'THE CORROSION OF SURGICAL IMPLANTS'

A THESIS SUBMITTED FOR THE DEGREE OF

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BY

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Summary

A study of implant corrosion has been undertaken. The work fell into two parts, the first consisted of an examination of contact corrosion on approximately four hundred used implants. Further information on these implants was obtained from the survey conducted by Dr. J. T. Scales of the Royal National Orthopaedic Hospital, Stanmore. The observations were then subjected to multi-variate statistical with two objects, to assess any factors which may lead to an increased incidence of corrosion and to discover if any factors lead to an increased rate of removal of implants.

Several implants were then examined in the scanning electron microscope and a possible mechanism for contact corrosion of stainless steel implants is presented.

The later part of the work is concerned with the in vitro testing of materials to assess their possible value in surgery. The effect of surface finish and cathodic activation on potentiostatic polarisation tests on stainless steel are described. Test procedures to evaluate the sensitivity of alloys to surface damage have been developed.

Finally the significance of the results has been assessed and suggestions made for further research.

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I. Acceptability of Implants

The criteria for implant acceptability have been outlined by many authors among them Crimmins (1). Briefly they are as follows :-

1. The implant must function mechanically without permanent deformation or failure whilst leaving the tissues unaltered.

2. The implant must not cause any local or systemic noxious effects.

3. The material used must not degrade in the tissues, (unless this is a design feature of the implant).

4. The material must be capable of being sterilised by conveniently available techniques without deleterious changes occurring.

Thus there are two series of tests to be applied to a given implant, one to assess the material and the second to test the design.

When testing the material tests may be done in two ways, in vitro or in vivo. The latter is, of course, the final criterion since every implant used is, in one sense, an in vivo test of the materials' acceptability. But in vivo testing is time consuming and expensive so that preliminary in vitro tests which can eliminate grossly unsuitable candidates and indicate areas where particular materials may be suspect are most useful.

II. In Vitro Testing

1. Mechanical tests

These involve the measurement (for metals) of the yield strength, ultimate tensile stress, ductility, Young's modulus, bend modulus and information on the fatigue properties. In addition information on the effect of cold work and various types of heat treatment is desirable. Most of this information is readily available either in tables of

materials' constants or, for new alloys, in manufacturer's publicity.

2. Corrosion tests

For alloys specifically designed for corrosion resistance some tests and results are usually quoted by the manufacturer. However these rarely relate directly to medical needs and specific tests must be devised.

The first decision which must be made is on the type of corrosive environment to be used. In the body the implant is in contact with the intercellular fluid which, to a first approximation is that of blood or serum. Whole blood is, however, a very inconvenient fluid to use. Unless chemical substances are added clotting occurs when the blood is in contact with a foreign surface, the cells present haemolyse on storage, and large quantities are difficult to obtain.

From the first, therefore, substitute solutions have been employed. Mears (2) performed an extensive series of tests in citrated whole blood, plasma and Hank's solution. He came to the conclusion that the results in these cases were indistinguishable and that Hank's solution was acceptable for in vitro corrosion testing. Similar results were obtained by Averill (3) who used whole blood, plasma, serum and Tyrode's solution. In fact Mears showed that a simple solution of sodium chloride gave reasonable results but was not as good as the more complex 'physiological' salt solutions.

The simplest test is the measurement of weight loss. This is, however, rarely used for implant materials for the following reasons :-

1. The test is time consuming, since long periods of immersion must be used.

2. The test is not sensitive to pitting corrosion nor contact corrosion, both of which have been shown to occur in stainless steel implants.

Such tests have been carried out (4,5) but the weight losses

are very small (less than 0.4 mg dm^{-2} day^{-1}) and so differences are hard to detect. Cohen (6) constructed a stressing apparatus to test the corrosion of various plate and screw assemblies in a saline solution. The implants were weighed on a balance accurate to $4x10^{-5}$ gm and then placed in the cyclic stressing apparatus for approximately three months. Controls were placed in saline solution only and also weighed at three or six month intervals.

Weight changes were always small but the steel showed greater changes than vitallium. The saline had to be replenished and when analysed showed iron at 4 ppm. The significance of this is not known. Cohen postulates the existence of fretting corrosion as well as contact corrosion in this situation. The weight losses for the mixed metal assemblies are difficult to interpret since a combined corrosion / abrasion test was used and some weight gains were noted with vitallium components.

Attention has therefore turned to electrochemical tests. The earliest proposal was the anodic back emf (ABE) of Clarke and Hickman (5,7). The ABE is measured in a cell with the test material as anode and a calomel electrode as cathode; the original electrolyte used was equine serum. The potential difference across this cell was then measured and the 'IR drop' subtracted to give the ABE. This value is independent of current over a wide range and the values obtained for different metals correlated well with their recorded weight losses. Similar results were obtained from human serum and equine whole blood.

The authors state that metals having an ABE higher than 300 mV show minimal weight loss and are therefore candidates for implant materials. All the currently used alloys fulfil this criterion. However Hensler (8) states that the test results vary with current density and specimen dimensions and that much work needs to be done

if it is to become a standard test.

Mears with Hoar (9) used more conventional electrochemical methods. Potential - time curves were plotted and it was shown that for inert or passive materials the potential slowly rose with time then stayed steady, for materials subject to pitting corrosion the potential was liable to sudden fluctuations as pitting occurred and for 'active' or corroding alloys the potential dropped with time. Thus the potential - time curve offers a qualitative way of distinguishing the three types of behaviour.

The other method they used was potentiostatic polarisation. The theory of this technique will be discussed later but in essence it consists of measuring the current necessary to polarise a test specimen to a given potential with respect to a reference electrode. The current required to achieve this is a quantitative measure of the corrosion rate existing at that potential. Mears performed the tests under true potentiostatic conditions i.e. allowing the current to reach equilibrium before recording the value but Averill (3) using a similar technique operated under non-equilibrium conditions in a form of potentiodynamic test. The relationship between the two types has been discussed by Evans (10). The various forms of potentiodynamic test have the advantage of being less time consuming since the potential is altered a a constant rate throughout the test.

A further form of electrochemical test has been developed by Greene and co-workers (11, 12, 13), the linear polarisation technique. This involves polarisation measurements very near to the corrosion potential (within 10 mV) where the relationship between current and potential is linear. The slope of this curve has the dimensions of resistance and a high resistance implies a low corrosion rate.

$$R = \frac{\Delta E}{\Delta I} = \frac{\beta_a \beta_c}{2.3 I_{corr} (\beta_a + \beta_c)}$$

β_a, β_c are Tafel const

I_{corr} is corrosion current in Amps

For isotonic saline $I_{corr} = \frac{\beta_a}{2.3R} = \frac{0.0348}{R}$

Again it has been shown that if these measurements are taken under equilibrium conditions the time to reach equilibrium increases markedly at low corrosion rates. Theory shows that if the potential is increased in a number of steps and the current read at a set time after the increase, then the slope of this line is equal to the slope of the one obtained under equilibrium conditions. This non-equilibrium technique is known as 'transient linear polarisation'.

Emneus and co-workers have used chemical means to assess corrosion. They have pioneered the use of the 'ferroxyl test' (14, 15). The specimen is immersed in a gel containing 0.9 M sodium chloride and potassium ferricyanide. When corrosion occurs coloured complexes are formed by the metal ions and the ferricyanide, blue with iron, yellow with nickel, and brown with cobalt. The effects of cold work, surface damage and metal contact were evaluated, including the results when the metals in contact were of different types. Qualitatively the results followed the pattern observed in clinical practice but the ferroxyl test is stated to be more severe than insertion into soft tissue.

A Scandinavian steel 832 SL (0.05% C, 17.5% Cr, 14 - 15% Ni, 4.5% Mo) is stated to be superior to AISI 316 which is one of the steels approved by the British Standard. However no other assessments seem to have been made of this steel. The compatability of titanium and vitallium when used together in one device is confirmed by this test as is the incompatability of the other combinations.

3. Tissue culture tests

These can be considered a sort of half - way test between in vitro and in vivo testing. Mears (16) grew rat skin fibroblasts on a culture medium with metal grids. The grids were made of nickel and coated with gold, platinum, rhodium, 316 type stainless steel or left uncoated. The cells were then analysed for the given metal using an electronprobe microanalyser. Nickel was always found intracellularly if it was present in the test medium and in view of the high toxicity of nickel (17) Mears suggests that alloys containing nickel are unsuitable for permanent implantation. Gold and platinum were not associated with the cells and only trace amounts of rhodium were found. However iron, chromium and nickel were all found in the cells from the stainless steel grids. If copper contaminated the nickel the copper again was always found associated with the cells.

Menegaux (18, 19) also worked with cultures but in assessing the toxicity of metal ions to the cells. This type of work helps in assessing the effects of any corrosion which occurs on metal implants. It does not, unfortunately, allow one to assess the effect on the whole animal of accumulated corrosion products and it has been found that the presence of implants raised the amount of metal in the hair (20).

Campbell et al (21) also used fibroblasts to ascertain the growth rate of cell cultures in the presence of metal ions. They found gold, silver, ticonium, vitallium and stainless steel to be essentially non-toxic and copper and vanadium to be highly toxic.

4. Metal transfer

A series of papers (22, 23, 24, 25, 26) has been written by Bowden, Laing and co-workers on the significance of metallic transfer between the tools and appliances used in orthopaedic surgery.

Using radio - isotope techniques they showed transfer of metal to the screws and plates, in accordance with the theory of Bowden and Tabor (27). This leads to the presence of metals of different compositions in contact in the body producing galvanic corrosion. The best composition of drivers for various screws is considered (23) and also the effects of drilling through the holes of bone plates (25).

These articles have led to the production of vitallium tipped tools for use with vitallium appliances and these are in use in many hospitals. A welcome side effect is that it has increased the tendency for vitallium, titanium and stainless steel implants to be stored separately with their own tools thus reducing the incidence of mixed metals in the same multi-component implant.

III. In Vivo Testing

1. Tissue reaction to metal

The classical means of establishing the suitability, or otherwise, of a given material for implant manufacture was by inserting small pieces into an animal and some time later observing the histological changes. These changes are well documented in the literature. Briefly, a well tolerated implant should be surrounded by a thin, fibrous sheath. This should not be attached to the implant nor contain significant quantities of fluid. The tissue outside the sheath should not contain abnormal quantities of phagocytes nor polymorphonuclear leucocytes. There should be no increase in vascularisation and the tissue structure should appear normal.

Campbell et al (28) followed up their fibroblast experiments by inserting meshes of wrought and cast ticonium and vitallium into the bones of dogs. Vitallium was not felt suitable for cranioplastic work because of its poor ductility but the ticonium alloys were candidates. However vitallium was known to be inert and functioned

as a control.

For six months all the implants functioned well, except one which was thought to be infected. After six months the cast ticonium produced chronically inflamed tissue and the screws became loose. In this case only long term implantation had rejected an alloy with reasonable electrochemical properties and which had proved non-toxic to fibroblasts. This surely indicates the necessity of final in vivo testing of materials.

As well as documenting the histological changes several authors have attempted to locate various metals in the tissue surrounding the implant. Emneus and Stenram (29) examined the reaction to various materials inserted into the muscles of chickens. After three months a histological examination was carried out. In addition, platinum was inserted and examined at intervals from 1 - 12 weeks. Turnbull pigments were observed in all the sections including the early platinum ones. However, the Turnbull positive reaction disappeared from around the platinum in a few weeks and did not persist longer than two months. All implants containing iron showed positive Turnbull pigment, some phagocytised, some extra-cellular. In addition some Turnbull negative pigment (probably containing cobalt, nickel or titanium) was found around the vitallium and titanium rods.

The pigments were further investigated (30) by X-ray fluorescence analysis. The specimens were irradiated with a 'white' X-ray source and the emergent radiation analysed. Conclusive results were not obtained but the evidence supported the theory that the black pigment found in the previous experiment around titanium implants contained some titanium and the brown pigment around the vitallium contained cobalt.

Mears (16) also studied the concentration of metal ions

around stainless steel implants. He found that nickel was invariably present to a concentration of about 2%, the concentration decreasing away from the implant. Iron was also present but its concentration was higher waay from the immediate edge of the implant. The distribution is, however, reported as variable. Chromium and molybdenum were never detected above background. It would be interesting to repeat these experiments using the X-ray microanalysis attachment to the SEM which is capable of giving better resolution or possibly the X-ray attachment in EMMA-4 which is capable of subcellular resolution.

Leventhal (31) studied tissue reaction to titanium. He reported that no adverse soft tissue reaction was observed, bone tended to adhere to screws made from titanium and that the weight loss in $2\frac{1}{2}$ months was within the limits of experimental error. A similar reaction to titanium screws is briefly reported by Wakamatsi (32).

Hickman et al (33) followed up previous work on ABE (5, 7) by correlating the ABE with histological changes. All the alloys tested with ABE greater than 300 mV were well tolerated after a year, 18:8 stainless steel having an ABE of 300 mV was partially tolerated but gave evidence of some reaction and the two metals with an ABE of less than 300 mV were rejected.

Ferguson et al (34) determined the corrosion around test metal cylinders spectrophotometrically, measuring the concentration of metal ions in the surrounding muscle. The concentrations were increased well above the controls in almost all cases. Iron was the main exception to this. Thus even 'inert' materials ionise to some extent when inserted into the body.

Histological reactions to various screws have been reported by Wagner (35), Mittelmeier reports on the histological reaction to the Smith - Peterson and Judet hip prostheses (36) and Fries (37)

uses the Turnbull pigment to assess the corrosion around a Steinman pin.

A recent paper by McFadden (38) has reviewed the tissue reactions to metals used in neurosurgery. The requirements for this type of surgery may be very different from those of orthopaedic surgery and he implanted metals in both vascular and neurological sites. Scarring is reported to occur from all the steels used, the amount varying with the known compatability of the steels. The noble metals produced so little scarring that the implants frequently migrated while sterling silver provoked a very severe reaction.

2. In vivo electrochemical tests

Two types of in vivo tests have been performed, potential - time and transient linear polarisation. The first was done by Mears (2) who obtained the curves from human volunteers with internal splints. These are pins about the thickness of a large darning needle which are inserted along the length of a digit leaving about one inch of metal free. Readings could be obtained at regular intervals for several weeks until the splints were removed.

A further series of results were obtained from a fracture plate inserted into a goat. The measurements in this case were taken via a probe inserted through a conventional cannula. On one occaision the cannula scratched the plate and the potential became unstable. It was uggested that mechanical damage may be one cause of corrosion initiation.

Colangelo (13) reports on in vivo transient linear polarisation and considers it a very useful technique for future corrosion testing of alloys.

IV. The Uses of Surgical Implants

After considering the types of test available it is useful to consider the different ways in which implants are used and thus the different requirements from the materials.

The implants inserted into the body can be divided into two classes, those whose removal would endanger or cripple the patient and those which can be removed after a given, usually reasonably short, period. The specifications applied to materials used in the first category must obviously be more stringent than those for the second. For, if comparatively young people are to have these implants inserted, then the implant should ideally have a lifetime of 50 - 60 years. In working towards this goal the quality of materials used in the second group will also improve, this will reduce the number of second operations currently performed for the routine, prophylactic removal of such implants.

1. Artificial hip joints

This is, perhaps, the most common of the permanent orthopaedic implants. In the early designs only the head of the femur was replaced. Many of these operations were quite successful and Martin (39) reported three patients who had had prostheses functioning for 16 years. These were manufactured from En 58J (18:8 Mo) and he reports no tendency to acetabular penetration but changes in bone structure in that part of the femur containing the stem.

Much work has been sone on the design of new hip joints, both for replacement of the femoral head only, and for total joint replacement. One of the most outstanding pieces of basic research in this connection was that of Rydell (40). Two specially manufactured hip joints were supplied with strain gauges and inserted into two volunteers. After healing had occurred and the patients were ambulatory, the wires attached to the gauges were brought through the

skin and could then be connected to suitable recorders. The forces applied to the neck of the femur during a wide range of normal movement were measured. These forces could be surprisingly high and even a gentle jog trot gave a force of 4.5 times body weight.

The action of a stick in reducing the load was quite clearly demonstrated, reducing the forces on walking to a maximum of 1.7 times body weight from an average maximum of about 4 times body weight. These figures are the basis of many biomechanical studies of artificial hip joints and, by extension of the results, the design of orthotic appliances.

All the other biomechanical work on hip joints has either been carried out in hip joint simulators or by inserting prostheses into cadaveric bones. A number of such simulators have been built in this country, one of the early ones being that at RNOH Stanmore (41). However many of the more recent ones have been designed more to investigate the wear of articular cartilage than the wear of artificial joints e.g. Clarke (42) and Swanson (43).

As well as the problems of friction and wear considerable care must be taken to ensure a firm fit of the prosthesis into the bone. One of the major causes of pain to such patients is a loosening of one or other component. The early Austin - Moore design had holes in the stem where bone chips could be inserted. It was hoped that a bony bridge would grow across the inside of the marrow cavity thus achoring the stem more firmly.

Most surgeons now use acrylic cement to anchor the prosthesis. The use of this material was pioneered by Charnley (44, 45, 46). He showed that by using this technique slip between the prosthesis and the bone could virtually be eliminated. This, he felt, would reduce much of the persistent pain. In 1968 he and his co-workers reported on a follow-up study of patients in whom this cement had been

used (47). They state that in 81% of cases (190 patients) the bone remained radiologically normal. Only 2% of patients showed potentially harmful changes and the authors feel that the use of the cement is therefore justified.

Scales (48) considered whether the cement actually attached chemically to the bone or whether it was merely a very well fitting plug and came to the conclusion that it was the latter. Thus the function of the cement is to distribute the load over a large surface area and to provide a solid fixation of the prosthesis.

Wilson (49) considered the problem of the fixation of the acetabular component and described the development of the Stanmore metal on metal total hip joint. Three divergent spikes, grouted in acrylic cement were now used and seemed to give a reasonably good fixation.

A novel approach to the problem is that of Galante et al (50) who used sintered titanium fibre composites. They demonstrated bony ingrowth with good fixation. A projected design for a hip joint in the dog is shown in which a sleeve of composite is bonded to the solid core of the stem. Cobalt - chrome alloy samples have been manufactured in the same laboratory but test results are not given.

A further type of bone bonding is described by Beckham et al (51) using a glass - ceramic implant. This is non-porous unlike the type of ceramic used by Hubbert (52) and Smith (53). However the authors claim that by using a composition similar to hydroxyapatite preferential deposition of bone around the implant is stimulated. They suggest that further investigations of implants producing an active response should be carried out.

In this connection the stimulation of heterotopic bone growth by samples of Hydron (107) is worthy of note. The response in human bone has not so far been evaluated but may prove intersting in

the future.

Allied to the problem of fixation of hip joints is the problem of friction. A high friction coefficient produces high loads on the stem, which in turn tends to loosen the implant. Charnley decided to opt for metal on plastic hip joints for his arthritic patients. The first design used metal heads in PTFE (polytetrafluorethylene) sockets. Preliminary results were good (54) but problems developed and high density polythene is now used for the sockets. In the same paper Charnley suggests that when a femoral head is used as a replacement after femoral neck fracture the excellent results are obtained because of the effect of the intact acetabular cartilage. He contrasts those results with the results obtained in arthritic patients which are generally mediocre.

Judet when designing a hip replacement also opted for low friction and used nylon bearings. The initial results were good but the wear particles formed produced severe tissue reaction (55, 56). The only plastic now in clinical use for bearings is the high density form of polyethylene.

Many articles have been published giving the results of clinical experience and outlining the criteria used in selecting specific operations. A report of the Committee on Fractures and Traumatic Surgery of the American Academy of Orthopaedic Surgeons is worthy of note (57). The basic criterion expressed still holds today, a natural hip joint in good condition is still preferable to an artificial one. However the results obtained from artificial joints are now much more reliable and the use of primary replacement is growing.

Evaluations of large numbers of operations were carried out by Anderson et al (58), Hinchey and Day (59), Stinchfield et al (60)

and Barr et al (61). Criteria for the primary replacement of a fractured head of femur are given by the latter authors as :-

1. Poor general health contra-indicating a second operation.
2. Parkinson's disease, spastic hemiplegia or arthritis.
3. Pathological fractures.
4. A need for early ambulation because of blindness or other systemic disease.
5. Elderly patients who frequently suffer from non-union. The latter criterion is, however, felt to be only relative.

Satisfactory results were achieved in 84% of cases after one year and 90% of cases followed for more than four years with no evidence of deterioration.

Anderson again reports 80% or more patients with satisfactory results but is much more reluctant to use a prosthesis for primary replacement and is more dubious about late results than Hinchey.

Stinchfield et al do not have such a high percentage of satisfactory results and this is possibly due to the use of a different assessment system. They do, however, throw doubts on the long term success of the acrylic head Judet prosthesis which were later fully justified. In addition they publish very useful breakdowns on their results by operative procedure and various clinical factors as a guide for the future.

Barr et al publish a review of 105 patients operated on 9 - 12 years previously. On the second assessment of these patients over 80% were noted as satisfactory. However the authors point out that the prognosis is poor for patients with rheumatoid and pyogenic arthritis and not good for those with degenerative arthritis or congenital dislocation.

Thus, summarising the four papers, on a long term basis about 80%

of the patients achieved satisfactory results. The replacement hips have been found to function adequately over a period of years, the all metal ones being better in this respect than designs such as the Judet. However all these papers dealt with femoral head replacement only which according to Charnley does not yield such good results as a total replacement for arthritic patients.

2. Knee joint replacement

Several patterns of artificial knee joint exist usually based on a hinge design. Adkins (62) used the Shiers knee but found that the stem tended to loosen and there was a loss of active extension. However, when he began using acrylic resin to hold the stem, no loosening had occurred after two years. The operation had also been modified to retain the patella and the loss of active extension became minimal.

Young (63) also used a hinged vitallium prosthesis. Originally he had used the Walldius knee which was of metal and acrylic construction but found that infection, due to faulty sterilisation, was a big problem. He therefore designed a hinge prosthesis in vitallium from which satisfactory results were obtained in about 60% of cases.

Girzadas et al (64) report on a post mortem examination of a patient with a functioning vitallium prosthesis. The capsule surrounding the implant was thick and discoloured and there were marked concentrations of lymphocytes and plasma cells. Prussian blue staining revealed deposits of phagocytised iron. Spectrographic analysis of surrounding tissue showed the presence of all the constituents of the vitallium alloy. Wear could be seen on the hinge part of the joint where the vapour blasted finish was destroyed.

The operation for knee joint replacement is less common than the one for the hip. The hinge design commonly used has problems of

wear around the bolt and also fracture of the bolt. Freeman et al (43) are working on the design of a non-hinge knee replacement where a shaped femoral bearing articulates on a flat tibial one. The integrity of the joint is preserved by the muscles and ligaments normally present.

3. Finger joints

Early designs for these were based on the hinge and made of metal. Long term results were in general poor. A one piece implant in silicone rubber is now commonly used (66). They have now gained a wide acceptability and may be inserted on an outpatient basis.

4. Elbow and shoulder joints

These are not so widely used. The shoulder, although a ball and socket joint, has a much shallower socket than the hip which gives it a tendency to dislocate. All plastic and metal on plastic versions are available. Elbow joints are difficult to replace since, unlike the knee, rotation must be incorporated. Work is continuing to improve the designs.

5. Hernia repair

Large or recurrent hernias are difficult to close without some form of strengthening. Various tissues have been tried. Fascia lata strips tend to stretch although patches are reported to be satisfactory. In some large defects the amount of fascia required is too great to be practicable. Skin has also been used but unfortunately the sebaceous glands continue to function making cyst formation a troublesome problem.

Various types of prosthetic materials have been used and a report is given by Zimmerman (67). He states that metal meshes tend to become friable with subsequent mechanical irritation and the scar formed through the mesh has a tendency to stretch. Plastic meshes tend to degrade but are less likely to lead to serious injury if they

become displaced. However serum tends to accumulate aroung the meshes which makes infection a hazard.

6. Nails and rods

Moving from the permanent (joint replacement) and semi-permanent (hernia repair) we consider the temporary implant. Nails and rods are usually inserted as internal splints with the object of stabilising a fracture. Theoretically, as soon as radiological union has been shown, the implant may be removed. Thus corrosion has a different significance. In the joint replacement corrosion may be a cause of chronic inflammation (which is rare) or may cause systemic changes in the body. In the fracture repair the corrosion may delay or prevent union but since the time scale is shorter the systemic effects are less.

