm surface replacement device. During the first million cycles wear rates increased from approximately 2.5 to 7.0 mm^3/Mcycle. Al-Hajjar *et al.*[27] reported an increase from approximately 1.2 to 4.62 mm^3/Mcycle for 28 mm MoM bearings subjected to microseparation over the first two million cycles of articulation. Previous studies with metal-on-metal have demonstrated increased wear with increased cup angle both in vitro and in vivo [28]. However, clinical studies suggest a larger variation in wear rates and also generally a greater increase in wear than found in vitro. This implies other variables may be playing a large role in determining wear rates in vivo.

Real-time corrosion measurements are providing evidence that one factor that is radically affected by misalignment is the "wear enhanced corrosion, C_w".

In work by Beadling *et al* [29] a standard twin-peak loading cycle was used at a frequency of 1 Hz. The loading cycle comprised 3 kN and 300 N peak and swing-phase loads respectively, +30° -15° Flexion / Extension and ±10° Internal / External rotation in part reference to ISO-14242 Part One [9]. Bearings were tested under either standard walking cycle conditions or subjected to 0.8 mm microseparation. The microseparation was effected by applying a negative load during the swing phase to separate the head and cup. Figure 8a shows the stark difference between the cumulative volume loss calculated from *in-situ* corrosion measurements under standard gait and with microseparation. The current measurements demonstrate that the wear-enhanced material loss rate is an order of magnitude greater when microseparation is present and is double what would be considered acceptable for a well performing bearing.

Assessing the current transients for standard gait and for microseparation in Figure 8b it is clear that there is a very prominent peak current which is ten times greater than the corresponding standard gait peak; this occurs at the point of "toe-off" and the start of the swing phase [30].

(a)

(b)
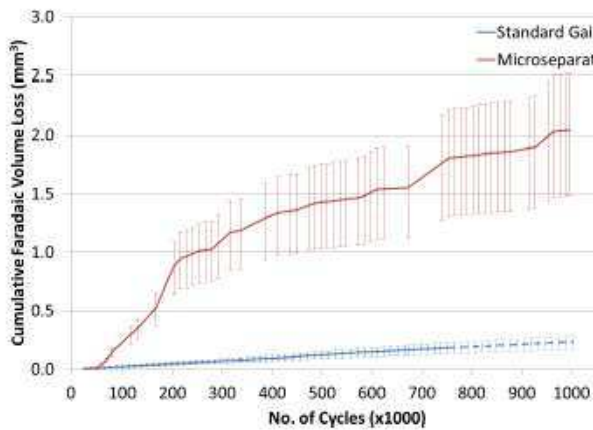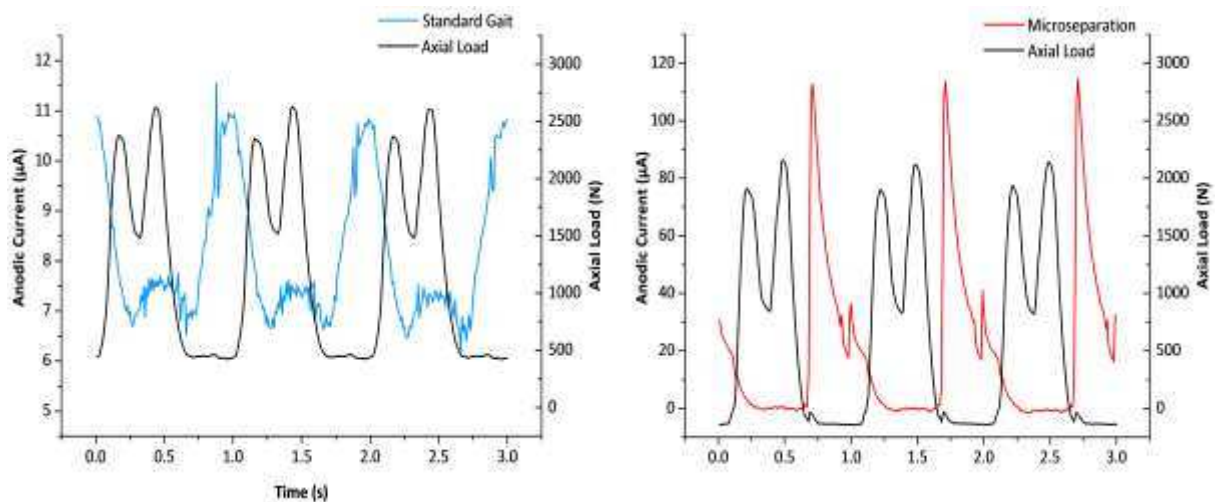
Figure 8 (a) Cumulative volumetric loss of material from calculations of the Faradaic charge transfer and the assumption that all charge transfer contributes to a "corrosion" mass loss. (b) Large variations in current transients associated with the motion cycle when microseparation is introduced. The current values suggest an order of magnitude greater corrosion for microseparation. [29]