In fracture fixation correct positioning of the fragments is essential for correct anatomical functioning. However the role of compressive forces in promoting healing are still a matter of dispute. Kuntscher (68) developed a clover leaf nail for the fixation of long bones. To achieve firm fixation the nail should occupy as much of the intramedullary canal as possible. Since the canal changes cross-section even after reaming it is difficult to achieve the maximum utilisation of the cross-sectional area with a solid rod. The clover leaf nail is compressible in two planes and so should deform to fit the shape of the canal.

The nail may often be inserted into the femur through a stab incision without exposing the fracture site and the patient should require no external immobilisation. Early weight bearing is possible providing that a close check is kept to ensure that union is not too long delayed otherwise there is a danger of fatigue fracture.

The mechanical principles of intramedullary fixation have been summarised by Allen et al (69). They show that an open nail is

mechanically poor in torsion. However they have not yet shown the type of contact surfaces required to reduce the 'working distance' (the distance between points of contact either side the fracture line) to a minimum. The rigidity in torsion is inversely proportional to this distance and that in bending to its square. Therefore, in assessing the properties of a given nail, the working distances produced must be considered with the modulus.

Wickstrom et al (70) reviewed over 300 patients whose fractured femurs had been nailed, usually by the Kuntscher technique. Out of these 4 deaths occurred, 20 cases of infection, 10 of which were deep infections and 2 eventual cases of non-union out of 11 cases of delayed union. The authors seemed well pleased with the technique particularly in the case of pathological fractures where the reduction of morbidity and ease of nursing offer considerable advantages.

7. Plates and screws

For some fractures a plate held onto the bone with screws is preferred to intramedullary nailing. In fractures of the neck of the femur a pin is inserted up the centre of the neck and an attached plate screwed onto the shaft. It may be an integral arrangement such as that of the Wainwright Spline or a composite device as in the Nissen Off - Set design. The introduction of these types of implants gives rise to two further sets of problems :-

1. The ability of screws to retain a hold in bone.

2. Metal to metal contact leading to the possibility of fretting and / or crevice corrosion.

Peterson in 1947 (71) reviewed the deficiencies in the then current orthopaedic practice. Poor design and workmanship was very evident and materials were very variable both in hardness and composition. Venable and Stuck (72) also reviewed the materials and

design of implants at the same period. The report on design deficiencies was very similar but the materials supported by the latter included 19:9 passivated steel and tantulum. Tantulum was rejected for fracture fixation because of its mechanical properties. Recommendations on practice e.g. use of self-tapping screws or the necessity of using a tap prior to insertion were made. Some disagreement over vitallium occurred (72, 73) but this may have been due to the extreme variation between different batches.

Ansell and Scales (74) reviewed the factors affecting the holding power of screws in bone. They analyse typical causes of failure, use of wrong size drill or tap, incorrect alignment and overstressing. A torque-limiting screwdriver is described which they hope will reduce or eliminate the latter.

A report on the problem of screw holding in horses was given by Boyd et al (75). The problem of fracture fixation in horses is even more difficult than in humans and one of the major reasons for failure is screws pulling out of bone. None of the commercially available appliances satisfied their tests and they suggest that fundamental changes in the design of equine implants must be made.

Many authors have described techniques for dealing with complicated fractures with one or more separated fragments. Funk et al (76) describe the use of screws and a nail to stabilise such fractures while Sargent et al (77) used double plates in forearm fractures. However, it should be noted that the more metal placed in a bone the more meticulous the technique must be, otherwise union may actually be prevented by periosteal destruction or separation of the fragments.

One of the problems with any internal splint is that bone and splint have different mechanical properties. This leads to refracture caused by stress concentrations at points along the plate or nail.

Chrisman and Snook (78) considered the refracture of the tibia in skiers. They show that even after removal of the plate and screws any cortical weakness tends to lead to refracture when the bone is subjected to severe stress as in skiing. The use of laminography to detect any remaining cortical defects before allowing the resumption of strenuous athletics is recommended.

Parrish and Jones (79) report several cases of fracture of the femur after an arthroplasty. Most of these patients suffered loss of function as a result of the fracture. The majority of femurs fractured after a fall or were pathological fractures. In patients suffering falls the presence of a prosthesis would obviously predispose that femur to fracture to fracture but the statistical significance of the results is not evaluated unlike Chrisman (78) who gives convincing evidence that the incidence of refracture he observed could not be due to chance.

V. Clinical Case Reports

Many authors have presented clinical reports on one or more failed implants. A small number are reviewed in the next section.

Heck and Chandler (80) reported ten failures of the Judet femoral head prosthesis showing that in each case degradation of the plastic was to blame. Similar experiences by other surgeons led to the discontinuation of the composite prosthesis.

McDougall (81) reported the first malignancy in a human associated with the site of a bone plate. The plate had been inserted 30 years previously and healing had occurred. A subsequent refracture at the site of a screw hole had also healed. In 1954 the plate was shown to be detatched and angled away from the bone. A swelling had appeared at this site. At operation a grossly corroded plate was seen and also a vascular malignant growth. Amputation was refused and the

patient died within 18 months. On examination the plate was found to be 18:8 steel with 12% Cr steel screws. This appears to be the only case of its type reported.

A high percentage of implant failure was reported by Emneus (82). Out of 17 cases of fracture treated by the McLaughlin method, 6 nails and plates had to be removed after union of the fracture. In each case inflammation was found and usually sinus formation. However no bacterial culture could be obtained and healing always occurred after removal of the implant. The last two cases had biopsies taken and the results showed foreign body reaction and iron particles in the tissues. The author blamed transfer of steel from the drill to the plate (vitallium) for the reaction following the articles by Laing et al (25)

An interesting case of corrosion of a nail and plate device with a detailed examination of the possible corrosion mechanisms was described by Cohen and Hammond (83). A feature of the metallurgical is the general indecision concerning galvanic corrosion in the body. In this implant contact corrosion was not a noticeable feature and a more generalised type of corrosion occurred.

Cohen and Foultz reported a further case of gross tissue reaction due to corrosion (84). The really significant fact is that this paper was written in 1960 and an examination of the corroded pin showed it to be of type 420 whose use was contra-indicated some 20 years previously. The reason for this material still being in circulation was not given.

The deleterious effects of corrosion on the body with subsequent production of inflammation and possible secondary sepsis or milder reactions such as eczema was described by Hicks and Cater (85). In a series of 500 bone platings they report removal rates of 3% for vitallium, 20% for 18:8 SMo, 18% for mixed 18:8 SMo / En 58E / En 58M

and 56% for En 58E / En 58M. Hicks (86) also wrote a general report on the corrosion of implants for Chemistry and Industry outlining the materials in use, the conditions in the body and their subsequent interaction.

Tate (87) described reaction to mild steel in an implant inserted in the late 1930's. On post-mortem (the cause of death was not connected with the implant) an ununited fracture was found with a highly corroded remnant of a screw and plate assembly. A thick capsule, the inner lining of which was necrotic, enclosed the remnant. The bone showed rarefaction and a gross foreign body reaction and the author suggests that the corrosion may have contributed to the non-union.

An attempt to use stainless steel mesh as a chest wall replacement and its subsequent failure because of corrosion has been described by Bucknall (88). The mesh was made from 304 type stainless steel with the wires of warp and weft of different hardness. Gross corrosion had occurred in under 18 months with severe tissue reaction. The implant had to be removed and the patient died from pneumonitis. Post-mortem examination revealed a recurrence of the cancer which had cecessitated the original implant.

A series of 113 biopsies was analysed by Emneus and Stenram (89). These consisted of prophylactically extracted functioning implants and implants which had failed because of chemical or mechanical irritation and some which had failed for reasons unconnected with the foreign material. The amount of Turnbull pigment found in the tissues was much higher when the metal was removed because of chemical irritation.

VI. Metallurgical Observations on Failed Implants

Wright and Axon (90) describe loosening of screws in bone saying that a purely mechanical loosening produces a narrow bony defect whereas tissue reaction to corrosion products produces a shallow conical defect. They point out that not all 'stainless steel' screws are in fact the 18:8 SMo that are specified and that En 58M (the free machining 18:8 steel) had been supplied. The insertion of these 'mixed metals' caused electrolytic corrosion. A smaller change in electrode potential may occur if part of a device is cold-worked more than another part; this may also cause corrosion. They suggest that to avoid loosening due to corrosion all components should be of the same alloy and as far as possible in the same metallurgical state. Handling of implants must be done carefully to minimise metal transfer and surface damage.

Scales et al have written on implant corrosion (91, 92). All the implants made of non-corrosion resistant steel showed gross corrosion, three of these had been inserted post-war but all the others had been inserted considerably earlier. Eventually those implants produce chronic inflammatory reactions. They detected no corrosion of the cobalt-chrome alloys.

Their results for the 18:8 series showed that 18:8 had just over half the components slightly corroded, mainly on contact surfaces, and similar behaviour in the 18:8 Ti components. Of the 18:8 SMo components only a quarter showed corrosion, a very significant reduction. Scales states that he was unable to prove a relationship between hardness and corrosion rate.

When cannulated nails were examined half showed corrosion in the cannula. This was associated with poor finish and carburisation, which is known to reduce corrosion resistance, and the authors suggested a change in manufacturing technique.

Twelve implants were removed because of corrosion (six mild steel) and in fifteen cases corrosion may have caused the condition leading to removal. However, there was no evidence that corrosion prevented union although it may have caused delay.

In a second paper (92) the same authors consider the corrosion of Smith - Peterson hip nails. Again they found no evidence of corrosion in the cobalt-chrome alloy nails. Nine nails made from 13% Cr steel were removed and all were inserted after it had been shown to be insufficiently corrosion resistant. Two other hails made from unsuitable steel (17:2) were removed, again both were used after 18:8 SMo was recommended, one as late as 1959. Eleven out of 69 items had been incorrectly labelled for alloy (17%) which is a very high proportion.

Considering the 18:8 SMo nails, 9 out of 30 showed corrosion which is a similar percentage to the one quoted in the previous paper (91). Once again hardness was not found to correlate with corrsion rate.

Cohen (93, 94) has discussed in general terms the reasons for implant failure. He considers that the surgeon could usefully contribute to a better understanding of the causes by planning implant removal with a view to investigating the cause of failure. This would include bacteriological culture and the collection of a biopsy sample as well as the careful labelling of the implant with avoidance of further damage.

He points out that there are three people who may call a given implant a failure (94), the surgeon, the patient and the metallurgist. It is conceivable that these may disagree and so the criteria for 'failing' an implant must be specified. A problem in the USA when investigating implant failure is that surgeons are unwilling to provide information which could be used in a charge of 'failure to

honour contract' in a court of law.

Brussatis and Nonhoff (95) examined the corrosion in a number of steel plates and screws of the AO type. A high incidence of contact corrosion was observed compared to that at other sites. They claim to have shown that surface damage during insertion and also defects due to manufacturing techniques may also increase the corrosion, However, in no case did corrosion prevent union although two cases of skin necrosis were observed.

A further series of failed implants has been studied by Cahoon and Paxton (96). Eight implants were thoroughly examined, six of these were removed because of fracture. Five fractures were due to a fatigue mechanism, usually caused by faulty design or production. In one case the mechanism was obscure and the authors were unable to decide whether the mode of failure was fatigue, corrosion fatigue, or stress corrosion. A further nine implants were examined but no details were given.

It is perhaps worthy of note that five out of seven 316L implants had a molybdenum content of less than 2%, which is outside the ASTM specification. However only one of these showed pitting corrosion, the implant actually failed by fatigue, the crack initiating at a pit. Implants which were metallurgically sound performed satisfactorily. The authors therefore recommend greater attention to design, manufacture and quality control.

A large series has been studied by Colangelo and Greene (97) in which they find that 37% of components showed corrosion and 3% were fractured. That corrosion on implants is mainly caused bu metal to metal contact is shown by the incidence of 91% of multi-component devices exhibiting corrosion but only 10% of the single component ones.

Analysing corrosion incidence with the duration of implantation the indications were that the incidence of corrosion did not increase

with time although the severity of the reaction probably did.

Homsy et al (98) have also observed contact corrosion in steel appliances and felt that if rupture of the oxide film could be prevented then corrosion would be reduced. They developed and tested a reinforced fluorocarbon membrane which fitted between the counter-sink of the plate and the screw head. They report that in all cases where the membrane had remained intact no corrosion had been found.

VII. Plastics as Implants

The main competitors to metals as implants are plastics. In certain applications plastics are infinitely superior, soft tissue augmentation, blood vessel replacement and various types of indwelling tube. However, in orthopaedics, the advantages of plastics are usually outweghed by their lack of strength. As previously indicated, nylon has been used in femoral head replacement and found to provoke severe tissue reaction (55, 56). Acrylics used in the same type of prosthesis degraded or cracked (60). The main uses at present are for the acetabular cup of the Charnley prosthesis and for finger joints.

Plastics, of course, do not corrode but they have their own material's problems. Completely pure polymers provoke little or no tissue reaction (99) but very few pure polymers can be used. Most available plastics contain molecules of a range of molecular weights (ranging from the monomer to units with molecular weights of the order of 10^6 or higher) with traces of catalyst and often additives such as fillers, plasticisers, stabilisers and anti-oxidants (100). Many of these additives are toxic. Nimni (101) showed the toxicity of organo-tin complexes used as stabilisers in many PVC preparations. Reaction occurred in less than a week at concentrations as low as $1:10^9$ and dibutyl tin dilaurate proved teratogenic when injected into

egg yolk.

The problems are not confined to toxicity. Loss of strength on implantation may be marked. Nylon, for example, loses 50% of its tensile strength after one years implantation (102) and the same author stated that if radioactively labelled polyethylene is implanted the label appears in the urine after 30 days. Some plastics, of course, are intended to degrade, one example being the tissue adhesives.

A further problem is carcinogenicity. Many of the tests for reaction to implants are done on small animals and if sheet plastic is inserted into rodents then tumours develop (99, 103, 108). If the same plastic is inserted as perforated sheet or powder the incidence is either much reduced or zero. It is worth stating that no tumour production has yet been shown in man.

But, not only do plastics degrade, they may also absorb substances from the body. An exampoe is the silicone rubber balls which were used in Starr - Edwards heart valves. These functioned well for a time but then began to swell and jam in the metal cage. Careful study implicated lipid absorption into the rubber (104). They have now been replaced by balls made from titanium.

The silicone rubbers are, however, widely used. As already stated in finger joints but also in the general field of plastic surgery. Nedelman (105) reports the acceptability of injected fluid silicone. A review of the uses of silicone rubber has been prepared by Braley (106) although he fails to mention its orthopaedic uses.

A preliminary report on the development of a hydrophilic polymer - Hydron - was given by Simpson (107) in which he reports favourably on its properties. This was later qualified (108) when heterotopic bone formation in the pig demonstrated.

IMPLANT SURVEY AT THE ROYAL NATIONAL ORTHOPAEDIC HOSPITAL STANMORE

The Medical Materials and Bioengineering Group at Stanmore had collected all implants removed in the hospital over a period of ten years. These implants were fully documented and the group generously made this material available to me.

I. Description of Survey Material

The survey consisted of all implants removed at RNOH and two associated hospitals, Great Portland Street and Queen Elizabeth's Hospital, Hadfield. The latter hospital used titanium where these were available and the other two hospitals used no titanium. Thus, since only steel implants were of interest in this project, all the samples came from two hospitals.

Each implant inserted at the hospitals was accompanied by a form detailing the date, type of impoant inserted, the patient's name, hospital number, age and sex, and details of the condition treated. This form was sent to the research group and filed until the implant was removed.

On removal, each component of the implant was placed in a separate sterile jar and sent for bacteriological investigation. Each screw was numbered, screw number one being the most proximal. In the case of plates which could be inserted either way up, hole number one (again the most proximal) was marked with a nylon thread. After culture the implants were autoclaved to eliminate the risk of viral hepatitis. Unfortunately this coagulated any blood or serum on the implant surface and the deposit had then to be removed. This could be difficult and the usual procedure was to soak the components overnight in an enzyme solution and then to scrub them with a soft brush.

The case notes of patients were then obtained from Medical Records and the remainder of the clinical information put onto the record sheet. Each component was then examined for corrosion under a low power binocular microscope and the X-rays examined to see if the corrosion had any detectable influence on the bone.

The hardness of each component was then determined using a Vickers Diamond Pyramid Indentor. The diameter and pitch of thread was measured for each screw and the implants despatched for chemical analysis. This was done at Firth Brown's steel works for the steel implants and at B.N.F. for the remainder. Both groups used a spark test only doing a more accurate analysis if the spark test indicated that the composition lay outside the British Standard Specification.

The information was then transferred to a feature card index. Each card then represented a 'feature' of the implant e.g. corrosion present on hole 1 and each implant showing this feature would have a hole punched through its number. Thus, tabulations could be carried out by placing the cards over a coloured light source and counting the number of spots.

II. Material Used for Statistical Analysis

It was decided to only include those stainless steel implants where the screws and plates conformed to British Standard Specification. Types of implants where only a small number appeared in the survey were also excluded because of difficulty in drawing meaningful conclusions from very small samples.

After considering the remainder it was decided to concentrate on six types of implants, Sherman and Burns bone plates, Wainwright and Nissen hip splines and McKee and Nissen - McKee hip nails. The Nissen - McKee set also included Nissen Off - Set plates which were classified in the same 'feature' by the Stanmore group.

III. Examination of Implants in the Binocular Microscope

The original intention was to assess the degree of corrosion of each implant by counting the corrosion pits on the surface. However, after examining two or three implants under a binocular microscope it became obvious that this would not be possible.

Some other means of assessing the corrosion was therefore sought and eventually a system of grading was devised. This suffers from the disadvantage that it is subjective and cannot be checked by an independent observer. When implants were re-examined only very small differences were found in the grading so that the assessment is at least self-consistent.

The final system was to allocate six grades to the corrosion, 1 being essentially uncorroded and 6 showing gross and massive corrosion. To indicate position within these categories + and - signs were used. Finally therefore there were 16 classifications possible (grade 6 was used without subdivision). On re-grading a selection of implants no re-grade differed from the original by more than one class.

Each hole and screw was assessed separately and in cases where a separate nail bolted to a plate was used, each contact surface. Thus the number of surfaces assessed was six for the Wainwright and Nissen Splines, eight for the Sherman and Burns bone plates (larger plates were not included in the material), and eleven for the McKee and Nissen - McKee devices. This naturally broke the implants into three main groups according to the number of contact surfaces present. In addition the non-contact surfaces were examined but less than 1% showed visible corrosion and in only one case was this significant.

Qualitative observations

When considering a screw and its matching hole the shape of the corroded areas was usually very similar. In fact, in occasional cases where the screws had not been labelled in theatre the corroded areas were matched in order to assign numbers to the screws.

There were two very noticeable patterns of corrosion on bone plates. The first was a single thin ring of corrosion around the countersink and if the X-rays were consulted the screws were invariably almost perpendicular to the axis of the plate. The other consisted of a patch of corrosion on one side of the countersink and almost opposite a patch on the vertical hole. This was caused by surgeons attempting to obtain extra rigidity by putting the screws at an angle to the plate which caused asymmetric contact. In early implants there were cases where the shaft of the screw was the correct size for the hole but the countersink was not correctly matched. This produced recognisable changes in the normal corrosion patterns.

Initially some difficulty was experienced in distinguishing serum which had not been removed from crevices in the surfaces from corrosion products. On closer examination the serum deposits usually had a more fibrous appearance and parts of the deposit were not attached to the metal. These deposits proved particularly troublesome if they occurred on finishing defects and then the only way to be certain was to either re-clean the component or to take an orange stick and gently rub the deposit while observing the results under the microscope.

The surface finish of many of the implants was poor, especially the early ones. The screw holes of plates usually showed machining marks and screws were, in general, badly machined. Threads were frequently not cleanly cut and slots in the head often had pieces of metal still attached. These pieces were usually sharp and it is

conceivable that if they were being handled without screw-holders they could snag the surgeon's gloves.

Many plates showed evidence of damage from tools used in the operating theatre but it was not always clear whether this had been inflicting while inserting or removing the implant. One type of damage was very noticeable and that was caused by drills. The usual practice when inserting a bone plate is to hold the plate onto the bone using bone holders and then to drill a hole (usually 1 or 4) using the plate as a drill guide. A screw is then inserted and the process repeated on the other side of the fracture. The bone holders are then removed and the remaining holes drilled. It is not uncommon for the drill to slip slightly during this process and part of the surface of the hole is then removed.

Signs of scratches caused by slipping screwdrivers are also common. Some of these are made while removing the screw but others are made duing its insertion. Many screws are still manufactured with single slots and there seems some resistance to a general use of non- slip screwheads.

When discussing the general problem of handling implants in the theatre with various surgeons a variety of attitudes was apparent. In generalmost surgeons would handle the implants more carefully if the procedure was no more complex than at present and took no longer. As one surgeon explained, "If I put in 30 screws in the course of a list, which is not uncommon, and doing it your way takes two minutes longer per screw then that list takes an extra hour. To get every one to do it properly it has to be easier to do it that way."

It is also very easy for the metallurgist or engineer to get this out of perspective. The vast majority of implant operations are successful, despite any shortcomings in surgical technique. A more profitable approach would seem to be in identifying those areas

where care is essential, persuading the surgeons to use better techniques there and then gradually extend these to all operations.

IV. Information Obtained from the Feature Cards

The first set of information obtained was the length of time the implant had been in the body. This was then expressed in months. The second vital piece of information was the reason for its removal. In children, for example, implants are rarely left in place for more than a few years, especially if they are made of steel. There are two reasons for this, one that trouble is expected in most cases before the patients dies and the other that the presence of implants near to a growing epiphysis can interfere with normal bone growth. Therefore most implants in children are removed as a 'routine'.

Further studies were carried out and the age and sex of the patient added to the data, also the clinical condition treated by the implant. Most of the children in the Stanmore survey had Sherman plates inserted for an osteotomy to correct a congenital dislocation of the hip.

It is known that the corrosion behaviour of stainless steel may be influenced by the amount of cold work done on the metal, this in turn alters the hardness. The hardness of each component had been measured and entered on the case sheet but on the feature card it was only entered as a range. Unfortunately time did not permit the retrieval of each individual case sheet and so hardness could only be entered as a category. On casual inspection of the figures it was obvious that, in general, plates were softer than screws.

It has also been postulated that the amount of corrosion depends on whether the plate has been subject to heavy load. Sherman and Burns plates may be inserted into any of the long bones and it was hoped to compare those inserted into legs with those in arms. Bones in the

arm are usually plated only after fracture and RNOH does comparatively little accident work. This meant that the sample of such plates was very small and was insufficient for an accurate statistical comparison. The impression was that the amounts of corrosion were less but the influence of other factors could not be assessed.

STATISTICAL CALCULATIONS

On returning from the first visit to Stanmore, the data obtained was assessed and it was decided to attempt a multi-variate statistical analysis of the observed corrosion.

At this stage the only information was the grade of corrosion on each contact surface, the time in the body, the reason for removal, and the bone plated (Sherman and Burns plates only).

The system of grading the corrosion 1- to 6 is obviously unsuitable for input to a computer and so the system of 16 classes was substituted. The problem then arose of combining these classes to arrive at an overall assessment of the amount of corrosion on a given appliance. If possible, the system adopted should be independent of the number of contact surfaces involved so that comparisons between implants are possible. The arithmetic mean was adopted as the most straightforward comparison, in the first analysis this was calculated by hand but later facilities became available for calculating it in the computer as part of the analysis.

Two means were calculated for each group of implants, that for the plate alone and that for the complete appliance. By comparing the two values it was hoped to test the impression that screws tended to corrode more than plates. The results are given in Table 3:1.

The results were then analysed on the statistical package supplied with the University's computer (an Elliot 803). This package was very limited and shortly afterwards an ICL 1905 became available with a more powerful package and most of the results were recalculated using the XDS 3 statistical package. The only exception was a series of results on the Sherman plates.

On examining the results an impression was formed that Hole 4

was more corroded than Hole 1. A regression equation was calculated between the Hole number and its class of corrosion with the following results :-

Class = 0.19 H + 0.28 H = hole number

Error in coefficient is 0.03

Correlation coefficient significant at 0.1%

This is a somewhat surprising result. All these implants had been inserted into the femur, usually in osteotomies to correct congenital hip dislocations. It could not be due to manufacturing technique since the plate is symmetrical and observations showed that the orientation with respect to the manufacturer's mark was random. Therefore physiological or mechanical factors must be responsible.