(V)   *Protein and tribofilm effects when coupled with advanced microscopy*

The interaction between a nascent CoCrMo surface and proteins in synovial fluid/serum has been reported from several authors including the authors of this paper in both tribometers and in simulators [19, 31]. The tribofilms formed at rubbing surfaces where tribocorrosion occurs are complex but access to the most advanced electron (transmission and scanning) microscopy enables the structures to be defined and their formation understood.

Figure 9 shows cross sectional Transmission Electron Microscopy images of the tribofilms formed on the bearing surfaces of simulator tests; in other publications the similarities in terms of tribofilms from simulators and retrieved hip implants has been

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demonstrated [20]. Two features are of particular interest; the apparent non-uniform thickness of the film (Fig 9a) and the presence of embedded particles in the tribofilm (dark regions in the intermediate layer in Figure 9b). EDX mapping provides very useful information on the nature of the particles; they are Co rich and are a combination of Co metal and Co_3S_4 as determined by electron diffraction. This shows definitively that there are constituents of the protein (sulphur) in the tribofilm; something that has been doubted in many publications where it was presented as a purely mechanically "worked" layer.

The effect of the tribofilm on subsequent corrosion rates is still very much a subject of debate. In work by Yan *et al* [31] he reported very low currents at periods in tribometer and simulator tests and associated these with periods when the tribofilm offered charge transfer resistance. This was referred to as a "wear-induced passivation". Schymura *et al* [32] also reported a "passivation" effect of the tribofilm. Others have not seen this effect and rather just a steady decrease in the corrosion rate in simulator tests as time passes [19, 29].
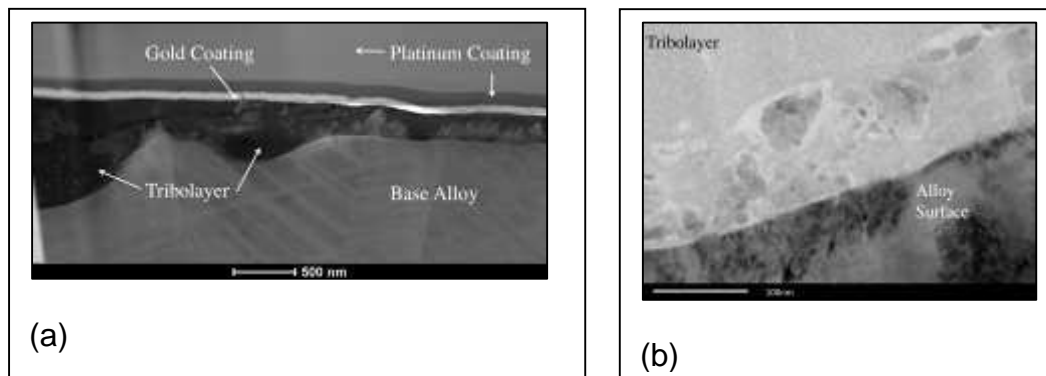
Figure 9 (a) Non-uniform thickness of the tribofilm formed after 1 million cycles using a standard walking cycle (scale bar 500nm) (b) Embedded particles evident in the tribofilm (scale bar 100nm)

The tribofilm is important for three main reasons

(i)   It can potentially reduce the charge transfer at the interface and have an impact on the corrosion-related damage
(ii)   It affects the mechanics of the interface; the film has different modulus and hardness to the base metal and will have different wetting and shear characteristics
(iii)   The production of debris in many cases is postulated to be from the tribofilm since the debris size is generally less than the thickness