Considering the physiological factors first, the most obvious variables are the electrolyte concentration and the oxygen partial pressure. There is no apparent reason for the first to vary but the second may alter with the blood supply. Since the osteotomy fracture is placed between holes 2 and 3 the variation in blood supply is unlikely to be vertical so mechanical factors are the most likely.

The plates are placed on the lateral aspect of the femur below the greater trochanter and so if the patient stands on the affected leg the plate will tend to be bent (the line of action of the centre is medial to the plate). Weight-bearing is not normally allowed until partial healing has occurred so that the effect of the fracture would be diminished. It is possible that the forces would vary in the necessary but experimental tests would need to be undertaken because the actual geometry of the situation is complex.

If the pressure on the screw in hole 4 was found to be significantly greater than on hole 1 then this observation provides evidence that pressure, and hence likely surface damage, influences the amount of corrosion.

Further evidence for the role of mechanical stress in corrosion comes from a comparison of mean corrosion for Sherman plates in the femur compared with Sherman plates in non-weight bearing bones. Only six samples were obtained but the difference is quite marked.

Femoral plates - mean = 2.5 ± 0.9 (148 samples)

Others - mean = 1.8 ± 0.8 (6 samples)

F (147, 5) =1.08

t (152) = 1.90

However there are insufficient samples for statistical significance.

When the mean corrosion for plate only and the complete appliance were compared there seemed to be a tendency for the latter to be higher. A statistical comparison was made but again the results were not significant.

Sherman plate - 2.427 ± 0.745 (148 samples)

appliance - 2.533 ± 0.841

F (147, 147) = 1.2742

t (294) = 1.1509

Wainwright plate - 2.471 ± 1.419 (34 samples)

appliance - 2.588 ± 1.417

F (33, 33) = 1.0028

t (66) = 0.3353

Burns plate - 2.294 ± 0.920 (9 samples)

appliance - 2.353 ± 0.996

F (8, 8) = 1.1720

t (16) = 0.1231

Nissen - McKee plate - 3.436 ± 1.330 (55 samples)

appliance - 3.382 ± 1.340

F (54, 54) = 1.0150

t (108) = 0.2106

McKee plate - 2.806 ± 1.327 (36 samples)

appliance - 2.694 ± 1.283

F (35, 35) = 1.0698

t (70) = 0.3596

Nissen plate - 2.1111 ± 0.928 (11 samples)

appliance - 2.222 ± 1.093

F (10,10) = 1.3872

t (20) = 0.2448

II. Regression Analysis

The object of this analysis was to see if metallurgical or clinical features affected the observed corrosion on removed implants. The data as acquired was not ideally suited for this type of analysis containing categories (reason for removal) and variables having only integral values (hardness and corrosion grades). It was felt, however, that any results obtained would at least be suggestive and could then be further investigated by more powerful techniques.

As previously stated the XDS3 statistical package was used in this analysis. A brief outline of this system will now be given.

The XDS3 package

The package has existed in several versions, each version has either corrected programme faults from previous versions or added new routines or both.

Data is input in the form of an OBSERVATION MATRIX consisting of a number of ROWS each characterised by a ROW NAME and each with the same number of variables each characterised by a COLUMN NAME. In later versions the system has accepted rows with values of one or more variables missing. Once the observations have been input either statistical calculations may be done on the raw data or

the data may be re-arranged in a more useful form.

One of the most useful sections is that governed by the TRANSFORMATION control. This allows access to most of the common Fortran arithmetic statements and places the transformed data in a separate matrix characterised by a different matrix name. This control will not work on matrices with missing values and either incomplete rows must be eliminated or the missing values must be filled in. The former may be accomplished by means of the CROSS PRODUCT control and the latter by means of a MISSING VALUES routine. There are three of these, the first puts the mean of the variable in place, the other two do a type of regression to produce a better estimate of the value. The first produces a regression equation for the first missing value in any row and substitutes the mean for any others, the second produces regression equations for all missing values.

Matrix addition may also be accomplished by means of the transformation control. Compatible matrices i.e. those with the same column names arranged in the same order may be transformed into matrices having the same name and these will be added in the store.

When an acceptable observation matrix has been produced various forms of output may be obtained, transformed observations may be printed, means which include minimum and maximum values and variance, and matrices such as the CROSS PRODUCT, COVARIANCE and CORRELATION matrices. The latter can only be produced from an 'observation' matrix without missing values but is very informative when considering the results of analysis routines.

After this various analysis routines are available, two were tried in this project, regression analysis and discriminant analysis. The first tries to estimate values of one variable by a linear

combination of other variables and the other tries to separate the observations into groups depending on the values of different variables.

There are various ways of conducting a regression analysis. If the equation is to be forced through the origin the calculation is carried out from the cross product matrix but if the best fit line is required from the covariance matrix. Then the equation may be calculated in two distinct ways, by considering the statistical significance of the coefficients or by selecting the variables to minimise the total variance. Thus there are four tactics which can be employed.

In discriminant analysis the observations must be put into groups, either by arranging the rows in order in the observation or by producing a separate matrix for each group. The latter system was used in this analysis and is most easily accomplished by use of the cross product control to multiply the whole row by one variable, if this variable can only take the values 1 or 0 then it effectively splits the observation matrix. A series of such variables will split the data into as many groups as required. The discriminant scores are then calculated and a HITS AND MISSES table may then be output. This uses the calculated discriminant scores to assign the original data to groups and the success of the system may easily be seen for if the original data cannot be accurately split then the chances of accurately splitting new data are small.

Implant survey

There were 12 groups of data in the survey, six types of implant examined on two separate occasions. On the first visit data was not collected with a view to multi-variate analysis and was later re-modelled to suit the Elliot 803 package. This data was then transferred to cards in a format suitable for XDS3 but in the process redundant information, such as a hand calculated implant corrosion grade, was also transferred. On the second visit information was recorded directly onto data sheets ready for punching. Unfortunately the order of some variables was not the same for different implant types thus the 12 groups did not have compatible observation matrices.

Since transformations were necessary it was decided to transform the matrices into the same format and then to add them. The first attempts were unsuccessful, the programme ran through to the end without error messages but when the final 'observation' matrix was output only the observations from the first of the original observation matrices appeared. After consulting the firm concerned it was learned that if row names were not numbered consecutively the first row name of any matrices to be added must be specified. This was done but without affecting the net result.

A further modification was then suggested - the use of a 'double transformation'. This involved transforming each matrix into a compatible format but each transformed matrix having a distinct name and then transforming these matrices into the final 'observation' matrix, specifying row names as before. No arithmetic alterations were made in this second transformation, merely the transfer of information from one matrix to another. Unfortunately the only change in the net result was a virtual doubling of time used!

Attempts to use the transformation to add matrices were then abandoned. Perusal of the manual showed that observation matrices could be output and input onto paper tape, still using cards to control the analysis. Plans were made to output transformed matrices onto paper tape and then to splice the tapes together. However, when output was obtained the format was not compatible with the programme input requirements so that attempt had to be abandoned also.

The use of a data handling package DAEDAL prepared by the Social Science Laboratory was then attempted. This too would produce output in the form of paper tape although its transformation facilities were more limited. Again output could not be obtained in a form compatible with the XDS3 input format.

The groups of data had therefore to be handled as separate programmes although some groups from the second visit were not analysed because insufficient numbers were present.

1. Preparation of data for analysis routines

All the sets of data contained some rows with missing values and the more powerful of the two regression routines was used to fill the gaps. The completed observation matrix was then transformed. Overall corrosion grades were calculated as previously described and information on time in the body, age and sex of the patient and reason for removal transferred into the matrix. Scales had reported (91, 92) that he was unable to find any evidence that hardness influenced the incidence of corrosion. Since one of the mechanisms by which hardness is supposed to influence corrosion is galvanic corrosion i.e. components having different hardnesses will have different potentials and so an electrochemical cell will be set up, it seemed that hardness difference was more likely to be significant than absolute values. Therefore the plate hardness was

subtracted from the hardness values of the individual components (in general plates were softer). The information on clinical condition treated was not felt to be useful since, for any one type of implant, there was insufficient variation. All the implants studied had been inserted into the femur so that information on the bone repaired was redundant.

2. Analysis routines.

A correlation matrix was output, this enabled any relationships between 'independent' variables to be investigated.

It was decided to use the covariance matrix to calculate the regression. Although, at least in theory, corrosion should be zero when insertion occurs it is not immediately obvious that when variables other than time are included the equation must pass through the origin. The arguments for the regression line passing through the origin were not felt to be sufficiently strong to suppress the intercept term although there are grounds for thinking that its value should be small.

A minimum variance analysis was chosen since the object of this was to try to predict the corrosion of an implant. The amount of attention given to a particular variable would then depend on the statistics output with its regression coefficient.

3. Results

a) Original Wainwright Splines.

The correlation matrix and regression equations are given in Table 3:1. Of the original implants 29 were carried into the final survey and the conclusions are given below.

Correlation Matrix :-

There are no significant correlations with corrosion. There is a tendency for implants where the hardness difference between components is greater to be removed earlier. Large differences in

Wainwright (first visit)

CORRELATION MATRIX

	CORRPL	CORRNX	TIMEMN	HDIFF1	HDIFF2	HDIFF3
CORRPL	.100000E 1	.947712E 0	.227711E 0	-.269746E 0	-.217539E 0	-.162686E 0
CORRNX	.947712E 0	.100000E 1	.168670E 0	-.263518E 0	-.158245E 0	-.187995E 0
TIMEMN	.227711E 0	.168670E 0	.100000E 1	-.381431E 0	-.545478E 0	-.380841E 0
HDIFF1	-.269746E 0	-.263518E 0	*-.381431E 0	.100000E 1	.732757E 0	.779149E 0
HDIFF2	-.217539E 0	-.158245E 0	*-.545478E 0	*.732757E 0	.100000E 1	.683335E 0
HDIFF3	-.162686E 0	-.187995E 0	*-.380841E 0	*.779149E 0	*.683335E 0	.100000E 1
AGEYRS	.108475E 0	.775621E- 1	-.524954E- 1	-.237317E- 1	.241530E 0	.230455E 0
FEMALE	.182136E 0	.507583E- 1	.952130E- 1	.555112E- 1	.345558E- 1	.223807E 0
ROUTIN	-.186068E 0	-.202039E 0	.567896E- 1	-.225340E 0	*-.375130E 0	*-.363726E 0
MALPSN	.104766E 0	.126010E 0	.153483E 0	.129942E 0	-.356857E- 1	.705539E- 1
MALPSN	.104766E 0	.126010E 0	.153483E 0	.129942E 0	-.356857E- 1	.705539E- 1
PAINXX	.119554E 0	.183999E 0	-.237695E 0	-.295578E 0	-.307541E- 1	-.164834E 0
PAINXX	.119554E 0	.183999E 0	-.237695E 0	-.295578E 0	-.307541E- 1	-.164834E 0
INFECT	-.223814E 0	-.246205E 0	*-.413299E 0	*.351020E 0	.241601E 0	*.318307E 0
MECHBR	-.223814E 0	-.268588E 0	* .323572E 0	*-.305639E 0	-.264520E 0	-.226837E 0
GXXXXX	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0
HXXXXX	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0

TABLE 3:1

Wainwright (first visit)

CORRELATION MATRIX

	AGEYRS	FEMALE	ROUTIN	MALPSN	MALPSN	PAINXX
CORRPL	.103475E 0	.182136E 0	-.186068E 0	.104766E 0	.104766E 0	.119554E 0
CORRNX	.775621E- 1	.507583E- 1	-.202039E 0	.126010E 0	.126010E 0	.183999E 0
TIMEMN	-.524954E- 1	.952130E- 1	.567896E- 1	.153483E 0	.153483E 0	-.237695E 0
HDIFF1	-.237517E- 1	.555112E- 1	-.225840E 0	.129942E 0	.129942E 0	-.295578E 0
HDIFF2	.241530E 0	.345558E- 1	-.375130E 0	-.356857E- 1	-.356857E- 1	-.307541E- 1
HDIFF3	.230455E 0	.223807E 0	-.363726E 0	.705539E- 1	.705539E- 1	-.164834E 0
AGEYRS	.100000E 1	.191593E 0	-.443959E 0	-.570839E- 1	-.570839E- 1	.462626E 0
FEMALE	.191593E 0	.100000E 1	-.306186E 0	-.656759E- 1	-.656759E- 1	-.357143E- 1
ROUTIN	*-.443959E 0	*-.306186E 0	.100000E 1	-.965234E- 1	-.965234E- 1	-.306186E 0
MALPSN	-.570839E- 1	-.656759E- 1	-.965234E- 1	.100000E 1	.100000E 1	-.656759E- 1
MALPSN	-.570839E- 1	-.656759E- 1	-.965234E- 1	.100000E 1	.100000E 1	-.656759E- 1
PAINXX	* .462626E 0	-.357143E- 1	* -.306186E 0	-.656759E- 1	-.656759E- 1	.100000E 1
PAINXX	* .462626E 0	-.357143E- 1	* -.306186E 0	-.656759E- 1	-.656759E- 1	.100000E 1
INFECT	-.110095E 0	-.136487E 0	-.514344E- 1	-.139010E 0	-.139010E 0	-.136487E 0
MECHBR	.171618E 0	-.136487E 0	-.514344E- 1	-.139010E 0	-.139010E 0	-.136487E 0
GXXXXX	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0
HXXXXX	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0

TABLE 3:1

Wainwright (first visit)

CORRELATION MATRIX

	PAINXX	INFECT	MECHBR	GXXXXX	HXXXXX
CORRPL	.119554E 0	-.223814E 0	-.223814E 0	.000000E 0	.000000E 0
CORRNX	.183999E 0	-.246205E 0	-.268538E 0	.000000E 0	.000000E 0
TIMEMN	-.237695E 0	-.413299E 0	.323572E 0	.000000E 0	.000000E 0
HDIFF1	-.295578E 0	.351020E 0	-.305639E 0	.000000E 0	.000000E 0
HDIFF2	-.307541E-1	.241601E 0	-.264520E 0	.000000E 0	.000000E 0
HDIFF3	-.164834E 0	.318307E 0	-.226837E 0	.000000E 0	.000000E 0
AGEYRS	.462626E 0	-.110095E 0	.171618E 0	.000000E 0	.000000E 0
FEMALE	-.357143E-1	-.136487E 0	-.136487E 0	.000000E 0	.000000E 0
ROUTIN	-.300186E 0	-.514344E-1	-.514344E-1	.000000E 0	.000000E 0
MALPSN	-.656759E-1	-.139010E 0	-.139010E 0	.000000E 0	.000000E 0
MALPSN	-.656759E-1	-.139010E 0	-.139010E 0	.000000E 0	.000000E 0
PAINXX	.100000E 1	-.136487E 0	-.136487E 0	.000000E 0	.000000E 0
PAINXX	.100000E 1	-.136487E 0	-.136487E 0	.000000E 0	.000000E 0
INFECT	-.136487E 0	.100000E 1	-.740741E-1	.000000E 0	.000000E 0
MECHBR	-.136487E 0	-.740741E-1	.100000E 1	.000000E 0	.000000E 0
GXXXXX	.000000E 0	.000000E 0	.000000E 0	.100000E 1	.000000E 0
HXXXXX	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.100000E 1

TABLE 3:1

Wainwright (first visit)

Dependent variable is corrosion degrees of freedom start at 27

VAR NAME	REGRESSION COEFF	STANDARD ERROR	CONFIDENCE INTERVAL	T STAT	PART CORR	MULTIPLE CORRELATION	E S S
HDIFF1 =	0.6635018	.467436E 0		1.42	-0.26		.119111E 3
INTERCEPT TERM		3.4683853					

VAR NAME	REGRESSION COEFF	STANDARD ERROR	CONFIDENCE INTERVAL	T STAT	PART CORR	MULTIPLE CORRELATION	E S S
HDIFF1 =	0.8202229	.469652E 0		1.75	-0.32	0.202	.114249E 3
ROUTIN =	3.0611881	.207176E 1		1.48	-0.28	0.264	.110840E 3
RESIDUAL ERROR	.193314E 1						
MULT CORR	0.376						
INTERCEPT TERM		3.8814110					

TABLE 3:1

Wainwright (first visit)

VAR NAME	REGRESSION COEFF	STANDARD ERROR	CONFIDENCE INTERVAL	T STAT	PART CORR	MULTIPLE CORRELATION	E S S
HDIFF1 =	0.6701004	.5037646 0	.	1.33	-0.26	0.327	.106386E 3
ROUTIN =	3.0068679	.2083596 1		1.44	-0.28	0.310	.107630E 3
INFECT =	1.3333339	.1560926 1		0.85	-0.17	0.376	.102254E 3

RESIDUAL ERROR .199353E 1

MULT CORR 0.407

INTERCEPT TERM 3.6769685

VAR NAME	REGRESSION COEFF	STANDARD ERROR	CONFIDENCE INTERVAL	T STAT	PART CORR	MULTIPLE CORRELATION	E S S
HDIFF1 =	0.7262831	.5180492 0		1.40	-0.28	0.334	.105793E 3
ROUTIN =	2.9218529	.2114146 1		1.38	-0.27	0.337	.105567E 3
MALPSN	0.5921440	.9542516 0		0.62	0.13	0.407	.993538E 2
INFECT =	1.1359534	.1612176 1		0.70	-0.14	0.403	.998078E 2

RESIDUAL ERROR .201851E 1

MULT CORR 0.423

INTERCEPT TERM 3.6481360

TABLE 3:1

have a slight tendency to be associated with infection. Of the other significant results the main effect is to confirm ideas on standard clinical practice e.g. young people have a greater incidence of prophylactic removal of implants.

Regression equations :-

There are no statistically significant results, this may be anticipated from a study of the correlation matrix.

b). Nissen - McKee hip nails

The correlation matrix is given in Table 3:2. There are 55 of the implants in the analysis. Again there is a tendency for a large difference in hardness between screws and plate to lead to an earlier removal and some evidence of it leading to increased corrosion. Mechanical breakage of the implant seems to occur in implants with less corrosion. This time there is some evidence that increased hardness difference is not associated with infection.

Comparing this matrix with the one for implants studied on the second visit (16 implants) it is immediately obvious that there are far fewer significant correlations. An interesting one is the association of increased corrosion with implants removed because of pain. A low hardness difference seems to lead to fewer mechanical breakages but this is possibly because of harder plates than softer screws.

Considering the regression equations for the implants from the first visit, hardness difference seems the most significant factor in accounting for the observed corrosion. An improvement is obtained when the age of the patient is included.

Comparing this with the early stages of regression in the set of implants from the second visit it can be seen that although pain is the single variable which accounts for the most variance a combination of routine removal and the patient being of the male

Nissen - McKee (first visit)

CORRELATION MATRIX

	TIMEMN	CORRNX	HDIFFN	HDIFF4	HDIFF3	HDIFF2
TIMEMN	.100000E 1	-.674749E-1	.225045E 0	-.277486E 0	-.287089E 0	-.224313E 0
CORRNX	-.674749E-1	.100000E 1	-.428588E-1	.989755E-1	.276414E 0	.195123E 0
HDIFFN	* .225045E 0	-.428588E-1	.100000E 1	.389178E 0	.246292E 0	.382305E 0
HDIFF4	*-.277486E 0	.989755E-1	*.389178E 0	.100000E 1	.724785E 0	.680142E 0
HDIFF3	*-.287089E 0	*.276414E 0	*.246292E 0	*.724785E 0	.100000E 1	.750640E 0
HDIFF2	-.224313E 0	.195123E 0	*.382305E 0	*.680142E 0	*.750640E 0	.100000E 1
HDIFF1	-.148262E 0	*.264180E 0	*.322293E 0	*.687977E 0	*.754904E 0	* .811713E 0
AGEYRS	.107560E 0	*.270368E 0	*-.243951E 0	-.144027E 0	-.112210E 0	-.209999E 0
FEMALE	.194816E 0	.347412E-2	.170238E 0	-.191240E 0	*-.264472E 0	* -.328421E 0
MALEXX	-.180127E 0	-.246777E-1	-.508394E-1	* .342905E 0	* .285408E 0	* .350885E 0
HXXXXX	-.121375E 0	-.202846E 0	* .426554E 0	* .272205E 0	* .291776E 0	* .482682E 0
GXXXXX	-.145142E 0	*-.230064E 0	-.896342E-1	-.527217E-1	-.682153E-1	-.720015E-1
MECHBR	-.976083E-1	*-.230064E 0	-.896342E-1	-.527217E-1	.111780E 0	.112893E 0
INFECT	-.769901E-1	.135738E 0	*-.287567E 0	-.748850E-1	-.128080E 0	* -.254022E 0
PAINXX	.211494E 0	.155242E 0	* .293894E 0	.192015E 0	-.118656E-2	.144769E 0
MALPSN	-.164481E 0	-.255172E-1	-.128522E 0	.179787E 0	.925877E-1	.906166E-1
ROUTIN	.981890E-1	-.224583E-1	-.514497E-2	.407126E-1	.159332E 0	.291967E-1

TABLE 3:2

Nissen - McKee (first visit)

CORRELATION MATRIX

	HDIFF1	AGEYRS	FEMALE	MALEXX	HXXXXX	GXXXXX
TIMEMN	-.148262E 0	.107560E 0	.194816E 0	-.180127E 0	-.121375E 0	-.145142E 0
CORRNX	.264180E 0	.270368E 0	.347412E- 2	-.246777E- 1	-.202846E 0	-.230064E 0
HDIFFN	.322293E 0	-.243951E 0	.170238E 0	-.508394E- 1	.426554E 0	-.896342E- 1
HDIFF4	.687977E 0	-.144027E 0	-.191240E 0	.342903E 0	.272205E 0	-.527217E- 1
HDIFF3	.754904E 0	-.112210E 0	-.264472E 0	.285408E 0	.291776E 0	-.682153E- 1
HDIFF2	.811713E 0	-.209999E 0	-.328421E 0	.350885E 0	.482682E 0	-.720015E- 1
HDIFF1	.100000E 1	-.897656E- 1	-.155366E 0	.210603E 0	.273966E 0	-.382963E- 1
AGEYRS	-.897656E- 1	.100000E 1	.519963E- 1	-.653251E- 1	-.533102E 0	-.406637E 0
FEMALE	-.155366E 0	.519963E- 1	.100000E 1	-.961621E 0	-.164614E 0	.116823E 0
MALEXX	.210603E 0	-.653251E- 1	* -.961621E 0	.100000E 1	.171184E 0	-.112340E 0
HXXXXX	* .273966E 0	* -.533102E 0	-.164614E 0	.171184E 0	.100000E 1	-.192308E- 1
GXXXXX	-.382963E- 1	* -.406637E 0	.116823E 0	-.112340E 0	-.192308E- 1	.100000E 1
MECHBR	.117835E 0	-.167029E- 1	-.164614E 0	.171184E 0	-.192308E- 1	-.192308E- 1
INFECT	-.690927E- 1	.709376E- 1	-.103241E 0	.127119E 0	-.830864E- 1	-.830864E- 1
PAINXX	.735498E- 1	.179740E 0	* .248585E 0	-.198825E 0	-.185507E 0	-.185507E 0
MALPSN	.201570E 0	-.192519E- 1	-.121115E 0	.134465E 0	-.447572E- 1	* .429669E 0
ROUTIN	.567909E- 1	-.464261E- 1	-.341232E- 1	.420155E- 1	-.274618E- 1	-.274618E- 1

TABLE 3:2

Nissen - McKee (first visit)

CORRELATION MATRIX

	MECHBR	INFECT	PAINXX	MALPSN	ROUTIN
TIMEMN	-.976083E-1	-.769901E-1	.211494E 0	-.164481E 0	.981890E-1
CORRNX	-.230064E 0	.135738E 0	.155242E 0	-.255172E-1	-.224583E-1
HDIFFN	-.896342E-1	-.287567E 0	.293894E 0	-.128524E 0	-.514497E-2
HDIFF4	-.527217E-1	-.748850E-1	.192015E 0	.179787E 0	.407126E-1
HDIFF3	.111780E 0	-.128080E 0	-.118656E-2	.925877E-1	.159332E 0
HDIFF2	.112893E 0	-.254022E 0	.144769E 0	.906166E-1	.291967E-1
HDIFF1	.117835E 0	-.690927E-1	.735498E-1	.201570E 0	.567909E-1
AGEYRS	-.167029E-1	.709376E-1	.179740E 0	-.192519E-1	-.464261E-1
FEMALE	-.164614E 0	-.103241E 0	.248585E 0	-.121115E 0	-.341232E-1
MALEXX	.171184E 0	.127119E 0	-.198825E 0	.134463E 0	.420153E-1
HXXXXX	-.192308E-1	-.830864E-1	-.185507E 0	-.447572E-1	-.274618E-1
GXXXXX	-.192308E-1	-.830864E-1	-.185507E 0	.429669E 0	-.274618E-1
MECHBR	.100000E 1	-.830864E-1	-.185507E 0	-.447572E-1	-.274618E-1
INFECT	-.830864E-1	.100000E 1	-.533761E 0	-.193373E 0	-.118648E 0
PAINXX	-.185507E 0 *	-.533761E 0	.100000E 1	-.279364E-1	-.264906E 0
MALPSN	-.447572E-1	-.193373E 0	-.279364E-1	.100000E 1	-.639137E-1
ROUTIN	-.274618E-1	-.118648E 0 *	-.264906E 0	-.639137E-1	.100000E 1

TABLE 3:2

Nissen - McKee (second visit)

CORRELATION MATRIX MAT999

	TIMEMN	CORRNX	HDIFF1	HDIFF2	HDIFF3	HDIFF4
TIMEMN	.100000E 1	-.488804E- 1	-.140200E 0	-.255673E 0	-.141528E 0	-.387238E 0
CORRNX	-.488804E- 1	.100000E 1	.207746E 0	-.381917E- 1	.670131E- 1	-.159169E 0
HDIFF1	-.140200E 0	.207746E 0	.100000E 1	*.848229E 0	.794374E 0	.768508E 0
HDIFF2	-.255673E 0	-.381917E- 1	*.848229E 0	.100000E 1	.940306E 0	.849732E 0
HDIFF3	-.141528E 0	.670131E- 1	*.794374E 0	*.940306E 0	.100000E 1	.709608E 0
HDIFF4	-.387238E 0	-.159169E 0	*.768508E 0	*.849732E 0	*.709608E 0	.100000E 1
HDIFFN	-.116714E 0	.173464E 0	*.759190E 0	*.717185E 0	*.677419E 0	*.733663E 0
ROUTIN	.144559E 0	-.426411E 0	.951105E- 1	.160380E 0	.139122E 0	.121032E 0
MALPSN	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0
PAINXX	.121040E 0	*.472571E 0	.169450E 0	.156300E 0	.201319E 0	-.536149E- 1
INFECT	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0
MECHBR	-.120035E 0	-.388177E 0	*-.525279E 0	-.206205E 0	-.231869E 0	-.155612E 0
GXXXXX	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0
HXXXXX	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0
AGEYRS	.251267E- 1	.921740E- 1	-.180745E 0	.350171E- 1	.193299E- 1	.122520E 0
FEMALE	-.373531E 0	-.363749E 0	-.605111E- 2	.687343E- 1	-.463739E- 1	.328515E 0
MALEXX	.373531E 0	.363749E 0	.605111E- 2	-.687343E- 1	.463739E- 1	-.328515E 0

TABLE 3:2

Nissen - McKee (second visit)

CORRELATION MATRIX MAT999

	HDIFFN	ROUTIN	MALPSN	PAINXX	INFECT	MECHBR
TIMEMN	-.116714E 0	.144559E 0	.000000E 0	.121040E 0	.000000E 0	-.120085E 0
CORPNX	.173464E 0	-.426411E 0	.000000E 0	.472571E 0	.000000E 0	-.388177E 0
HDIFF1	.759190E 0	.951105E- 1	.000000E 0	.169450E 0	.000000E 0	-.525279E 0
HDIFF2	.717183E 0	.160380E 0	.000000E 0	.156300E 0	.000000E 0	-.206203E 0
HDIFF3	.677419E 0	.139122E 0	.000000E 0	.201319E 0	.000000E 0	-.231869E 0
HDIFF4	.733663E 0	.121032E 0	.000000E 0	-.536149E- 1	.000000E 0	-.155612E 0
HDIFFN	.100000E 1	.231869E 0	.000000E 0	.287599E- 1	.000000E 0	-.139122E 0
ROUTIN	.231869E 0	.100000E 1	.000000E 0	-.537484E 0	.000000E 0	-.666667E- 1
MALPSN	.000000E 0	.000000E 0	.100000E 1	.000000E 0	.000000E 0	.000000E 0
PAINXX	.287599E- 1	*-.537484E 0	.000000E 0	.100000E 1	.000000E 0	.124035E 0
INFECT	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.100000E 1	.000000E 0
MECHBR	-.139122E 0	-.666667E- 1	.000000E 0	.124035E 0	.000000E 0	.100000E 1
GXXXXX	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0
HXXXXX	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0
AGEYRS	-.966496E- 1	-.120417E 0	.000000E 0	.173084E 0	.000000E 0	.277385E- 1
FEMALE	-.139122E 0	-.333333E 0	.000000E 0	-.413449E- 1	.000000E 0	.200000E 0
MALEXX	.139122E 0	.333333E 0	.000000E 0	.413449E- 1	.000000E 0	-.200000E 0

TABLE 3:2

Nissen - McKee (second visit)

CORRELATION MATRIX MAT999

	GXXXXX	HXXXXX	AGEYRS	FEMALE	MALEXX
TIMEMN	.000000E 0	.000000E 0	.251267E- 1	-.373531E 0	.373531E 0
CORRNX	.000000E 0	.000000E 0	.921740E- 1	-.363749E 0	.363749E 0
HDIFF1	.000000E 0	.000000E 0	-.180745E 0	-.605111E- 2	.605111E- 2
HDIFF2	.000000E 0	.000000E 0	.350171E- 1	.687343E- 1	-.687343E- 1
HDIFF3	.000000E 0	.000000E 0	.193299E- 1	-.463739E- 1	.463739E- 1
HDIFF4	.000000E 0	.000000E 0	.122520E 0	.328515E 0	-.328515E 0
HDIFFN	.000000E 0	.000000E 0	-.966496E- 1	-.139122E 0	.139122E 0
ROUTIN	.000000E 0	.000000E 0	-.120417E 0	-.333333E 0	.333333E 0
MALPSN	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0
PAINXX	.000000E 0	.000000E 0	.173082E 0	-.413449E- 1	.413449E- 1
INFECT	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0
MECHBR	.000000E 0	.000000E 0	.277885E- 1	.200000E 0	-.200000E 0
GXXXXX	.100000E 1	.000000E 0	.000000E 0	.000000E 0	.000000E 0
HXXXXX	.000000E 0	.100000E 1	.000000E 0	.000000E 0	.000000E 0
AGEYRS	.000000E 0	.000000E 0	.100000E 1	.120417E 0	-.120417E 0
FEMALE	.000000E 0	.000000E 0	.120417E 0	.100000E 1	-.100000E 1
MALEXX	.000000E 0	.000000E 0	-.120417E 0	-.100000E 1	.100000E 1

TABLE 3:2

Nissen - McKee - first visit

VAR NAME	REGRESSION COEFF	STANDARD ERROR	CONFIDENCE INTERVAL	T STAT	PART CORR	MULTIPLE CORRELATION	E S S
HDIFF3	0.6647282	.325623E 0		2.05	0.28		.181935E 3
RESIDUAL ERROR	.181515E 1						
MULT CORR	0.276						
INTERCEPT TERM		2.1571073					

VAR NAME	REGRESSION COEFF	STANDARD ERROR	CONFIDENCE INTERVAL	T STAT	PART CORR	MULTIPLE CORRELATION	E S S
HDIFF3	0.7470927	.312110E 0		2.39	0.32	0.270	.168636E 3
AGEYRS	0.0429769	.182741E- 1		2.35	0.32	0.276	.168034E 3
RESIDUAL ERROR	.173953E 1						
MULT CORR	0.410						
INTERCEPT TERM	=	0.3453373					

TABLE 3:2

sex are the best pair. As variables are added into the regression set different combinations are used to achieve the best result, on examination of the output for the number of equations tried before the best combination was selected it became obvious that there were many combinations yielding similar results. The final equation in the set (5 variables) is worthy of note, all the variables have t-statistics which are significant at 5% and 3 are significant at 1%. The opposite senses of the dependence of corrosion on hardness difference on hole 4 and on the nut are explained by the very high positive correlation between the two variables.

c) McKee - first visit

Again hardness difference appears important, a greater difference tends to lead to earlier removal of the implant, but the less likely it is to be removed because of pain.

Considering the regression equations, the only two factors which seem important in assessing the corrosion appear to be the time of implantation and the various hardness differences. Too much reliance cannot be placed on the details of the equations because of the very high correlations which exist between the various hardness differences but the importance is obvious.

d) Nissen - first visit

There are only 9 observations in this set so that it is difficult to interpret the results accurately. Corrosion is negatively correlated with hardness difference, which is the opposite sense to many types of implants. Routine removals also seem to have more corrosion than others but the sample is so small that this is probably a spurious correlation.

Of the regression equations the most useful one is probably the one with 5 variables. Apart from female all the included

McKee - first visit

	TIMEMN	CORRNX	HDIFF1	HDIFF2	HDIFF3	HDIFF4
TIMEMN	.100000E 1	.370064E 0	-.334262E 0	-.288297E 0	-.131551E 0	-.257938E 0
CORRNX	.370064E 0	.100000E 1	-.255306E 0	-.270568E 0	-.265376E 0	-.351622E-1
HDIFF1	-.334262E 0	-.255306E 0	.100000E 1	.588799E 0	.634718E 0	.768286E 0
HDIFF2	-.288297E 0	-.270568E 0	.588799E 0	.100000E 1	.593539E 0	.682866E 0
HDIFF3	-.131551E 0	-.265376E 0	.634718E 0	.593539E 0	.100000E 1	.727294E 0
HDIFF4	-.257938E 0	-.351622E-1	.768286E 0	.682866E 0	.727294E 0	.100000E 1
HDIFFN	-.633416E-1	-.166731E 0	.298285E 0	.193487E 0	.293218E 0	.320791E 0
AGEYRS	.243277E-2	-.165653E 0	.350417E-1	-.471514E-1	.212825E-1	.201889E-1
FEMALE	.144315E 0	.107205E 0	.102293E 0	.175079E 0	.191489E 0	.135953E 0
MALEXX	-.144315E 0	-.107205E 0	-.102293E 0	-.175079E 0	-.191489E 0	-.135953E 0
ROUTIN	-.143567E 0	.232172E-1	.240308E 0	.404376E 0	.406268E-1	.123971E 0
MALPSN	-.127972E 0	.662357E-1	-.758184E-1	.223362E-1	-.120218E-1	-.987861E-1
PAINXX	.212580E 0	.132721E 0	-.283647E 0	-.268384E 0	-.349127E 0	-.121885E 0
INFECT	-.161467E 0	-.674510E-1	.251095E-1	-.526041E-1	-.143865E-1	-.559920E-2
MECHBR	-.217232E 0	-.809101E-1	-.510368E-1	-.742154E-1	.406268E-1	-.213096E-1
GXXXXX	-.587392E-1	-.164510E 0	.117403E 0	.584120E-1	.773319E-1	.150811E 0
HXXXXX	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0

TABLE 3:3

McKee - first visit

CORRELATION MATRIX

	HDIFFN	AGEYRS	FEMALE	MALEXX	ROUTIN	MALPSN
TIMEMN	-.633416E- 1	.243277E- 2	.144315E 0	-.144315E 0	-.148567E 0	-.127972E 0
CORONX	-.166731E 0	-.165653E 0	.107205E 0	-.107205E 0	.282172E- 1	.662357E- 1
HDIFF1	.293285E 0	.350417E- 1	.102293E 0	-.102293E 0	.240308E 0	-.758184E- 1
HDIFF2	.193487E 0	-.471514E- 1	.175079E 0	-.175079E 0	.404876E 0	.223362E- 1
HDIFF3	.293218E 0	.212825E- 1	.191489E 0	-.191489E 0	.406268E- 1	-.120218E- 1
HDIFF4	.320791E 0	.201889E- 1	.135953E 0	-.135953E 0	.123971E 0	-.987861E- 1
HDIFFN	.100000E 1	.170721E 0	-.352189E- 1	.352189E- 1	-.168086E 0	.294058E 0
AGEYRS	.170721E 0	.100000E 1	.214722E 0	-.214722E 0	-.394955E 0	-.441694E- 1
FEMALE	-.352189E- 1	.214722E 0	.100000E 1	-.100000E 1	.614341E- 2	-.150586E 0
MALEXX	.352189E- 1	-.214722E 0	-.100000E 1	.100000E 1	-.614341E- 2	.150586E 0
ROUTIN	-.168086E 0	-.394955E 0	.614341E- 2	-.614341E- 2	.100000E 1	-.139272E 0
MALPSN	.294058E 0	-.441694E- 1	-.150586E 0	.150586E 0	-.139272E 0	.100000E 1
PAINXX	-.880994E- 1	.438755E- 1	.997890E- 1	-.997890E- 1	-.297560E 0	-.138680E 0
INFECT	-.250625E 0	.916750E- 1	.106486E 0	-.106486E 0	-.166667E 0	-.247594E 0
MECHBR	.121077E 0	.325484E 0	-.208876E 0	.208876E 0	-.937500E- 1	-.139272E 0
GXXXXX	.273257E- 1	.131867E 0	.123876E 0	-.123876E 0	-.525105E- 1	-.780076E- 1
HXXXXX	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0

TABLE 3:3

McKee -first visit

CORRELATION MATRIX

	PAINXX	INFECT	MECHBR	GXXXXX	HXXXXX
TIMEMN	.212380E 0	-.161467E 0	-.217232E 0	-.587392E- 1	.000000E 0
CORRNX	.152721E 0	-.674510E- 1	-.309101E- 1	-.164510E 0	.000000E 0
HDIFF1	-.283647E 0	.251095E- 1	-.510368E- 1	.117405E 0	.000000E 0
HDIFF2	-.268384E 0	-.526041E- 1	-.742152E- 1	.584120E- 1	.000000E 0
HDIFF3	-.349127E 0	-.143865E- 1	.406268E- 1	.773319E- 1	.000000E 0
HDIFF4	-.121885E 0	-.559920E- 2	-.213096E- 1	.150811E 0	.000000E 0
HDIFFN	-.380994E- 1	-.250625E 0	.121077E 0	.273257E- 1	.000000E 0
AGEYRS	.438755E- 1	.916750E- 1	.325484E 0	.131867E 0	.000000E 0
FEMALE	.997390E- 1	.106436E 0	-.203876E 0	.123876E 0	.000000E 0
MALEXX	-.997390E- 1	-.106436E 0	.203876E 0	-.123876E 0	.000000E 0
ROUTIN	-.297560E 0	-.166667E 0	-.937500E- 1	-.525105E- 1	.000000E 0
MALPSN	-.138680E 0	-.247594E 0	-.139272E 0	-.780976E- 1	.000000E 0
PAINXX	.100000E 1	-.392856E 0	-.933520E- 1	.176471E 0	.000000E 0
INFECT	-.392856E 0	.100000E 1	-.166667E 0	-.933520E- 1	.000000E 0
MECHBR	-.933520E- 1	-.166667E 0	.100000E 1	-.525105E- 1	.000000E 0
GXXXXX	.176471E 0	-.933520E- 1	-.525105E- 1	.100000E 1	.000000E 0
HXXXXX	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.100000E 1

TABLE 3:3

McKee - first visit

VAR NAME	REGRESSION COEFF	STANDARD ERROR	CONFIDENCE INTERVAL	T STAT	PART CORR	MULTIPLE CORRELATION	E S S
TIMEMN	0.0384880	.168194E- 1		2.29	0.37	0.000	.101206E 3

RESIDUAL ERROR .1626916 1

MULT CORR 0.370

INTERCEPT TERM 1.2049954

VAR NAME	REGRESSION COEFF	STANDARD ERROR	CONFIDENCE INTERVAL	T STAT	PART CORR	MULTIPLE CORRELATION	E S S
TIMEMN	0.0354710	.167461E- 1		2.12	0.35	0.265	.940783E 2
HDIFF3 -	0.3579830	.201397E 0		1.37	-0.24	0.370	.873458E 2

RESIDUAL ERROR .160575E 1

MULT CORR 0.430

INTERCEPT TERM 1.8619616

TABLE 3:3

McKee - first visit

VAR NAME	REGRESSION COEFF	STANDARD ERROR	CONFIDENCE INTERVAL	T STAT	PART CORR	MULTIPLE CORRELATION	E S S
TIMEMN	0.0437119	.163830E- 1		2.67	0.43	0.351	.887252E 2
HDIFF3 =	0.9076552	.390010E 0		2.52	-0.41	0.375	.869517E 2
HDIFF4	1.1615534	.550746E 0		2.11	0.35	0.430	.825099E 2
RESIDUAL ERROR	.152565E 1						
MULT CORR	0.536						
INTERCEPT TERM		0.9593589					

TABLE 3:2

McKee - first visit

VAR NAME	REGRESSION COEFF	STANDARD ERROR	CONFIDENCE INTERVAL	T STAT	PART CORR	MULTIPLE CORRELATION	E S S
TIMEMN	0.0381221	.166124E- 1		2.29	0.39	0.462	.795698E 2
HDIFF1 =	0.7452548	.529585E 0		1.41	-0.25	0.536	.721563E 2
HDIFF3 =	0.8074329	.361535E 0		2.23	-0.38	0.469	.789422E 2
HDIFF4	1.6576058	.646744E 0		2.56	0.42	0.430	.825095E 2
RESIDUAL ERROR	.150209E 1						
MULT CORR	0.575						
INTERCEPT TERM		1.3043447					

TABLE 3:3

Nissen - first visit

CORRELATION MATRIX

	CORRPL	CORRNX	TIMEMN	HDIFF1	HDIFF2	HDIFF3
CORRPL	.100000E 1	.986731E 0	.183272E 0	-.518194E 0	-.573711E 0	-.720683E 0
CORRNX	.986731E 0	.100000E 1	.195441E 0	-.425471E 0	-.484411E 0	-.642447E 0
TIMEMN	.183272E 0	.195441E 0	.100000E 1	.350070E-1	-.160422E 0	.194745E 0
HDIFF1	-.518194E 0	-.425471E 0	.350070E-1	.100000E 1	.927426E 0	.860946E 0
HDIFF2	-.573711E 0	-.484411E 0	-.160422E 0	.927426E 0	.100000E 1	.737043E 0
HDIFF3	-.720683E 0	-.642447E 0	.194745E 0	.860946E 0	.737043E 0	.100000E 1
AGEYRS	-.860774E 0	-.830439E 0	-.186884E 0	.625092E 0	.650130E 0	.743156E 0
FEMALE	-.250783E 0	-.185836E 0	.121268E 0	.288675E 0	.944911E-1	.573539E 0
MALEXX	.250783E 0	.185836E 0	-.121268E 0	-.288675E 0	-.944911E-1	-.573539E 0
ROUTIN	.830142E 0	.775386E 0	-.151585E-1	-.577350E 0	-.614192E 0	-.802955E 0
MALPSN	-.259417E 0	-.288224E 0	-.263551E 0	.436436E 0	.357143E 0	.346844E 0
PAINXX	-.208696E-1	.648459E-1	.335547E 0	-.912871E-1	-.209165E 0	.253917E 0
INFECT	-.171588E 0	-.176224E 0	-.515388E 0	-.144338E 0	.236228E 0	-.286770E 0
MECHBR	-.439013E 0	-.484411E 0	.423973E 0	.109109E 0	.357143E-1	.346844E 0
GXXXXX	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0
HXXXXX	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0

TABLE 3:4

Nissen - first visit

TABLE 3:4

CORRELATION MATRIX

	AGEYRS	FEMALE	MALEXX	ROUTIN	MALPSN	PAINXX
CORRPL	-.860774E 0	-.250783E 0	.250783E 0	.838142E 0	-.259417E 0	-.208696E- 1
CORRNX	-.830439E 0	-.185836E 0	.185836E 0	.775386E 0	-.288224E 0	.648459E- 1
TIMEMN	-.186884E 0	.121268E 0	-.121268E 0	-.151585E- 1	-.263551E 0	.335547E 0
HDIFF1	.625092E 0	.288675E 0	-.288675E 0	-.577350E 0	.436436E 0	-.912871E- 1
HDIFF2	.650130E 0	.944911E- 1	-.944911E- 1	-.614192E 0	.357143E 0	-.209165E 0
HDIFF3	.743156E 0	.573539E 0	-.573539E 0	-.802955E 0	.346844E 0	.253917E 0
AGEYRS	.100000E 1	.344889E 0	-.344889E 0	-.905880E 0	.397668E 0	-.552221E- 2
FEMALE	.344889E 0	.100000E 1	-.100000E 1	-.500000E 0	.377964E 0	.632456E 0
MALEXX	-.344889E 0	-.100000E 1	.100000E 1	.500000E 0	-.377964E 0	-.632456E 0
ROUTIN	-.905880E 0	-.500000E 0	.500000E 0	.100000E 1	-.188982E 0	-.316228E 0
MALPSN	.397668E 0	.377964E 0	-.377964E 0	-.188982E 0	.100000E 1	-.478091E 0
PAINXX	-.552221E- 2	.632456E 0	-.632456E 0	-.316228E 0	-.478091E 0	.100000E 1
INFECT	.960451E- 1	-.500000E 0	.500000E 0	-.125000E 0	-.188982E 0	-.316228E 0
MECHAR	.145207E 0	-.188982E 0	.188982E 0	-.188982E 0	-.285714E 0	.597614E- 1
GXXXXX	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0
HXXXXX	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0

Nissen - first visit

CORRELATION MATRIX

	INFECT	MECHBR	GXXXXX	HXXXXX
CORRPL	-.171588E 0	-.439013E 0	.000000E 0	.000000E 0
CORRNX	-.176224E 0	-.484411E 0	.000000E 0	.000000E 0
TIMEMN	-.515388E 0	.423973E 0	.000000E 0	.000000E 0
HDIFF1	-.144338E 0	.109109E 0	.000000E 0	.000000E 0
HDIFF2	.236228E 0	.357143E-1	.000000E 0	.000000E 0
HDIFF3	-.286770E 0	.346644E 0	.000000E 0	.000000E 0
AGEYRS	.960451E-1	.145207E 0	.000000E 0	.000000E 0
FEMALE	-.500000E 0	-.188982E 0	.000000E 0	.000000E 0
MALEXX	.500000E 0	.188982E 0	.000000E 0	.000000E 0
ROUTIN	-.125000E 0	-.188982E 0	.000000E 0	.000000E 0
MALPSN	-.188982E 0	-.285714E 0	.000000E 0	.000000E 0
PAINXX	-.316228E 0	.597614E-1	.000000E 0	.000000E 0
INFECT	.100000E 1	-.188982E 0	.000000E 0	.000000E 0
MECHBR	-.188982E 0	.100000E 1	.000000E 0	.000000E 0
GXXXXX	.000000E 0	.000000E 0	.100000E 1	.000000E 0
HXXXXX	.000000E 0	.000000E 0	.000000E 0	.100000E 1

TABLE 3:4

variables have significant t-statistics, the entry of plate corrosion (corrpl) merely indicates that there is a very high correlation between appliance corrosion (corrnx) and plate corrosion and that in this set, unlike some others, variance is reduced by its inclusion.

On the second visit only 4 implants of this type were examined and were not analysed.

e) Sherman.

Although these plates also show interesting correlations with hardness differences only holes 1 and 2 can be regarded as significant since the data for holes 3 and 4 is very fragmentary. The correlations with the two hardnesses differences seem to have no obvious explanation and do not seem consistent between the two variables.

Regression data was extremely difficult to obtain on the sherman plates and is not included in the thesis. Many of the variables had extremely low average values and this tended to produce errors. The only variable to enter the data set before a programme cut off occurred was the hardness difference on hole 1 but the equations were not significant.