Wear particles have been extracted from simulator tests of metal-on-metal implants in many studies and consistently their size is estimated to be in the range from 50-80nm [33]. From volumetric wear calculations it has been estimated that in excess of 6.7 x 10^{12} particles can be produced per year. Notwithstanding the inevitable errors in

assuming a uniform size for the particles, it is clear that for every step taken >1.5 million particles are produced. The nature of the particles is complex; many reports show the absence or very low levels of Co compared to the bulk alloy. The particles are typically rich in Cr; primarily oxidised Cr species. Some authors postulate that the debris is derived from the passive film on the alloys. However, it would seem unlikely that all particles are derived from the virgin passivefilm; it is much more likely that it is derived from the partial removal of the tribofilm. Wimmer *et al* [34] and Yan [20] reported the incorporation of proteins into tribofilms with no detail on exactly how these proteins interacted with the metallic species. Hesketh [19] reported Co_3S_4 particles; definitive evidence of protein/Co interactions.   Goode *et al* [35] did report varying levels of Co in wear particles. It is feasible that the Co ions in tissue in-vivo and found in the serum solution in simulator studies could have been derived from preferential of Cr and Co containing particles.

Measurements of real-time corrosion rates in simulators cannot directly assist in the determination of wear particle or tribofilm composition but assessing changes in the charge transfer at the bearing surface, coupled with advanced microscopy, the kinetics of tribofilm formation can be followed.

Outlook: Prediction/management of degradation

It is acknowledged across the literature that it is very difficult, and in some instances impossible, to predict *in-vivo* performance from *in-vitro* simulator tests. Whilst there are great efforts in trying to make the simulations more realistic through incorporation of realistic motion cycles [36], understanding stop/start effects in simulations and stratifying simulations [37], this paper has shown how incorporation of real-time corrosion measurements can enable information relating to the tribocorrosion processes at hip joint surfaces to be accessed that cannot be revealed in other ways. We find that there is strong evidence that corrosion and corrosion-related damage can account for anywhere from 40%-50% of damage in the running-in phase to lower values of ca. 20-30% in steady state in a normal walking cycle. This is increased significantly in adverse loading there is no real rationale for advocating that we can proceed with simulations that do not quantify corrosion effects.

Two final points are discussed here (a) how modelling can be anything other than empirical if corrosion is not incorporated and (b) how simulations that approximate 1 million cycles to be equivalent to one year of implantation in patients fundamentally miss some of the subtle effects of corrosion.

Modelling tribocorrosion

There have been many recent attempts at modelling the tribocorrosion damage in CoCrMo alloys in relation to hip joints. Most of the work has used electrochemical data

fused with gravimetric data collected from tribometers in a pin-on-reciprocating plate mode [38]. Whilst the depassivation and repassivation events associated with tribocorrosion can be properly represented and controlled with such a set up it is important to note that the complexities that arise in a hip joint simulator due to the 6-axis loading system and the complex lubrication regimes are not captured. However, such models enable an understanding of how corrosion and wear interact and also mass balances to be completed which account for all the modes of material damage in a tribocorrosion contact. In some of our recent work we have also modelled the repassivation kinetics of CoCrMo alloys in sliding contacts and shown that the lubricant and the sliding conditions affect the repassivation kinetics [39]. Translating this to a hip joint simulator is now possible and will be done in due course. In the hip joint simulator depassivation is not a simple process; the combination of flexion-extension, adduction-abduction mean that the depassivation and repassivation are continuously occurring across the contact patch of the femoral components.

Cao et al. [40] have used a composite model approach to model the mechanical and chemical aspects of tribocorrosion damage and have reported good fits to experimental data (shows within 20% of the experimental values). Uhlig [in 41] was the first to split tribocorrosion damage into two components as in (4)

$$V_{tot} = V_{chem} + V_{mech} \quad\quad \text{--(4)}$$

The volumetric chemical damage (v_{chem}) and volumetric mechanical damage (v_{mech}) are isolated. Mechanistically this seems like a good approach but it should be appreciated that if the definitions of corrosion and wear effects are used as in (1) and (2) previously the interactions between the process are captured. It should be noted that a portion of v_{mech} is the wear that is enhanced by the presence of corrosion; the question arises whether this is *corrosion* or *wear* damage and in fact it is an interaction.