The existance of a cut off in the programme is an unfortunate hindrance but is designed to prevent wastage of computer time while trying to divide two extremely small numbers. Several runs were attempted removing different variables from the dataset but no useful output was obtained. Further work will be carried out in an attempt to produce meaningful regression equations.

f) Burns

There were insufficient examples of these to attempt a useful analysis. The means quoted from the previous work are valid but with the inclusion of other variables some of the

Sherman - first visit

CORRELATION MATRIX

	CORRNX	TIMEMN	HDIFF1	HDIFF2	HDIFF3	HDIFF4
CORRNX	.100000E 1	.154599E 0	-.161930E 0	-.270884E-1	-.232601E-1	.203957E-1
TIMEMN	.154599E 0	.100000E 1	-.838633E-1	-.192085E 0	.250464E 0	.228218E 0
HDIFF1	-.161930E 0	-.838633E-1	.100000E 1	.463254E 0	.521621E-1	.232111E-1
HDIFF2	-.270884E-1	-.192085E 0	.463254E 0	.100000E 1	-.488564E 0	-.516655E 0
HDIFF3	-.232601E-1	.250464E 0	.521621E-1	-.488564E 0	.100000E 1	.973659E 0
HDIFF4	.203957E-1	.228218E 0	.232111E-1	-.516655E 0	.973659E 0	.100000E 1
AGEYRS	-.223622E-1	-.743575E-1	-.111574E 0	-.414188E-1	-.168104E-1	-.699252E-2
FEMALE	.265137E-1	-.210154E 0	.301478E 0	.888545E-1	.965507E-1	.999887E-1
MALEXX	.314009E-1	.250583E 0	-.200114E 0	-.526829E-1	-.544419E-1	-.590438E-1
ROUTIN	-.256269E-1	-.118115E 0	-.805996E-1	-.239584E 0	.166164E 0	.175801E 0
MALPSN	.107173E 0	.373308E-1	.748640E-1	.451047E 0	-.313463E 0	-.378646E 0
PAINXX	.102166E-1	.543180E-1	.102177E 0	.236829E-1	-.901728E-1	-.149335E 0
INFECT	-.414700E-3	-.574782E-1	-.107980E-1	-.104464E-1	-.786903E-1	-.822249E-1
MECHBR	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0

TABLE 3:5

Sherman - first visit

CORRELATION MATRIX

	AGEYRS	FEMALE	MALEXX	ROUTIN	MALRSN	PAINXX
CORRNX	-.223622E- 1	.265137E- 1	.314009E- 1	-.256269E- 1	.107173E 0	.102166E- 1
TIMEMN	-.743575E- 1	-.210154E 0	.250583E 0	-.118115E 0	.375308E- 1	.543180E- 1
HDIFF1	-.111574E 0	.301478E 0	-.200114E 0	-.805996E- 1	.748640E- 1	.102177E 0
HDIFF2	-.414188E- 1	.888545E- 1	-.526829E- 1	-.239584E 0	.451047E 0	.236829E- 1
HDIFF3	-.166104E- 1	.965507E- 1	-.544419E- 1	.166164E 0	-.313463E 0	-.901728E- 1
HDIFF4	-.699252E- 2	.999887E- 1	-.590438E- 1	.175801E 0	-.378646E 0	-.149335E 0
AGEYRS	.100000E 1	-.260782E- 1	-.434789E 0	-.130026E 0	.425367E- 1	-.302019E 0
FEMALE	-.260782E- 1	.100000E 1	-.827712E 0	.855109E- 1	-.141389E- 1	.416636E- 1
MALEXX	-.434789E 0	-.827712E 0	.100000E 1	-.228369E- 1	-.352349E- 2	.986583E- 1
ROUTIN	-.130026E 0	.855109E- 1	-.228369E- 1	.100000E 1	-.116584E 0	.151835E 0
MALRSN	.425367E- 1	-.141389E- 1	-.352349E- 2	-.116584E 0	.100000E 1	-.101547E- 1
PAINXX	-.302019E 0	.416636E- 1	.986583E- 1	.151835E 0	-.101547E- 1	.100000E 1
INFECT	-.965339E- 2	-.183773E- 1	.222025E- 1	.316536E- 1	.447910E- 2	.154226E- 1
MECHBR	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0	.000000E 0

TABLE 3:5

Sherman - first visit

CORRELATION MATRIX

	INFECT	MECHBR
CORRNX	-.414700E- 3	.000000E 0
TIMEMN	-.574782E- 1	.000000E 0
HDIFF1	-.107980E- 1	.000000E 0
HDIFF2	-.104462E- 1	.000000E 0
HDIFF3	-.786903E- 1	.000000E 0
HDIFF4	-.822249E- 1	.000000E 0
AGEYRS	-.965339E- 2	.000000E 0
FEMALE	-.183773E- 1	.000000E 0
MALEXX	.222025E- 1	.000000E 0
ROUTIN	.316536E- 1	.000000E 0
MALPSN	.447910E- 2	.000000E 0
PAINXX	.154226E- 1	.000000E 0
INFECT	.100000E 1	.000000E 0
MECHBR	.000000E 0	.100000E 1

TABLE 3:5

rows were left incomplete and there were insufficient examples in the set for the missing values routine to produce meaningful results.

III. Discriminant Analysis

1. XDS3 Package

After the data has been transformed (see previous section) the observation matrix must be split into groups. In the system used in this analysis CROSS PRODUCT control blocks were used to multiply whole rows by one particular variable. The variables chosen were the reasons for implant removal which were coded either as 1 or 0. Separate matrices containing all the implants removed for the different reasons were thus produced.

These matrices formed the groups of the discriminant analysis. The objective was to discover a formula whereby the implants could be assigned to one or other group from a knowledge of the other variables. The routine is initiated by a DISCRIMINANT ANALYSIS control and output by PDISCRIMINANT. If a check on the efficacy of the routine is required a HITS AND MISSES table may be produced by an IDENTIFICATION routine. This routine takes the original and assigns it to a group using the formula previously produced. Thus, some idea of the ability of the programme to deal with this type of data can be gained.

2. Use on implant survey

Attempts were made to use this routine to assign implants to groups characterised by different reasons for removal. It was felt that this may bring to light some of the conditions leading to an increased rate of removal. The observation matrix was split as previously described and the routine initiated. In every case a tape error occurred and after examining one set of output it was discovered that the sample means produced as part of the discriminant analysis output had two variables with a mean and variance of zero although the means printed in the earlier data preparation section had non-zero values. The presence of these two

values at this point in the analysis is likely to lead to an attempt to divide zero by zero with obvious results. A representative of ICL was contacted and is currently investigating the fault. Storage problems have been encountered before in this package and it is possible that there is a further package error.

This part of the project has therefore not been completed although the routines exist. It is hoped that when the source of this fault has been found and rectified the analysis will be completed.

SCANNING ELECTRON MICROSCOPE STUDIES

I. Theory of the Instrument

The scanning electron microscope was developed in its present form by Oatley and co-workers at the University of Cambridge (109). In their system electrons are emitted from a tungsten hairpin filament and formed into a high energy beam by a conventional triode gun. Three lenses of variable power successively demagnify the image of the tip of the filament until the final diameter of the beam may be as small as 15nm. Between lenses 2 and 3 a set of scanning coils are mounted. These electromagnetically deflect the beam so that the spot scans a raster pattern on the specimen. The ratio of the raster scanned on the specimen to the size of the display cathode ray tube determines the magnification. Focussing is carried out by adjusting the strength of the final lens so that the minimum diameter of the beam is put into the plane of the specimen surface.

As the beam of electrons hits the surface of the specimen a number of interactions between the beam and the atoms in the specimen occur.

1. Electrons may undergo elastic collisions with nuclei and be deflected through large angles with minimum loss of energy. Those undergoing deflections of about 180° may escape from the specimen and are then referred to as high energy primaries.

2. Interaction may occur with other electrons resulting in transfer of momentum to orbital electrons. The electrons may then escape from the atom and those which succeed in reaching the surface of the specimen are termed secondary electrons. Their energies are typically in the range 0 - 100 eV. One high energy electron may produce many secondaries before it either loses too much energy or penetrates too deeply into the specimen for the freed electron to

have a reasonable probability of reaching the surface.

The loss of these electrons leaves atoms in the solid in excited states which then decay into the ground state. These decay processes cause the emission of electromagnetic radiation which may be collected and used to obtain information about the specimen.

3. Under the correct conditions a type of diffraction pattern may be observed. This is analogous to the Kikuchi lines formed in the transmission electron microscope and yields information on the crystallography of the underlying area.

4. Complex electronic transitions occur in semi-conductors and SEM studies are very useful in the study of integrated circuits. Further information may be obtained in the book by Thornton (110).

The basic system studies the emitted electrons. Referring to Fig 4:1, after the beam has come down the column onto the specimen the emitted secondary electrons are attracted to the collector by a positive potential applied to the outer case of the collector. The tip of the scintillator is held at a potential of 12 KV to ensure that all the electrons entering the outer case reach the tip. A plastic light guide conveys the light produced to a variable gain photomultiplier. The brightness of the visual gain is determined by the output from the photomultiplier. This CRT is scanned synchronously with the beam on the specimen, thus the image produced is a map of the electron emission over the specimen.

On a perfectly flat specimen, changes of intensity will be due to changes in composition which may affect primary or secondary electrons. This atomic number effect is, however, small compared with the changes in intensity which occur when the specimen is no longer perfectly flat. Consider a specimen which has a cross-section as in Fig 4:2 and the electron beam at points A to E.

Providing that the step height is not so great that the specimen

Fig 4:1

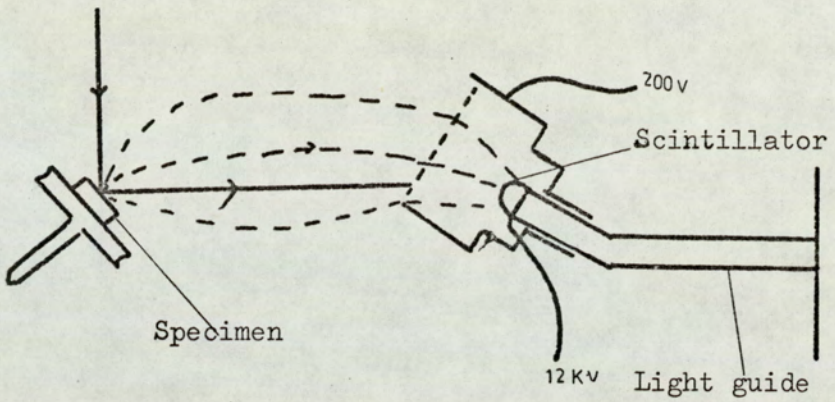
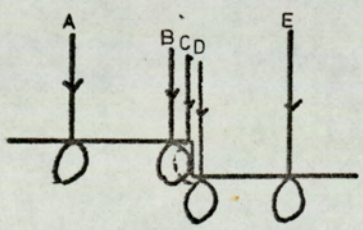


Fig 4:2



is out of focus, the intensities of emission at A and E will be almost identical. Theory shows that the only electrons escaping are produced in a pear shaped volume under the beam (Fig 4:2). At points B, C, D the surface over this volume is no longer flat. At point B the step intersects the side of the pear leading to icreased emission. This is more pronounced at point C but at point D there is an increased depth of material to the left of the beam reducing the emission. Thus edges are characterised by increased emission and therefore increased brightness.

When the intensity distribution is compared to the surface topography, the picture obtained is similar to that found in reflected light microscopy with oblique illumination. There are slight differences since secondary electrons may follow curved paths to the collector. However, it should be noted that the view seen is the one from the filament and not that from the collector.

The image produced may be altered electronically. The simplest control for this is the 'black level' which reduces the intensity of the whole picture. The relationship between the photomultiplier voltage and the resultant intensity may be varied by means of the 'gamma' control. Use of this has the effect of enhancing contrast in the dark areas of the specimen while reducing it in the bright ones. Its greatest use is in the examination of holes or cracks.

A module has recently been introduced which puts the differential of the signal onto the screen. Again this allows specimens of very high contrast to be examined, for a better visual effect scans may be taken at right angles and superimposed on the negative or a normal and differentiated picture may be added. The study of pseudo-Kikuchi lines has been made considerably easier by this modification.

Further picture improvements may sometimes be made by using manual settings on the 'rise time' control. The circuit acts as a

filter which rejects signals occurring in shorter times than the setting. 'Noise' from the electronics usually has a fast rise time and therefore if a long exposure photograph (involving a slowly moving spot) is taken, a setting of the rise time control may be found which rejects a high proportion of the noise while retaining the fine detail in the picture.

Much useful information may be obtained if emissions other than electrons are collected. For example, if the secondary electrons are produced by ejecting electrons from the inner orbitals of atoms, X-rays having wavelengths characteristic of the atomic number of the atom will be produced. Thus the composition of small areas of the specimen may be analysed by measuring the intensities of characteristic wavelengths, alternatively,by selecting a given wavelength and scanning the specimen, the distribution of that element may be found. Unfortunately the attachment was not available for this research project.

II. Specimen Preparation

For metallic i.e. electrically conducting specimens there is little preparation necessary. The specimen must be of a suitable size, for the standard stage of the Cambridge Mark 2A less than 1 cm. cube. This is then mounted onto one of the standard stubs provided with the instrument. Grease and dust must be removed which is usually accomplished by washing in acetone or ether. To avoid a build up of charge on the specimen it must be in electrical contact with the stub. This may be achieved either by using a conducting adhesive or by joining specimen to stub with a conducting paint.

If the specimen is non-conducting e.g. biological specimens or painted metal, a thin conducting coat must be applied to the surface. The coat should be of uniform thickness and thinner than the maximum

resolution required. Evaporation of metals or graphite under vacuum is probably the most convenient method. If the metal used is in the form of a wire, calibration tests may be done to determine the length of wire corresponding to different thicknesses of coat for the particular geometry of coating unit. To achieve a uniform coat the specimen should be rotated, ideally in all three planes and devices have been made to do this automatically.

III. Examination of Surgical Implants

Several composite implants were examined. The implants had previously been rinsed in sterile saline and then autoclaved. Any deposits were then removed by scrubbing with a soft brush. The plate was then sawn into suitably sized pieces for examination on a conventional stage in the Cambridge Mark 2A Stereoscan. This will only accept specimens of maximum 1 cm. cube if full stage mobility is retained. If the sacrifice of certain movements is accepted slightly larger specimens may be accomodated.

On the small bone plates a hole could be selected and all the contact area examined but on the larger splines the holes had to be sectioned and care had to be taken to select the angle of cut so as to destroy the minimum amount of useful information. Small screws could be examined intact but larger ones had to be shortened.

After sectioning the implants were washed in acetone to remove debris and grease and then mounted onto stubs. The specimens were examined at an accelerating voltage of 30 KV.

IV. Results

Most of the visible corrosion appeared on contact surfaces. However, when the top surface of the implant was examined, small pits could be seen (Fig 4:3). These sometimes occurred singly but frequently in lines as shown. The mechanism of this attack is certainly a form of pitting but the initiation mechanism is uncertain. Many of the lines suggest that inclusions, broken up during the production processes, may be responsible. There is no proof that these pits occurred in the body, they may be defects in the electro-polishing process or else caused during sterilisation. The number of such pits is, however, small and they do not appear to be associated with surface damage.

Turning to the much larger problem of contact corrosion it was hoped that SEM studies would help to determine the mechanism of such corrosion. The precise shape of the patch of corrosion depended on the actual type of contact (see Ch 2). Surface damage or machining marks did not appear to initiate the attack. In Fig 4:4 there are no signs of damage close to the corrosion yet quite severe defects occur only a little way away. A higher magnification picture of the same area is shown in Fig 4:5. This reveals small machining marks at the bottom of the picture and to the left but these cannot be distinguished on Fig 4:4. Similar behaviour is shown in Fig 4:6.

The more severely corroded sample in Fig 4:7 shows definite horizontal lines at the bottom of the corroded area. This corresponds to the circumferential direction of the screw head. The area of corrosion and the amount of corrosion are so great that no conclusions can be drawn about the site and hence cause of initiation. In Fig 4:8 the general level of corrosion is much lighter but the indications are that although damage or defects do not appear to initiate corrosion, if the affected area spreads to a defect the corrosion

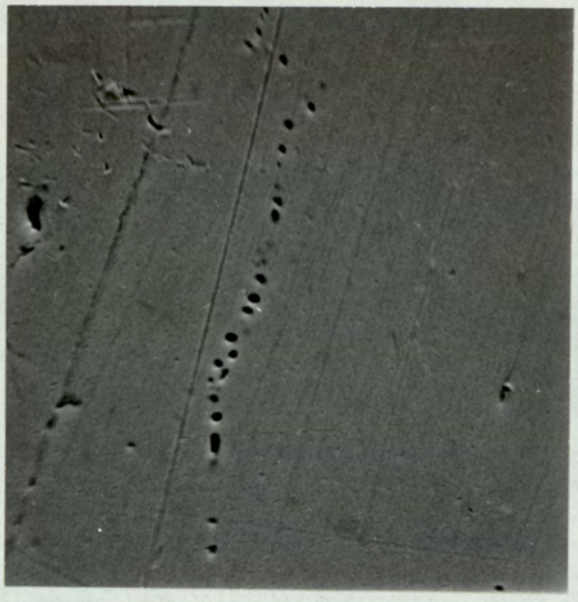


Fig 4:3 x1.1K Top surface of Wainwright Spline

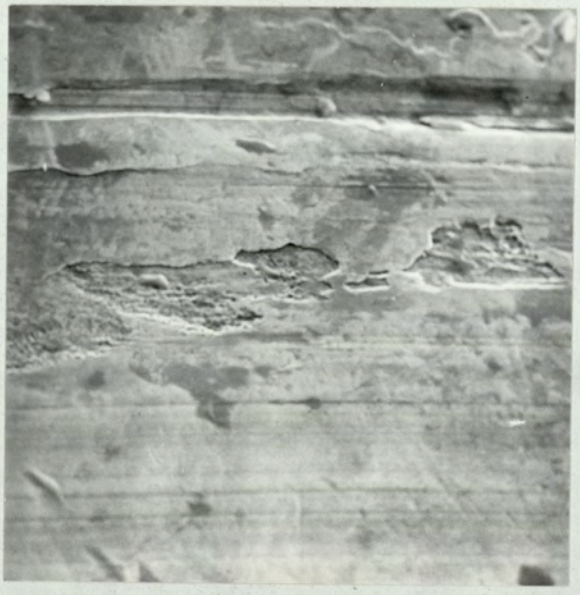


Fig 4:4 x170 Countersink of screw

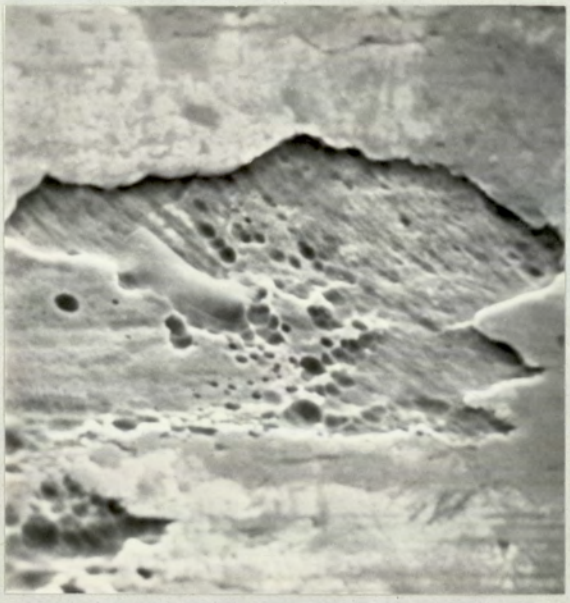


Fig 4:5 x840 Detail of Fig 4:4

Fig 4:6 x825 Countersink of screw from same appliance as Fig 4:4

Fig 4:7 x43 Countersink of screw 3 from Wainwright Spline

Fig 4:8 x1.7K Countersink of screw from bone plate

will spread preferentially along it.

Considering the mechanism of attack, the presence of quite large pits is obvious (Figs 4:4, 4:5, 4:6, 4:8). But as well as pits there are lines of attack (Figs 4:5, 4:6, 4:9). A high magnification view (Fig 4:10) reveals that these lines vary in direction and may have small pits in them. The lines are strikingly reminiscent of corroded fatigue striations. Waterhouse et al (111) have demonstrated that fatigue mechanisms are present in fretting attack and it is possible that these striations are the result of complex fretting action. The pits are then presumed to have initiated after the removal of the surface layer. Removal of an upper layer, possibly by fretting action, is supported by the low power photographs Figs 4:4, 4:5, 4:6, 4:9 but not by Fig 4:7. Fig 4:8 shows a pitting attack and the lines appearing on this photograph are closely related to surface damage.

Further examples of the supposed fretting / pitting attack are shown in Figs 4:10, 4:11, 4:12, 4:13. Fig 4:13 shows some of these striations at a high magnification. They are remarkably parallel and are punctuated by pits but do not seem to be caused by coalescence of pits.

Thus a mechanism is postulated in which destruction of the surface occurs by fretting action. This leads to sub-surface fatigue cracks which are later revealed as the striations on the now exposed surface. Concurrently a classical type of crevice corrosion is also occurring. This causes the large pits. The very large numbers of small pits are supposed to have initiated after the original surface layer has been destroyed.

A further mechanism is suggested by Figs 4:14 and 4:15. Instead of being vaguely circular the pits are angular and many of the sharp angles seem to be about 120°. This suggests an attack mediated

Fig 4:9 x840 Countersink of screw from bone plate

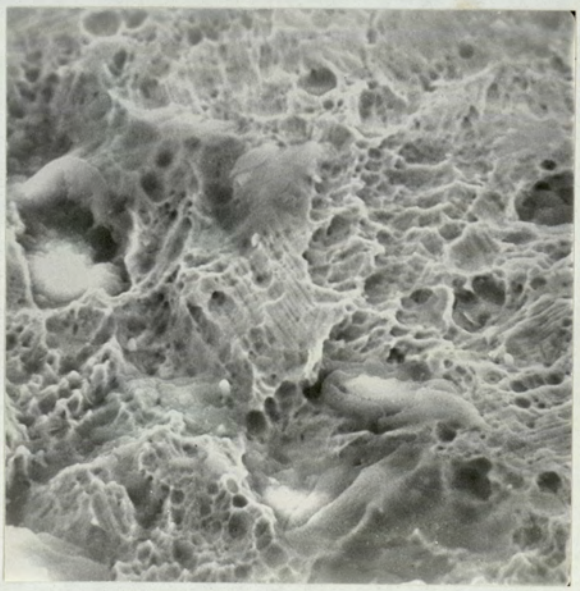


Fig 4:10 x1.1K Hole 3 Wainwright Spline

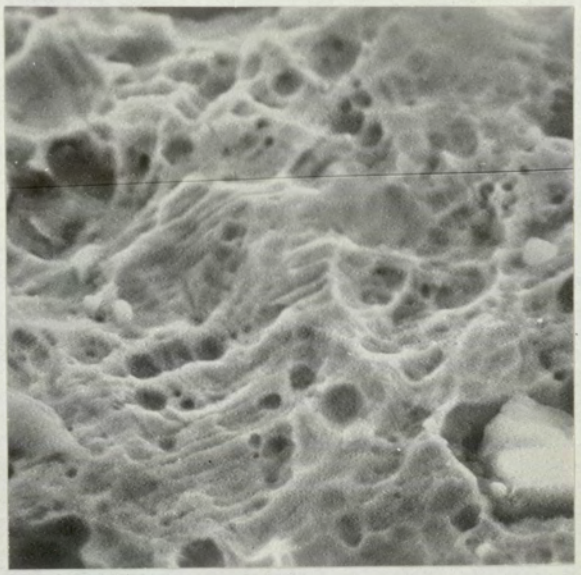


Fig 4:11 x2.2K Hole 3 Wainwright Spline

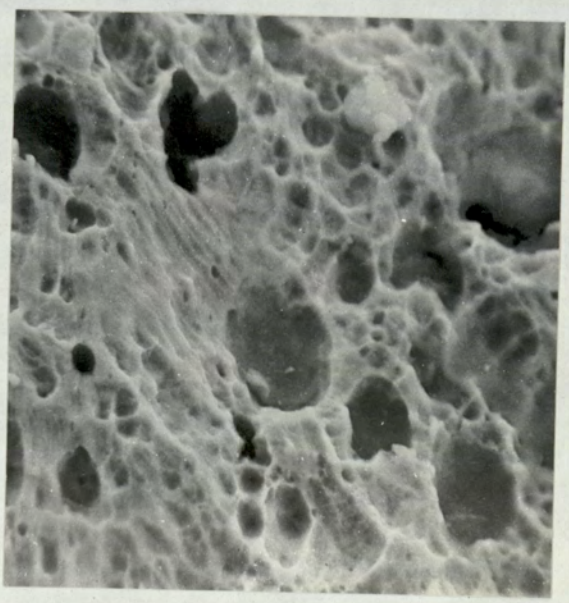


Fig 4:12 x1.4K Countersink of screw from bone plate

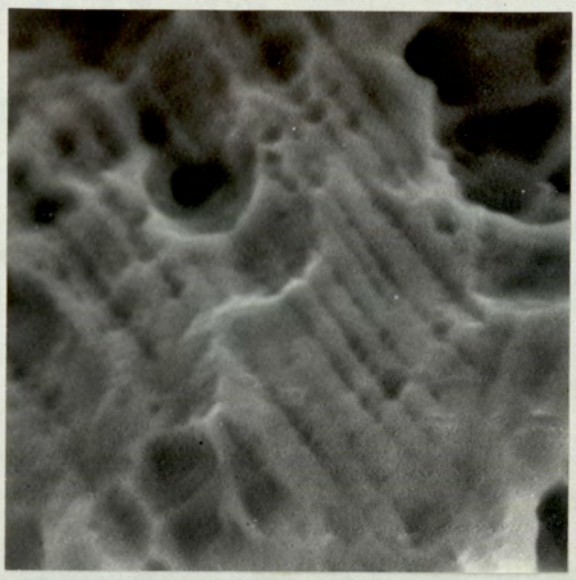


Fig 4:13 x5.5K Detail of Fig 4:10

Fig 4:14 x4K Hole 3 Wainwright Spline

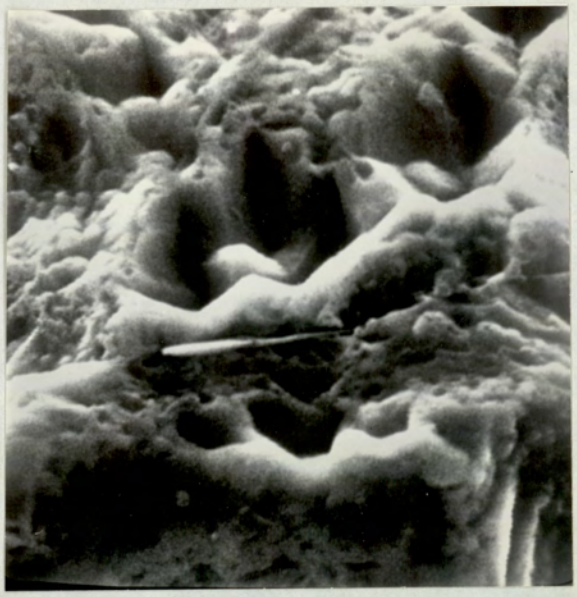


Fig 4:15 x8K Detail of Fig 4:14

by some sort of crystallographic factor. This is the only region where this type of attack has been seen so it is probably not important for the general understanding of implant corrosion.

POTENTIOSTATIC STUDIES

I. Theory

When a piece of metal is immersed in an electrically conducting solution it takes up a potential which may be measured with respect to a reference electrode. The value of the potential is often time - dependent and a plot of its variation is often used in corrosion studies (2). If a third electrode is added and current passed between it and the specimen, the potential of the specimen will alter. Two instruments have been devised which rely on this polarisation of specimens, the galvanostat and the potentiostat. The former delivers constant current to the specimen while the latter holds the sample at constant potential.

In the potentiostat current is passed between a counter electrode and the specimen, the potntial of the specimen is continuously monitored and compared with a set potential by a type of bridge. If the potential drifts away from the set value the current is altered to reduce the difference. The current actually flowing is displayed on a meter and outputs to chart recorders may be arranged.

There are three main ways of conducting tests with a potentiostat. A true potentiostic test is conducted at thermodynamic equilibrium. Each time the potential is changed sufficient time is allowed for the value of the current to stabilise (except in pitting corrosion where the current fluctuates violently as pitting occurs). Thus the production of a polarisation curve is a lengthy undertaking.

The other two methods do not work at equilibrium. The potential is varied at a pre-determined rate and the current flowing at a particular moment is measured. In one technique the potential is continuously varied and the current flowing output on a chart recorder. The other alters potential in steps at regular and takes the value of the current at a set time after the change.

The precise shape of the curves alters with the rate of change of potential. This is particularly marked around an active - passive transition since time to achieve passivity varies with current density. Therefore, if accurate comparisons are to be made between different specimens, the test conditions must be carefully standardised. This is easier to achieve with the continuous change than the step-wise one.

II. Potentiostatic Testing of Implant Materials

Mears (2, 9) pioneered the use of the potentiostat in the in vitro testing of implant materials. However, there are some factors in the preparation of specimens which need further clarification. Most corrosion processes are concerned with current density rather than absolute current and this is usually calculated by dividing measured current by apparent surface area. Because no surface is truly flat the real surface area is much greater. Therefore, if two specimens are being compared their surface roughness should be equal. There are different ways of preparing flat surfaces and it is conceivable that these may not give identical results in terms of corrosion resistance. Two types of mechanical polishing and three electropolishing solutions were tested.

Many testers report that prior to potentiostatic testing their specimens have been cathodically activated (e.g. 112, 113, 114) i.e. hydrogen has been bubbled against the surface. This, of course, has the effect of reducing any oxide film present. A series of tests was carried out with different pre-treatments to discover if specimen behaviour varied.

As a result it was hoped to be able to recommend more specific test routines for prospective implant materials.

III. The Effect of Surface Finish

1. Method.

Specimens were prepared in the following ways :-

a) Mechanically buffed on successively finer carborundum wheels.

b) Hand polished on silicon carbide paper followed by diamond paste, finishing with $\frac{1}{4}\mu$ paste.

c) Electropolished in Batelle's solution.

d) Electropolished in Batelle's solution with added chromium trioxide.

e) Electropolished in a saturated solution of chromium trioxide in acetic acid.

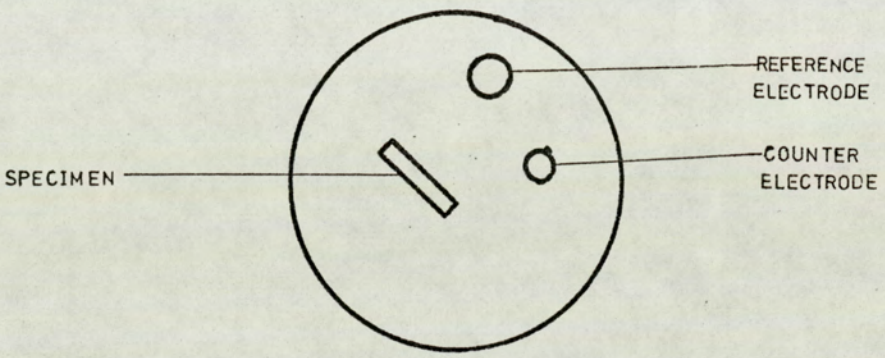
After polishing, the specimens were washed in acetone, dried, and then coated with two coats of Lacomit (a protective lacquer) leaving approximately 1 $cm.^2$ of surface exposed. The lacquer was allowed to harden for several hours before immersion of the specimen in a corrosive environment.

The anodic polarisation curves were measured in Tyrodes solution using a saturated calomel electrode as reference and a platinum basket as counter electrode. The relative positions of the electrodes were determined by a jig fitting the top of a 250 ml. beaker (Fig 5:1).

The potential of the specimen with no current flowing (U_r) was measured, then the same potential (U_s) set using the potentiometer. The potential was then increased by 50 units on the potentiometer each minute and the corresponding current read 45 seconds later. The increments were repeated until oxygen was evolved at the anode and then the process repeated decreasing the potential.

The nominal surface areas were measured and polarisation curves drawn. After finishing these experiments it was discovered that

Fig 5:1



instead of multiplying the potentiometer reading by a factor of 2 to obtain the potential, the instrument had been wrongly calibrated and the correct factor was 1.76 ± 0.02. Therefore instead of a rate of change of potential of 100 mV / min the true rate was only 88 mV / min. The values of U_r were not affected.

2. Results.

The results are given in Table 5:1 and the polarisation curves plotted in Fig 5:2. It is obvious from the graphs that all three electropolishings solutions produce a surface with the same corrosion resistance. The smooth curves shown by the electropolished samples should be contrasted with the more complex shapes for the two mechanically polished samples.

The complex behaviour of the buffed sample is not unexpected since buffing produces a variable finish over the surface and pieces of the polishing wheels may be found embedded in the specimen. Also the mechanical forces involved in buffing are much higher than in hand polishing and so the surface layers will be more distorted.

From the graphs the hand posished surface shows the best corrosion resistance but would be almost impossible to us in mass production. Electropolishing probably offers the best surface for mass - produced implants, especially since complex shapes are easier to electropolish than mechanically polish.

IV. Cathodic Activation

1. Method.

Samples were prepared by electropolishing and the specimens prepared for testing as described in the previous section. The test solution chosen was a phosphate buffer at a pH of 7.3. The absence of chloride eliminated pitting corrosion and no change of pH was observed during hydrogen evolution. After measuring U_r in the usual

TABLE 5:1

Effect of surface finish on anodic polarisation tests of steel

Hand polished		Buffed		Chrome-Acetic	
Potential (mV)	Log Current ($\mu A/cm^2$)	Potential (mV)	Log Current ($\mu A/cm^2$)	Potential (mV)	Log Current ($\mu A/cm^2$)
-165	0	-165	0	-55	0
-77	0	-77	0	33	0
11	0	11	0.6	121	0
99	0	99	1.48	209	0
187	0.3	187	1.71	297	0
275	0.6	275	1.73	385	0.45
363	0.7	363	2.33	473	0.85
451	0.7	451	2.63	561	2.15
539	0.95	539	2.82	649	2.99
627	1.59	627	2.88	737	3.59
715	2.24	715	3.04	815	3.84
803	2.61	803	3.13	903	4.03
891	2.81	891	3.14	991	4.15
979	2.95	979	3.24	1079	4.24
1067	3.03	1067	3.29	1167	4.32
1155	3.12	1155	3.33	1255	4.40
1243	3.19			1343	4.47
1331	3.23			1431	4.54
1419	3.29				

Batelle		Batelle + Chrome	
Potential (mV)	Log Current ($\mu A/cm^2$)	Potential (mV)	Log Current ($\mu A/cm^2$)
18	0	46	0
106	0	134	0
194	0	222	0
282	0.3	310	0
370	0.6	398	0.3
458	0.85	486	1.49
546	2.15	574	2.33
634	3.02	662	3.11
722	3.60	750	3.60
810	3.85	838	3.92
898	4.01	926	4.06
986	4.14	1014	4.15
1074	4.23	1102	4.23
1162	4.30	1190	4.30
1250	4.36	1278	4.36

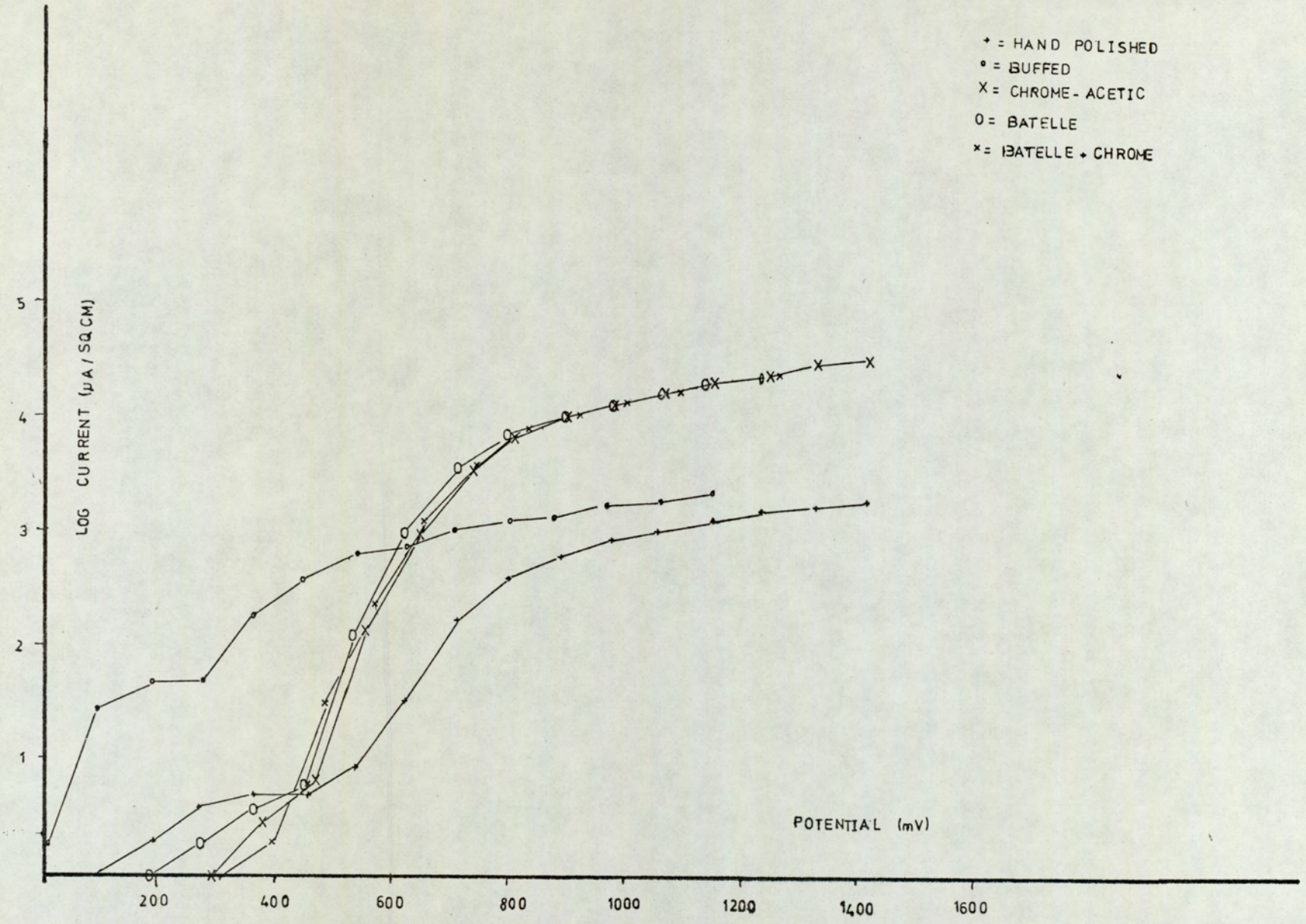

+ = HAND POLISHED
° = BUFFED
X = CHROME - ACETIC
0 = BATELLE
× = BATELLE + CHROME
LOG CURRENT (μA / SQ CM)
5
4
3
2
1
POTENTIAL (mV)
200
400
600
800
1000
1200
1400
1600

Fig 5:2

way the specimen was polarised cathodically until hydrogen was evolved at a current of 5 mA. This was maintained for periods of 2, 5, 10, 20 minutes then the potentiometer returned to U_s. The current was measured 45 seconds later and the test procedure of the previous section carried out.

2. Results

a) Ascending curves.

Considering first the unactivated control specimen, a measureable corrosion current appeared at about 400 mV and exhibited a plateau between 650 and 900 mV. The current then decreased prior to breakdown at just below 1100 mV. A further plateau appeared at 1300 mV denoting secondary passivity, this was quite short and oxygen evolution commenced shortly afterwards.

For all the activated samples a jump in potential of about 1500 mV occurred immediately after activation. The very short time which elapsed before measuring the current did not allow attainment of equilibrium and the current fell for the first few minutes of each test. After breakdown which always occurred between 1000 and 1200 mV the curves were essentially the same.

Prior to breakdown the curves varied. A plateau was still evident but the current flowing varied and was not directly related to the activation treatment.

b) Descending curves.

In some ways these are more interesting than the ascending ones. Above the breakdown potential the curves are once again identical. After that the control and 2 minute samples follow the same smooth path and the corrosion current became undetectable at about 900 mV. The 5 minute sample showed a slight tailing off and quite a long period with a 1μA corrosion current. The 10 and 20 minute samples showed plateaux before the corrosion current finally became negligible.

TABLE 5:2

Effect of activation on ascending polarisation tests of steel

Control		2 min at 5 mA		2 min at 5 mA	
Potential (mV)	Log Current ($\mu A/cm^2$)	Potential (mV)	Log Current ($\mu A/cm^2$)	Potential (mV)	Log Current ($\mu A/cm^2$)
-51	0	50	1.20	57	1.20
37	0	138	0.78	145	0.85
125	0	226	0.70	233	0.70
213	0	314	0.70	321	0.70
301	0	402	0.78	409	0.78
389	0	490	0.78	497	0.78
477	0.4	578	0.88	585	0.85
565	0.6	666	0.88	673	0.78
653	0.7	754	0.78	761	0.78
741	0.7	842	0.78	849	0.78
829	0.7	930	0.78	937	0.78
917	0.7	1018	0.78	1025	0.78
1005	0.5	1106	1.28	1103	1.30
1093	1.11	1194	2.32	1191	2.28
1181	2.27	1272	2.92	1279	2.80
1269	2.88	1360	3.09	1367	3.03
1357	3.06	1448	3.11	1455	3.07
1445	3.11	1536	3.33	1543	3.22
1523	3.3	1624	3.55	1631	3.44
1611	3.5	1712	3.74	1719	3.60
1699	3.78				

5 min at 5 mA		10 min at 5 mA		20 min at 5 mA	
Potential (mV)	Log Current ($\mu A/cm^2$)	Potential (mV)	Log Current ($\mu A/cm^2$)	Potential (mV)	Log Current ($\mu A/cm^2$)
102	2.07	150	1.92	-40	2.16
190	1.64	238	1.78	48	1.84
278	1.45	326	1.71	136	1.64
366	1.3	414	1.63	224	1.58
454	1.23	502	1.59	312	1.53
542	1.20	590	1.59	400	1.53
630	1.28	678	1.65	488	1.52
718	1.40	766	1.67	576	1.52
806	1.46	854	1.63	664	1.48
894	1.43	942	1.61	752	1.42
982	1.36	1030	1.59	840	1.42
1070	1.3	1108	1.77	928	1.38
1158	1.79	1196	2.25	1016	1.36
1246	2.49	1284	2.72	1104	1.46
1334	2.89	1372	3.04	1192	2.02
1422	3.05	1460	3.08	1270	2.68
1510	3.10	1548	3.21	1358	3.04
1598	3.28	1636	3.41	1446	3.12
1686	3.49	1724	3.60	1534	3.22
				1622	3.41
				1710	3.59

Fig 5:3

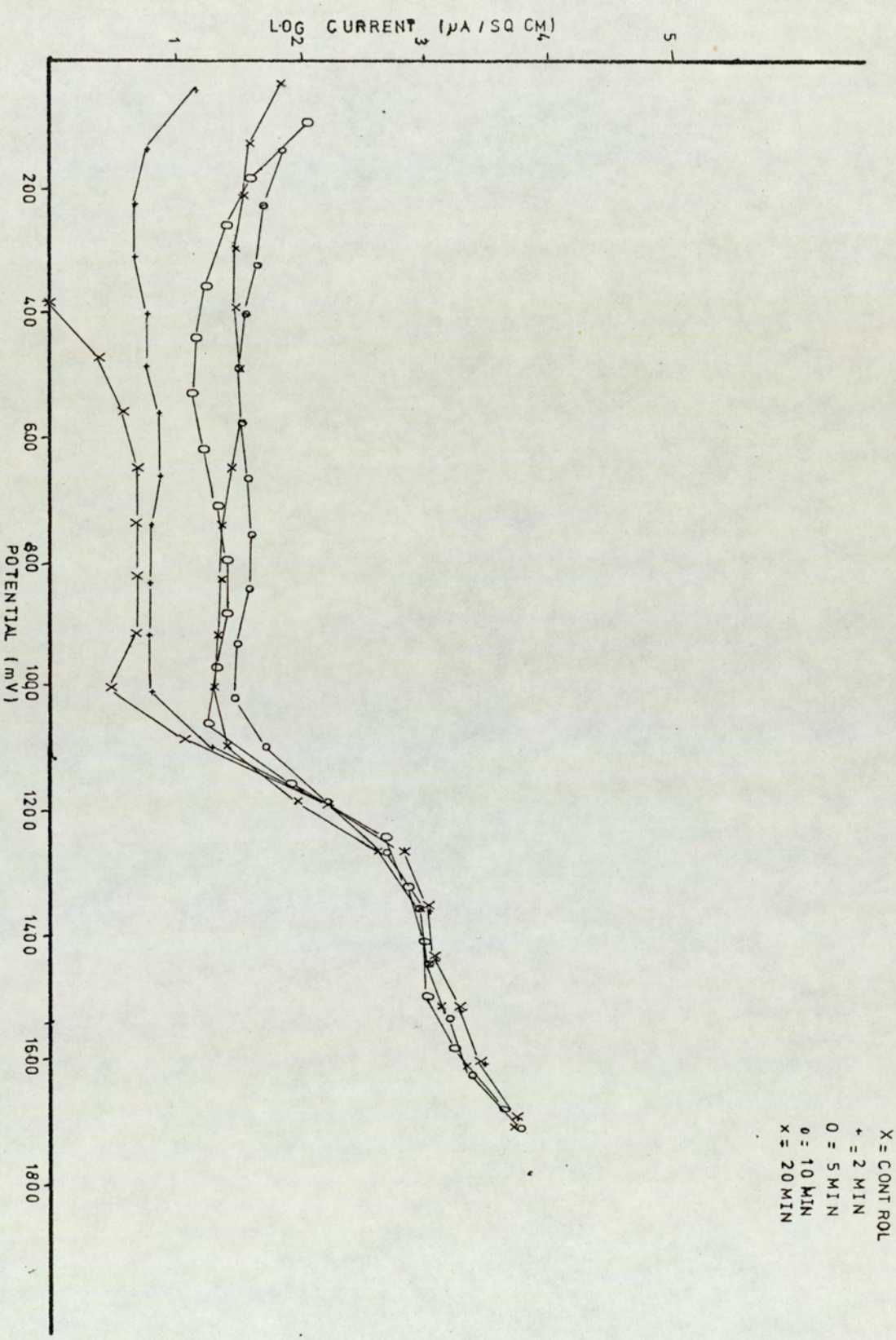

LOG CURRENT (μA / SQ CM)
1
2
3
4
5
POTENTIAL (mV)
200
400
600
800
1000
1200
1400
1600
1800
X = CONTROL
+ = 2 MIN
O = 5 MIN
o = 10 MIN
x = 20 MIN

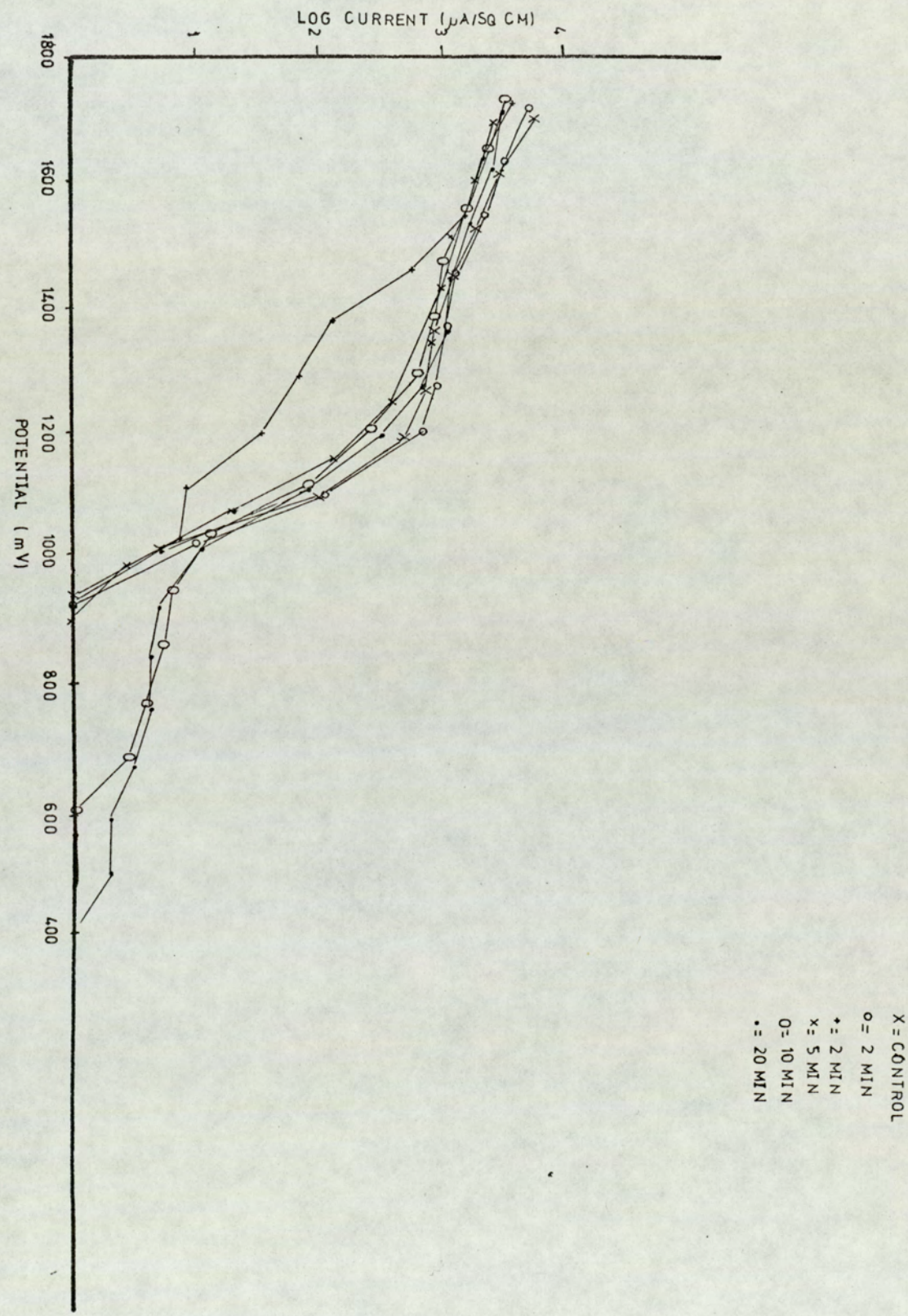
TABLE 5:3

Effect of activation on descending polarisation tests of steel

Control		2 min at 5 mA		2 min at 5 mA	
Potential (mV)	Log Current ($\mu A/cm^2$)	Potential (mV)	Log Current ($\mu A/cm^2$)	Potential (mV)	Log Current ($\mu A/cm^2$)
1699	3.78	1712	3.74	1719	3.60
1611	3.52	1624	3.57	1631	3.39
1523	3.31	1536	3.35	1543	3.25
1445	3.12	1448	3.16	1455	2.80
1357	2.98	1360	3.09	1367	2.13
1269	2.92	1272	2.96	1279	1.87
1181	2.71	1194	2.60	1191	1.56
1093	2.03	1106	2.04	1103	0.93
1005	0.72	1018	1.00	1025	0.90
917	0	930	0	937	0

5 min at 5 mA		10 min at 5 mA		20 min at 5 mA	
Potential (mV)	Log Current ($\mu A/cm^2$)	Potential (mV)	Log Current ($\mu A/cm^2$)	Potential (mV)	Log Current ($\mu A/cm^2$)
1686	3.49	1724	3.60	1710	3.59
1598	3.31	1636	3.43	1622	3.44
1510	3.13	1548	3.24	1534	3.26
1422	3.05	1460	3.07	1446	3.12
1334	2.95	1372	3.00	1358	3.07
1246	2.65	1284	2.84	1270	2.89
1158	2.17	1196	2.48	1192	2.52
1070	1.34	1108	1.93	1104	1.94
982	0.47	1030	1.12	1016	1.05
894	0	942	0.82	928	0.74
		854	0.72	840	0.65
		766	0.60	752	0.65
		678	0.42	664	0.52
		590	0	576	0.35
				488	0.35
				400	0

Fig 5:4


LOG CURRENT (μA/SQ CM)
1
2
3
4
POTENTIAL (mV)
1800
1600
1400
1200
1000
800
600
400
X = CONTROL
o = 2 MIN
+ = 2 MIN
x = 5 MIN
O = 10 MIN
• = 20 MIN

Thus, in some fundamental way the hydrogen had altered the surface of the metal. Despite showing the same breakdown behaviour as the unactivated sample the film did not show passivity in the same way. The effect could be due to atomec hydrogen diffusing into the metal surface and subsequently either interfering with oxide film formation or perhaps locally reducing the film. Since there are no aggressive ions present the film should heal rapidly and violent current fluctuations such as are seen in pitting corrosion may well not be observed.