The composite model in (5) represents an important advance in the prediction of the total tribocorrosion damage. However, the model relies on imposition of a potential on the tribocorrosion sample to determine the charge Q and no account is taken of what that shift from equilibrium does to the subsequent wear processes. The first term in the right hand side is an Archard type modification for wear which takes account of the boundary lubrication regime. The second term is the corrosion term and uses the minimum film thickness and the associated charge transfer to determine V_{chem}.

$$V_{tot} = k_m \left(\frac{k_0 F_n / h_{min}^{1.49}}{H} \right) v_s + k_c \frac{Q_P M v_s \left(\frac{k_0 F_n / h_{min}^{1.49}}{H} \right)^{0.5}}{nF\rho} \quad\quad \text{--------(5)}$$

Where k_m is a proportionality factor linking mechanical wear to an Archard type expression ($v_{mech} = k_m \frac{F_n}{H} L$). k_0 is a proportionality factor for effective load. F_n is

normal load. H_{min} is minimum film thickness. H is hardness. k_c is a proportionality factor. Q_P is the passivation charge density. M is atomic mass, v_s is sliding velocity, n is oxidation valence, F is Faraday's constant and ρ is density. Full explanation of the terms can be found in [40].

The authors of this paper believe that in order for the model to be fully predictive then the proportionality factors need defined; currently they are empirical. There needs to be a more precise linking between the tribological factors (h_{min}, h_c, instantaneous real contact area) and the corrosion currents occurring at the open circuit potential. Studies in tribometers and in simulators measuring corrosion rates *in-situ* and linking these to the changing tribological conditions will ensure progress is made.

Limitations of simulations when 1 million cycles equates to one year

In simulator studies one million cycles is equated to one year of total hip joint replacement implantation. Two aspects of this should be considered if there is an expectation that real lifetime of bearing surfaces can be predicted.

(a) What happens to wear, corrosion and their interactions when there is no motion? In simulator studies the assumption is made that wear occurs during the walking cycle and then no material loss occurs during the rest of the time when the patient is stationary. If corrosion measurements from simulators are considered then it can be deduced that corrosion is not zero when there is no motion. There are 31.5 million seconds in a year and so the static corrosion rates should be accounted for in the prediction of degradation (production of ions/wear etc). In the work by Hesketh [19] depending on the static corrosion rate adopted the increase in mass loss could be between 0.3 and 1.2mg against the total over a million cycles of ca. 3.5mg.

(b) Wear-enhanced corrosion represents the depassivation that occurs when the passive film protection is removed. For periods when motion ceases in a real hip joints the current remains high; the repassivation kinetics have been the subject of much debate and have been found to follow first order or bi-exponential decay. The simulator tests with one million cycles will normally be stopped every 300,000 cycles and so the additional current (corrosion) associated with the period after motion is ceased is not accounted for except for in 3 discrete periods. For a full year of hip joint implantation the number of "stops" could reach thousands of seconds and so the current decay characteristics are likely to be important. Without knowing exactly how the repassivation of the bearing surface occurs and the proportion of "active" area as a function of time it is hard to accurately estimate what this effect might be but there is evidence in the literature [42] that in tribocorrosion having more rest periods and the same number of cycles significantly increased the tribocorrosion material loss, In addition Hadley [43] found that increased "stop/start" cycles in simulators increased the total damage; the mechanism for this was not fully elucidated.

Conclusions

This paper has presented an appraisal of electrochemical techniques and their potential in hip joint simulation; the focus has been on bearing surfaces but the same potential exists for their use in other important interfaces in hip joints such as the taper junction and stem/cement interface. Several areas where they can provide access to information additional to conventional gravimetric analysis are presented. The greatest benefit from inclusion of *in-situ* corrosion measurements in hip joint simulation is in pushing forward the mechanistic understanding of a complex plethora of processes occurring at the bearing surfaces and on debris.

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