Whatever the mechanism it is clear that activation has an effect which is not quickly lost. Therefore, if it is deemed necessary to so treat the specimens, all specimens must be activated under the same conditions. However, it may well be safer to find some other way of cleaning the surface prior to testing.

CHAPTER 6

IRON SOLUTION TESTS

I. Introduction

The object was to assess the corrosion rate of steel in salt solutions by measuring the quantity of iron in the solution. A spectrophotometric method, capable of detecting 0.3 g in 200 mls. of solution, was chosen (115). Immersion tests were carried out on undamaged specimens and the corrosion rate calculated as a function of chloride and bicarbonate concentrations, pH and time.

II. Preparation of Equipment

All equipment used in the tests had to be free from iron. Glassware was first steeped in chromic - sulphuric acid overnight, then washed in de-ionised water. All equipment, glass and plastic, was then soaked in analytical grade hydrochloric acid for four hours, rinsed in de-ionised water and filled with acidified, dilute thioglycollic acid. Articles made from glass or polythene were then placed in a circulating air oven at 80°C for a minimum of 24 hours. Perspex apparatus was placed in a similar oven at 60°C for a minimum of 72 hours. The thioglycollic acid was then discarded, the equipment washed with double de-ionised water and filled with fresh, acidified, thioglycollic acid. All pieces of equipment were stored in this way when not in use.

III. Purification of Solutions

1. Hydrochloric acid

Analytical grade, concentrated acid was diluted with approximately its own volume of de-ionised water and distilled in a clean glass still using glass beads to control the tendency of the acid to 'bump'. It was found necessary (see section IV) to distill

three times to reduce iron contamination to acceptible levels.

2. Water

Double de-ionised water was prepared by coupling two 'Elgastat' resin columns together. The first 100 mls. was discarded and the rest collected in clean bottles (see section II).

3. Buffer

This is made from 250 mls glacial acetic acid, 300 mls water and 2.8 equivalents of ammonia solution. The whole is then diluted to 1 litre with water. Except for water the individual components were not purified prior to use (116). After mixing, 16 mls of thioglycollic acid were added to the buffer and the solution heated to 80°C in a polythene bottle for 72 hours. Four millilitres of bathophenanthroline solution were then added to each 200 ml portion and allowed to react. The iron was extracted with 20 mls amyl alcohol. This procedure was repeated until the amyl alcohol remained colourless after the extraction. The solution was kept at 80°C for 24 hours prior to each extraction. In addition, each 150 mls was re-purified immediately prior to use.

4. Thioglycollic acid

The acid used in the determinations, as opposed to that used for cleaning equipment, was purified by passing it through a column of Amberlite IR - 120.

5. Bathophenanthroline - 4,7-diphenyl-1,10-phenanthroline

A 1% w/v was made up by dissolving 0.50 gm in 500 mls amyl alcohol. The solution was then filtered through a Whatman 542 filter paper and stored in glass.

6. Industrial methylated spirits

This was filtered through a Whatman 542 filter paper and then stored in clean pyrex.

IV. Experimental Method

The solution under test was transferred to a cleaned, double - stoppered polythene bottle and 3 mls of purified hydrochloric acid added. Using an automatic pipette, 4 mls of purified thioglycollic acid were added, the bottle stoppered and then heated to 80°C for 24 hours. The solution was then placed in a stoppered glass separating funnel and allowed to cool to about 50°C when 10 mls of buffer were added. The mixture was then swirled until thoroughly mixed and 4 mls bathophenanthroline solution added. The mixture was then shaken (releasing the pressure every few seconds) for one minute and then left for 30 minutes. Approximately 21 mls of amyl alcohol were then added and the contents shaken for 2 minutes (the pressure again released as necessary) and the phases allowed to separate for at least 45 minutes.

The aqueous phase was discarded and the alcohol run into a dry 25 ml volumetric flask. The funnel was then washed through with approximately 5 mls industrial spirits and the contents made up to 25 mls with the same liquid. Any aqueous contamination could then be dispersed by shaking the flask.

Meanwhile the spectrophotometer cells had been rinsed in industrial spirits, dried, and filled with amyl alcohol. Blank readings were taken at 534 nm and the cells to be used in the determinations washed in industrial spirits and dried.

The iron solutions were then transferred to cells (the size used varied with amounts of iron) using a pipette and a minimum of three readings taken at 534 nm against amyl alcohol.

This procedure was repeated on a standard iron solution until consistent results were obtained. Double reagent blank tests were then carried out on all reagents. In these the amount of each reagent was either doubled or halved and if the reading fell outside

the normal limits of reproducibility the reagent was re-purified.

V. Calibration Curves

Using analytical grade ferrous ammonium sulphate an aqueous solution was prepared containing 1 gm of iron per litre. By serial dilution two further standard solutions were made containing 100 g/ml and 10 g/ ml. A solution containing 1 g/ ml was made as required. Calibration curves from 10 to 200 g were made using $\frac{1}{2}$, 1 and 2 cm cells and from 1 to 10 g using a 4 cm cell. The best fit lines were calculated on an Olivetti Programma 101 and the results plotted (Table 6:1, 6:2 and Figs 6:1, 6:2, 6:3, 6:4)

VI. Preparation of Specimens for Immersion Tests

Originally a chromium trioxide - acetic acid mixture was used to electropolish the stainless steel samples. The solution was prepared by adding chromium trioxide to glacial acetic acid containing 7 mls water per litre and stirring vigorously with a mechanical stirrer. Chromium trioxide was added until a saturated solution was formed, this usually took about 8 hours. During this time a further 4 - 5 mls of water was absorbed from the atmosphere.

Specimens were then polished at a temperature of 12°- 18°C in a covered bath. The bath was cooled by two steel pipes, which also functioned as cathodes, containing cold running water. This polishing system is unusual in that the current - plot contains no 'polishing plateau'. Polishing conditions have therefore to be determined by trial each time the solution is used. Extreme difficulties were experienced with this solution in hot weather as water vapour was absorbed from the air which quickly rendered the solution unusable, sometimes after only one day.

A new solution was then tried (117). This consisted of

TABLE 6:1

Calibration curves for 2 cm, 1 cm, $\frac{1}{2}$ cm cells

Iron (μg)	2 cm	1 cm	$\frac{1}{2}$ cm
5	0.33	0.165	
10	0.49	0.26	
15	0.60	0.297	0.165
25	0.84	0.415	0.23
35	1.115	0.54	0.278
50	1.64	1.0	0.53
75		1.215	0.62
100		1.53	0.80
125		1.62	0.86
150		2.06	1.16

TABLE 6:2

Calibration curve for 4 cm cell

Iron (μg)	Reading
1	0.27
2	0.40
3	0.54
4	0.64
6	0.621
8	0.745
10	0.95

Fig 6:1

2 cm. cell

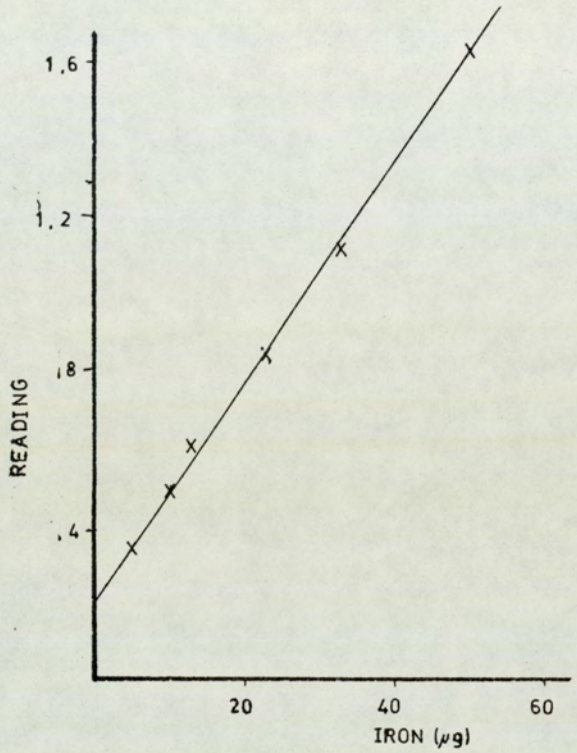


Fig 6:3

½ cm. cell

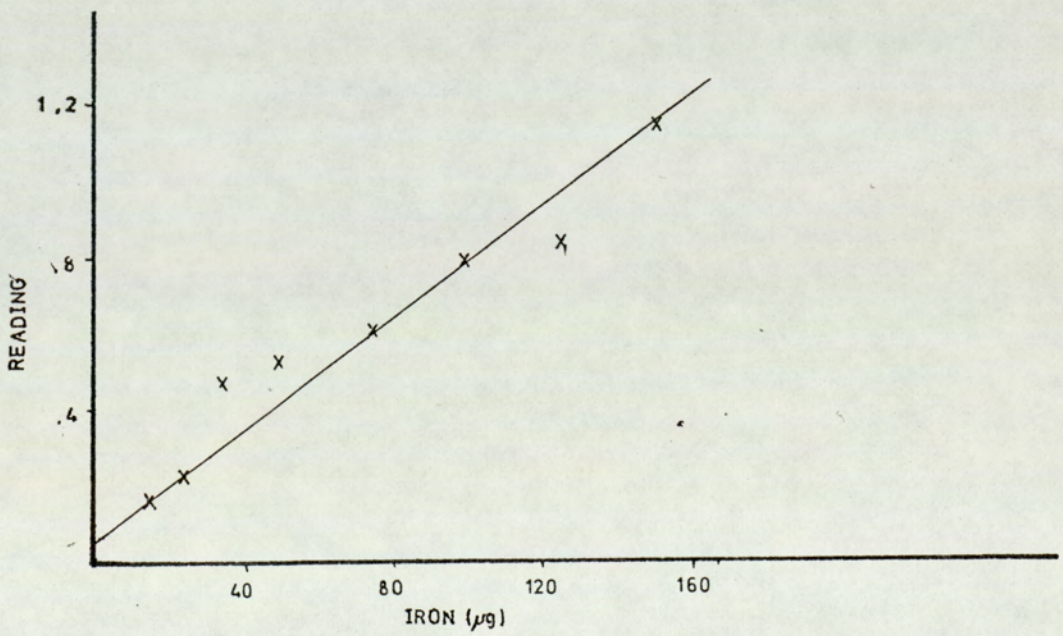


Fig 6:2

1 cm. cell

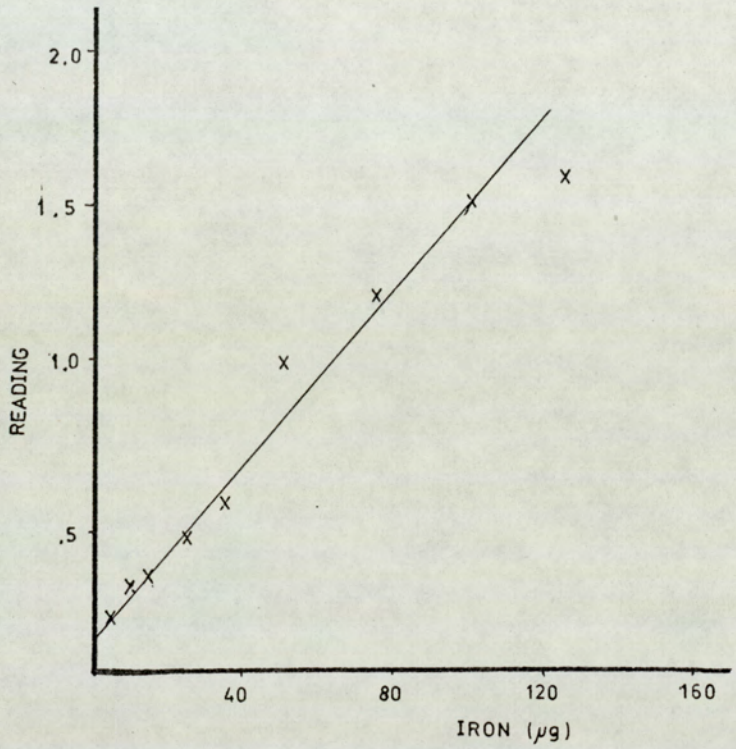
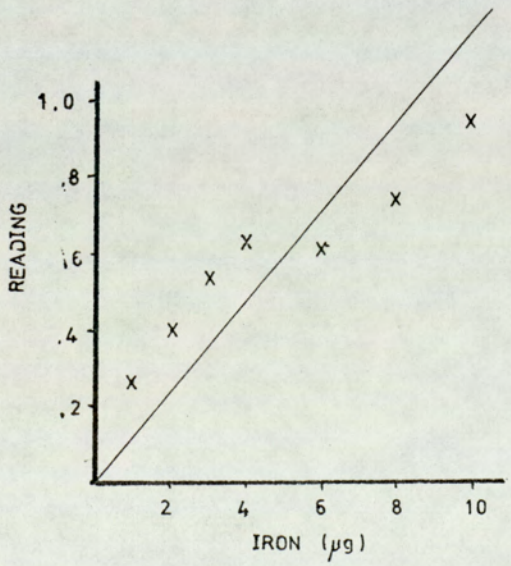


Fig 6:4

4 cm. cell



100 mls ethyl alcohol, 50 mls 2-butoxyethanol and 15 mls perchloric acid. Later industrial spirit was substituted for the ethyl alcohol and its polishing ability seemed unimpaired. When polishing, a film was formed over the specimen at a potential of 18 volts, on steel the film is brown and viscous, building up from the lower edge of the specimen. When the film began to flow off the base of the specimen the voltage was reduced to 9 volts until polishing was completed.

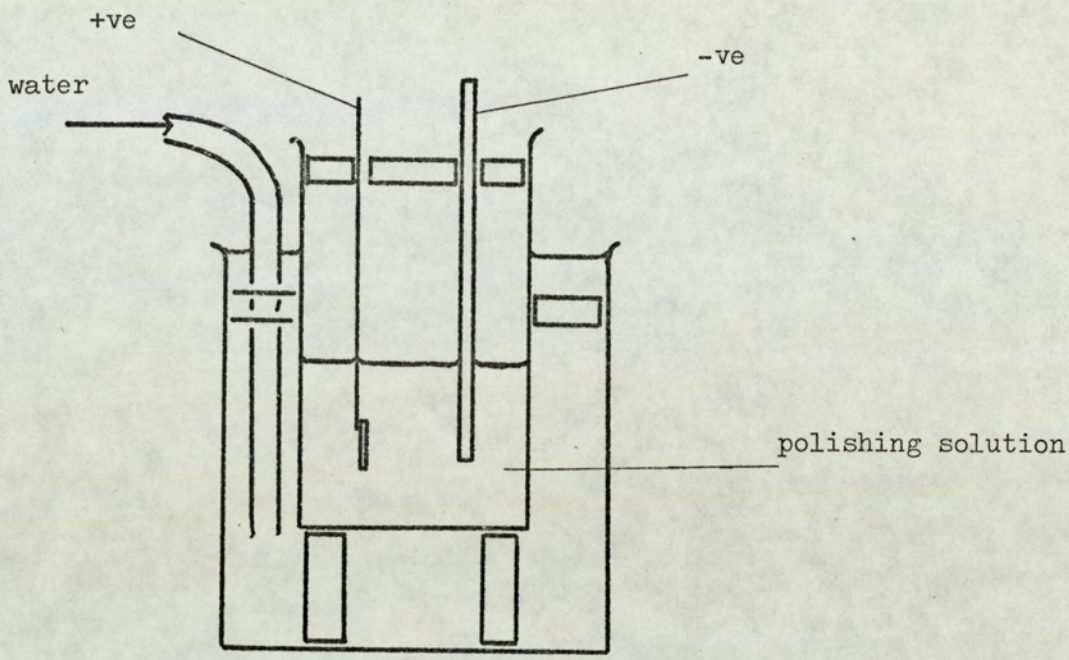
Blanking off areas of specimens with protective lacquer was found to be ineffective since the polishing film merely penetrated beneath them. It was frequently observed that despite using a single cathode both sides of the specimen were polished although the finish on the reverse side was usually inferior. It did, however, mean that accurate positioning of anode and cathode was unnecessary.

The system eventually adopted was to discharge nichrome wire to the back of the specimen, this was then held in a polystyrene jig fitted into a 400 ml beaker (Fig 6:5). One piece of wire usually lasted for about 40 minutes before it had been polished away at the surface of the solution.

Film breakdown occurred at a temperature of 20°C and pitting occurred. Water cooling, as shown in Fig 6:5 was effective for the 40 minute period and three beakers were used in rotation. When not in use they were stored in a deep freeze. Each specimen required three or four polishing periods to achieve a mirror finish.

The solution proved extremely versatile polishing all the austenitic steels tried and several martensitic ones. It was, however, unsuccessful on a complex cast iron. An interesting feature of the solution is that inclusions and other phases seem to be polished at the same rate as the matrix which makes it very useful for the production of thin foils for transmission electron microscopy.

Fig 6:5



VII. Immersion Tests

Small pieces of stainless steel which had previously been electropolished were coated with 'Lacomit' leaving approximately 1 sq.cm. exposed to the solution. A piece of nylon thread was attached to the reverse side of the metal using Lacomit as an adhesive. A trial experiment was carried out using 3 mls of triple distilled hydrochloric acid in 100 mls of double de-ionised water as a test solution.

The solution was placed in a cleaned, double - stoppered, polythene bottle and the specimen suspended in the medium by a thread held by the inner stopper. After completion of the test the specimen was rinsed with double de-ionised water, the rinse was added to the solution. No further hydrochloric acid was added, just 4 mls of thioglycollic acid. The solution was then heated to 80°C for 24 hours. Iron was then analysed as previously described, a standard solution of 50 g of iron tested with each batch of specimens to ensure reproducibility of results. Times of immersion from 1 to 48 hours were used. Reasonable results were obtained (Table 6:3) and further tests using salt solutions planned.

Originally it was planned to use Tyrodes solution as a test medium but apart from difficulty in obtaining such a complex solution iron - free it was found to be very difficult to achieve quantitative extraction of added iron. Tyrodes solution is a neutral, buffered, salt solution and thioglycollic acid will only extract iron in an acid environment, the amount of hydrochloric acid to achieve correct conditions would have introduced an unacceptible error. A trial was undertaken using a limited quantity of acid but as expected it was unsuccessful.

A simpler system using either sodium chloride only or a mixture of sodium chloride and sodium bicarbonate was employed. The

experiment was designed to investigate simultaneous variation of time and both components of the solution. Variation in bicarbonate concentration naturally altered pH and these values were recorded.

The results of these tests were analysed using the XDS3 statistical package on the ICL 1905 computer.

VIII. Results

From the trial tests in hydrochloric acid (Table 6:3) it can be seen that corrosion increases linearly with time over a period of 48 hours. The intercept term is rather high representing a contamination of 5 - 6 g. Some contamination occurred in the actual analysis (about 1 g) and the rest probably came from specimen contamination or faulty technique.

The multi-variate tests (Table 6:4) show somewhat puzzling features after statistical analysis. A negative regression coefficient for time is clearly meaningless in this experiment and the reason for this peculiar result can be seen by examining the correlation matrix. Time and iron are positively correlated, which is physically correct but so are time and chloride concentration. Thus, the two 'independent' variables are not truly independent. Multi-variate statistics are at their most effective when the variables are an orthogonal set (truly independent). If this condition is not met then either they must be transformed into an orthogonal set or a less effective analysis must be made.

An orthogonal set (with respect to time, chloride and bicarbonate) was originally planned but two results had to be rejected (corrosion rate more than three times the mean)) and an arithmetic error had been made in calculating the correlations. When the error was discovered it was no longer possible to repeat determinations and the data set had to be analysed as it stood.

TABLE 6:3

Immersion tests in dilute hydrochloric acid

Time (hours)	Iron (μg/sq.cm.)
1	4.6
2	5.0
4	11.9
6	12.9
12	13.4
16	13.6
22	20.4
24	18.2
36	27.9
48	27.4

Regression analysis :-

Slope = 0.49 μg Fe / sq.cm. / hr

Intercept = 7.2

Correlation coefficient = 0.94 - significant at 0.05%

TABLE 6:4

Saline and bicarbonate immersion tests

Time	Chloride Concentration	Bicarbonate Concentration	pH	Iron (μg/sq.cm)
0.5	2.1	1.0	6.2	2.6
1.0	1.7	0	4.5	2.8
1.2	7.5	0.08	6.5	4.5
1.5	1.4	0.03	6.2	1.2
1.6	6.8	0.06	3.9	9.2
1.8	6.4	0.05	3.9	6.7
2.0	1.0	0	4.5	2.2
2.2	6.2	0.09	6.5	4.5
2.4	6.1	0.09	6.5	6.8
2.5	0.73	0.1	6.8	3.5
3.0	3.0	0	4.5	1.9
3.5	2.6	0.31	7.0	5.5
4.0	8.8	0	4.5	3.3
4.5	2.3	0.47	7.2	3.2
5.0	6.0	0	4.5	3.5
5.5	2.3	0.16	7.0	4.5
6.0	3.0	0	4.5	3.3
6.5	1.3	0.23	6.9	3.5
7.0	4.4	0	4.5	3.1
7.5	3.2	0.19	6.8	2.9
8.0	1.2	0	4.5	3.7
8.5	4.5	0.56	7.2	6.2
9.0	4.6	0	4.3	3.5
9.5	3.9	0.82	7.6	9.0
10.0	4.2	0	4.4	3.1
10.5	3.8	0.3	7.0	3.1
11.0	3.7	0	3.9	3.8
12.5	5.7	0.02	4.0	5.7
13.0	5.5	0	3.8	7.2
13.5	5.2	0.04	4.1	5.8
14.0	5.1	0	3.9	5.2

Correlation Matrix

Conc Bicarb	Iron	Time	pH	
0.05	0.73	0.22	-0.09	Conc Cl
	0.35	0.08	0.75	Conc Bicarb
		0.19	0.01	Iron
			-0.26	Time

TABLE 6:4 (cont)

Regression Equations

1. $Fe = 0.68\ Cl + 2.12$

   $t(Cl) = 5.77$ (0.5%) 29 degrees of freedom

2. $Fe = 0.67\ Cl + 3.26\ HCO_3 + 1.78$

   $t(Cl) = 6.27$ (0.5%) 28 degrees of freedom

   $t(HCO_3) = 2.79$ (1%)

3. $Fe = 0.63Cl + 6.17\ HCO_3 - 0.56\ pH + 4.58$

   $t(Cl) = 6.17$ (0.5%) 27 degrees of freedom

   $t(HCO_3) = 3.69$ (0.5%)

   $t(pH) = 2.29$ (5%)

4. $Fe = 0.64\ Cl + 7.1\ HCO_3 - 0.07\ time - 0.7\ pH + 5.69$

   $t(Cl) = 6.34$ (0.5%) 26 degrees of freedom

   $t(HCO_3) = 3.89$ (0.5%)

   $t(time) = 1.21$ (25%)

   $t(pH) = 2.61$ (2.5%)

Regression equations have been produced with different numbers of variables. Selection of variables was made by minimising the variance and choosing the set which gave the lowest value. From a physical point of view the best equation is probably the one with two variables. It is highly significant (t - test better than 0.5%) and the coefficients are physically sensible.

If a principle components analysis were performed it is likely that two components would be extracted, one consisting of chloride concentration and time and the other bicarbonate concentration and pH. Therefore, if the two variable equation is regarded in such a way that the two variables selected also contain part of the variance from the others, it is quite reasonable. Unfortunately, in that form, it is not useful in interpreting the results of further experiments.

SURFACE DAMAGE TESTS

I. Potential - Time Tests

Potential - time curves characteristic of different types of corrosion behaviour have been described by Mears (2). A resistant metal or alloy will have a potential which gently rises with time or remains steady, an active one will fall with time and one subject to pitting corrosion will fluctuate. He also described a fall in potential during one of his in vivo tests when a probe accidently scratched an implant.

This chance observation gives the basis of a further test for implant materials. Many implants suffer small amounts of surface damage, either on insertion or during use, and if the material is not to suffer corrosion the damage must repair itself quickly. By plotting change in potential after damage, some idea of the expected behaviour can be obtained.

1. Method

Three steel specimens were used with three different surface finishes. One was buffed, another hand polished and the third electropolished in chrome - acetic acid. The specimens were prepared as previously described in Ch 5 and then immersed in Tyrodes solution with a saturated calomel reference. Potential was measured on a valve millivoltmeter and recorded every minute. After an hour the specimen was brought to the surface and scratched with a scalpel blade, 20 minutes later the process was repeated and the potential followed for a further 20 minutes.

2. Results

a) Buffed specimen.

Immediately after immersion the potential rose, then fell sharply before beginning a gentle rise. When the scratch was administered the potential fell, then fluctuated at a much lower mean value than previously (Table 7:1, Fig 7:1). A further slight fall occurred after the second scratch but this time the potential rose to a similar value to that of the undamaged specimen.

b) Hand polished specimen.

After scratching there was again an abrupt fall in potential which was followed by a smooth rise to a value slightly higher than that of the undamaged specimen.

c) Electropolished specimen.

Originally this had the highest potential. Again the potential fell sharply when the specimen was scratched but rose smoothly to a value slightly lower than the original one.

3. Conclusions.

The buffed sample is obviously unsuitable. Its behaviour is most erratic and although, in service, some specimens may give very good results, others may be equally disastrous. The mechanically polished sample appears marginally better than the electropolished one. It should be noted that the corrosion rate is not linked to the value of the potential (118) but that the likely type of behaviour is indicated by the change in potential (2).

Therefore, although the hand polished sample has a lower mean potential than the electropolished one, the continued rise in potential after damage is more favourable than the slight fall observed in the other. The difference, however, is not great.

TABLE 7:1

Potential - time tests

I. Buffed Specimen

Time (min)	Potential (mV)	Time (min)	Potential (mV)	Time (min)	Potential (mV)
¼	27	36	-54	75	-189
½	-2	37	-53	76	-183
¾	2	38	-52	77	-183
1	14	39	-51	78	-147
1½	33	40	-50	79	-183
2	44	41	-50	80	-159
3	50	42	-50	80¼*	-135
4	51	43	-49	81	-99
5	48	44	-48	82	-80
5½	44	45	-48	83	-71
6	40	46	-48	84	-65
7	32	47	-47	85	-60
8	26	48	-47	86	-56
9	20	49	-46	87	-54
10	9	50	-46	88	-51
11	0	51	-46	89	-50
12	-9	52	-45	90	-50
13	-18	53	-45	91	-49
14	-27	54	-45	92	-38
15	-35	55	-45	93	-37
16	-43	56	-45	94	-36
17	-47	57	-45	95	-36
18	-50	58	-45	96	-36
19	-52	59	-44	97	-35
20	-55	60	-44	98	-35
21	-55	60¼*	-147	99	-35
22	-56	61	-99	100	-35
23	-56	62	-150		
24	-57	63	-147		
25	-58	64	-147		
26	-59	65	-50		
27	-59	66	-144		
28	-59	67	-141		
29	-58	68	-180		
30	-57	69	-180		
31	-56	70	-180		
32	-55	71	-183		
33	-55	72	-186		
34	-55	73	-183		
35	-55	74	-186		

TABLE 7:1 (cont)

II. Hand polished specimen

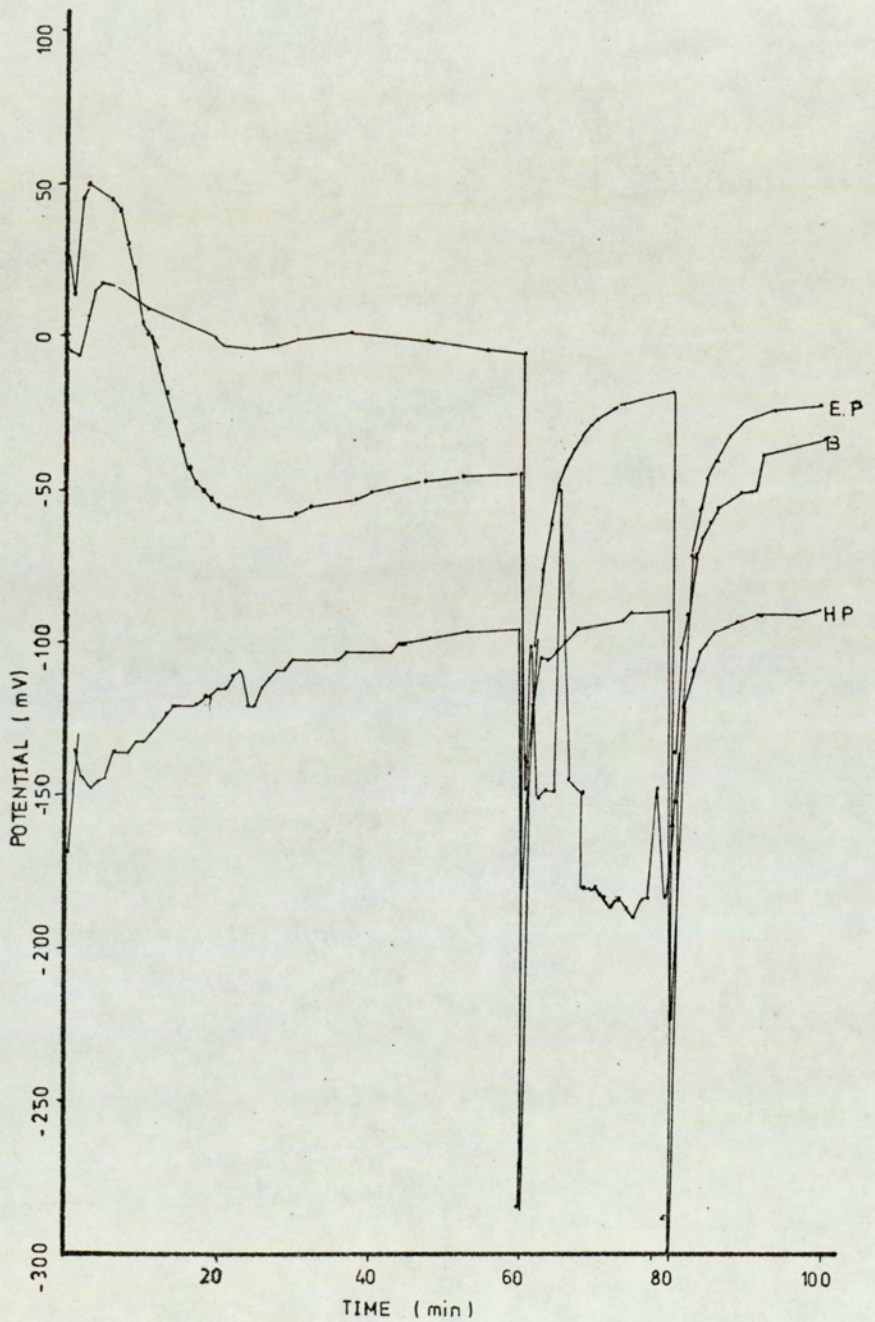
Time (min)	Potential (mV)	Time (min)	Potential (mV)	Time (min)	Potential (mV)
0	-168	36	-105	72	-93
½	-126	37	-102	73	-93
1	-135	38	-102	74	-92
2	-144	39	-102	75	-90
3	-147	40	-102	76	-90
4	-144	41	-102	77	-90
5	-141	42	-102	78	-90
6	-135	43	-102	79	-90
7	-135	44	-99	80	-90
8	-135	45	-98	80¼*	-222
9	-132	46	-98	81	-150
10	-132	47	-97	82	-120
11	-129	48	-97	83	-108
12	-126	49	-96	84	-102
13	-123	50	-96	85	-98
14	-120	51	-96	86	-95
15	-120	52	-96	87	-94
16	-120	53	-95	88	-93
17	-120	54	-95	89	-92
18	-117	55	-95	90	-91
19	-117	56	-95	91	-91
20	-114	57	-95	92	-90
21	-114	58	-94	93	-90
22	-111	59	-94	94	-90
23	-108	60	-94	95	-90
24	-120	60¼*	-180	96	-90
25	-120	61	-138	97	-90
26	-114	62	-120	98	-89
27	-111	63	-105	99	-89
28	-108	64	-105	100	-88
29	-108	65	-102		
30	-105	66	-99		
31	-105	67	-97		
32	-105	68	-95		
33	-105	69	-95		
34	-105	70	-95		
35	-105	71	-94		

TABLE 7:1 (cont)

III. Electropolished specimen

Time (min)	Potential (mV)	Time (min)	Potential (mV)	Time (min)	Potential (mV)
¼	-3	35	2	70	-26
1	-6	36	1	71	-24
2	-7	37	2	72	-23
3	6	38	2	73	-21
4	14	39	2	74	-20
5	17	40	2	75	-20
6	17	41	2	76	-19
7	16	42	2	77	-18
8	14	43	1	78	-18
9	13	44	1	79	-17
10	11	45	1	80	-17
11	10	46	1	80¼*	-300
12	8	47	0	81	-150
13	7	48	0	82	-96
14	6	49	0	83	-70
15	5	50	-1	84	-55
16	4	51	-1	85	-45
17	3	52	-1	86	-39
18	2	53	-2	87	-34
19	1	54	-2	88	-31
20	0	55	-2	89	-28
21	-2	56	-2	90	-26
22	-2	57	-2	91	-25
23	-3	58	-3	92	-24
24	-3	60	-3	93	-23
25	-3	60¼*	-282	94	-22
26	-3	61	-150	95	-22
27	-3	62	-99	96	-21
28	-2	63	-74	97	-21
29	-2	64	-59	98	-21
30	-1	65	-48	99	-21
31	0	66	-40	100	-21
32	1	67	-35		
33	1	68	-31		
34	1	69	-23		

Fig 7:1


100
50
0
-50
-100
-150
-200
-250
-300
POTENTIAL (mV)
20
40
60
80
100
TIME (min)
E.P
B
H P

III. Immersion Tests

The experiments described in the previous section indicated that an increase in corrosion rate may be expected as a result of surface damage. It was decided to try to detect this increase using analysis techniques similar to those used in the previous chapter.

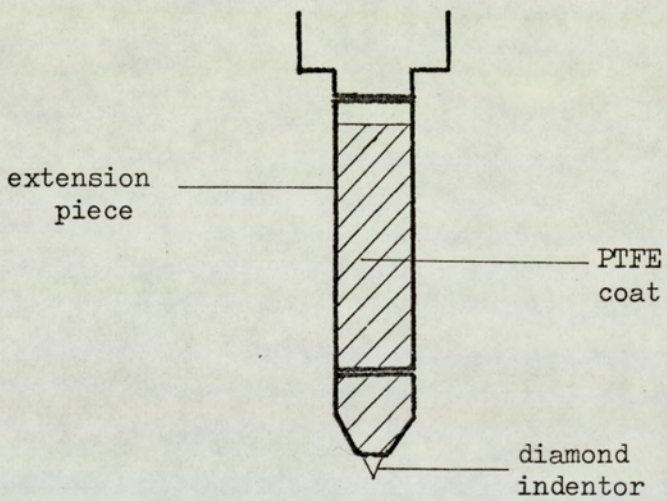
The first problem was to inflict damage without transfer of foreign, since according to the work of Bowden, Laing et al (22 - 27) this may in itself increase the corrosion rate and the second was to inflict a measured amount of damage. These problems were finally overcome by using a modified form of indentation test.

A standard Vickers Diamond Pyramid Indentor was modified by fitting an extension piece between the diamond mount and screw connector (Fig 7:2). With the exception of the diamond this was then coated with PTFE to prevent corrosive attack.

Specimens were prepared as described in Ch 6 except that a much smaller area was left exposed to the solution. An immersion cell was constructed from perspex and the indentation was carried out at the start of a period of immersion in salt solution. A similar test protocol to the previous experiments was adopted and it was hoped to be able to compare the average corrosion rates.

The immersion cell consisted of an open rectangular box and so had to be enclosed in an air-tight container to be cleaned with thioglycollic acid. A plastic luncheon box was tried and worked most satisfactorily. After the necessary pre-cleaning the box and cell were carefully washed with double de-ionised water, the components of the mixed salt solution added and the sealed box transferred to the modified Vickers Hardness Tester. It was decided to follow the potential changes during the exposure so a saturated calomel electrode was wiped with triple distilled hydrochloric acid (the outer case

Fig 7:2



had previously been cleaned in the same acid) and placed in the solution. The specimen had a piece of wire spot welded onto the side and the wire was carefully coated with Lacomit. As soon as the specimen could be positioned under the indentor a standard indentation was carried out while recording the potential on a chart recorder. The indentor was then withdrawn from the solution and rinsed with double de-ionised water, the rinsings were collected in the outer box. A polythene sheet was then used to cover the cell and an exposure of between half an hour and 24 hours carried out. During this time the potential was recorded.

At the end of the test the specimen was removed from the solution and rinsed as before. Thioglycollic acid was added both to the cell and the outer box and acidified with triple - distilled hydrochloric acid. After sealing the box it was placed in a circulating air oven at 60°C for at least 72 hours prior to an iron estimation carried out by the methods of the previous chapter.

A multi-variate regression analysis was then carried out on the data using the XDS3 package.

It had been hoped to use the potential - time curves to assess some of the corrosion. Unfortunately when the curves were studied there did not seem to be any features which lent themselves to statistical analysis. The curves followed the same general features as those in section I in that there was a sudden fall in potential at indentation followed by a rise to about the initial value but after that behaviour varied and was typical of that described by Mears (2) for alloys subject to pitting corrosion.

Results

The results are given in Table 7:2. When the correlation matrix is examined it is obvious that there is no significant correlation between the iron in solution and any parameter. The corrosion per square centimetre is however much higher than in the undamaged specimens.

The dependence on the different variables bears no relation to the previous experiments and as a multi-variate experiment it can probably be termed a failure.

	DSP005		DSP010		DSP015		DSP025		DSP030		DSP035	
CONST	.100000E	1	.100000E	1	.100000E	1	.100000E	1	.100000E	1	.100000E	1
CONCCL	.271161E	1	.139314E	1	.485920E	1	.167394E	1	.273604E	0	.000000E	0
CONBIC	.129554E	0	.266239E	0	.290200E	0	.114252E	1	.653604E	0	.345476E	0
FESQCM	.708840E	2	.745350E	2	.704125E	2	.719937E	2	.417029E	2	.373975E	2
TNITPH	.620000E	1	.650000E	1	.660000E	1	.780000E	1	.700000E	1	.510000E	1
DMGDAR	.130000E-	2	.120000E-	2	.600000E-	3	.200000E-	1	.270000E-	2	.160000E-	2
LOADKG	.200000E	2	.150000E	2	.100000E	2	.125000E	2	.500000E	1	.200000E	2
TRTIME	.500000E	0	.100000E	1	.150000E	1	.250000E	1	.300000E	1	.350000E	1

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OBSERVATION MATRIX MAT2

	DSP045		DSP065		DSP060		DSP070		DSP160		DSP200	
CONST	.100000E	1	.100000E	1	.100000E	1	.100000E	1	.100000E	1	.100000E	1
CONCCL	.102084E	1	.382614E	1	.202467E	1	.162696E	1	.516497E	1	.433857E	1
CONBIC	.914496E	0	.628386E	0	.725500E	0	.388661E	0	.108578E	1	.103643E	1
FESQCM	.254340E	3	.699828E	2	.501563E	2	.697873E	2	.481874E	2	.115371E	3
TNITPH	.760000E	1	.690000E	1	.750000E	1	.680000E	1	.800000E	1	.800000E	1
DMGDAR	.120000E-	2	.800000E-	3	.180000E-	2	.250000E-	2	.190000E-	2	.210000E-	2
LOADKG	.150000E	2	.100000E	2	.125000E	2	.100000E	2	.250000E	1	.125000E	2
TRTIME	.450000E	1	.650000E	1	.600000E	1	.700000E	1	.160000E	2	.200000E	2

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OBSERVATION MATRIX MAT2

	DSP240		DSP020	
CONST	.100000E	1	.100000E	1
CONCCL	.235629E	1	.589709E	0
CONBIC	.437802E	0	.704369E-	1
FESQCM	.566807E	2	.903000E	2
TNITPH	.700000E	1	.500000E	1
DMGDAR	.160000E-	2	.140000E-	2
LOADKG	.200000E	2	.500000E	1
TRTIME	.240000E	2	.200000E	1

TABLE 7:2

CORRELATION MATRIX

	CONCCL	CONBIC	FESOCM	TNITPH	DMGDAR	LOADKG
CONCCL	.100000E 1	.300725E 0	-.875162E-1	.495924E 0	-.135753E 0	-.230717E 0
CONBIC	.300725E 0	.100000E 1	.256893E 0	.862189E 0	.481994E 0	-.261293E 0
FESOCM	-.875162E-1	.256893E 0	.100000E 1	.246878E 0	-.712592E-1	.117187E 0
TNITPH	.495924E 0	.862189E 0	.246878E 0	.100000E 1	.313483E 0	-.201666E 0
DMGDAR	-.135753E 0	.481994E 0	-.712592E-1	.313485E 0	.100000E 1	-.144026E-1
LOADKG	-.230717E 0	-.261293E 0	.117187E 0	-.201666E 0	-.144026E-1	.100000E 1
TRTIME	.438933E 0	.400671E 0	-.365755E-1	.471693E 0	-.136778E 0	.434189E-1

CORRELATION MATRIX MAT2

	TRTIME
CONCCL	.438933E 0
CONBIC	.400671E 0
FESOCM	-.365755E-1
TNITPH	.471693E 0
DMGDAR	-.136778E 0
LOADKG	.434189E-1
TRTIME	.100000E 1

TABLE 7.2

VAR NAME	REGRESSION COEFF	STANDARD ERROR	CONFIDENCE INTERVAL	T STAT	PART CORR	MULTIPLE CORRELATION	E S S
CONBIC	110.4800739	.622125E 2		1.78	0.51	0.146	.371470E 5
DMGDAR	= 5200.0499462	.397476E 4		1.31	=0.40	0.371	.327393E 5
LOADKG	3.0769176	.294090E 1		1.05	0.33	0.433	.308537E 5
TRTIME	= 2.9596726	.252951E 1		1.17	=0.36	0.406	.316924E 5

VARIABLES NOT IN THE REGRESSION SET

VAR NAME	T STAT	PART CORR	MULTIPLE CORRELATION	E S S
CONCCL	0.47	=0.17	0.543	.267556E 5
TNITPH	0.14	0.05	0.526	.274368E 5

E.S.S.	.275080E 5
RESIDUAL ERROR	.552852E 2
MULT CORR	0.525
INTERCEPT TERM	142.5564169

TABLE 7:2

CHAPTER 8

CONCLUSIONS

The multivariate statistical analysis has yielded disappointing results. There is no consistent trend over the various types of implant and many of the results are merely confusing. Two main factors emerge, one is that even larger samples of implants are necessary to keep enough implants of one type for a reasonable analysis and the other is more work on the effect of hardness difference between components.

The results on hardness were somewhat confusing but definitely suggested that some form of relationship between corrosion rate and hardness difference exists. It would be interesting to go back to the original figures and to carry out a study on accurate hardness differences instead of using ranges and to compare this with the actual contact corrosion between those two surfaces. At the moment the comparison is always made on plate or appliance grades which obscures any relationship.

The results on stress effects by comparing corrosion on Sherman plates inserted into the femur with those in non-weight bearing bones should also be further investigated. In this connection a study of stress distribution along the Sherman plates used in osteotomies to see whether the observed variation in hole corrosion could be due to stress effects should also be undertaken.

Considering the proposed mechanism of corrosion suggested as a result of the SEM study, in vitro tests should be made to try to simulate the effects. This will not be easy, some fretting corrosion specimens were studied for another research group and using conventional fretting apparatus corrosion of this type is not produced. However if fretting corrosion exists in the body it will not be of the usual uniaxial high speed type. It will be of varying direction, at low rates with rests between groups of oscillations

and under conditions where crevice corrosion is likely. In order to simulate this type of attack a device must be constructed which will produce similar conditions in the laboratory.

Turning now to the materials' tests again the results were disappointing. Differences in behaviour between surfaces produced by various techniques were demonstrated. The effect of cathodic activation was perhaps more significant. The oxide films formed during the test would probably include anions from the solution. Chief among thes is probably phosphate and by disturbing the integrity of the film passivity may be made harder to achieve. A disturbed film would probably have increased cationic permeability and this too would tend to increase the passive current. It would be interesting to repeat these experiments at different polarisation rates to measure the kinetics of the change.

The surface damage test was perhaps the most disappointing. Errors in the experimental design were only discovered after the author had left the University of Aston and facilities no longer existed to complete the series satisfactorily. A major problem in the test as a whole was contamination. The best way to overcome this is perhaps a 'clean room' environment which would cut down atmospheric contamination and also reduce the chance of pick - up from solid surfaces.

Measuring increase in corrosion as a result of surface damage seems a valid test for implants but perhaps a simpler test protocol would have yielded more useful results. Other methods of analysing the solutions should also be considered. The obvious alternatives are atomic absorption spectrophotometry and neutron activation analysis. The former has difficulty in handling complex solutions of transition elements and correction factors have to be calculated for a wide range of concentrations. The latter is theoretically

the most promising although measurements are likely to be tedious. Since a range of active isotopes is likely to be produced a combined energy and time discrimination would be necessary. A careful study of isotope tables giving modes of decay and half-lives would yield a test protocol. Whether this would be superior to an improved experimental design based on spectrophotometry is open to question but for development of the test should certainly be considered more fully.

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