A STUDY BY X-RAY PHOTOELECTRON SPECTROSCOPY, OF SULPHUR CHEMISTRY IN RELATION TO CORROSION

by

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A thesis submitted to the Faculty of Engineering at the University of Surrey for the Degree of Doctor of Philosophy

Materials Science and Engineering Department,
University of Surrey,
Guildford,
April 1990.
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REFERENCES
Thanks are extended to all members of the Materials Science and Engineering Department, in particular past (Dr Mike Edgell, University of Alabama in Huntsville, USA and Dr Roy Paynter, University of Laval, Canada) and present members of the Surface Analysis Group, in especially Dr J Watts and Chris Burt.

Thanks are also extended to the members of the Laboratoire des Physico Chimie des Surfaces, University Pierre et Marie Curie for all their help on my visits there, in particular Drs Phillip Marcus and Elie Protopopoff.

Thanks also to Dr Glyn Smith, Chemistry Department, University of Surrey, for help with inter-ionic calculations, to Dr Chandrasekaran, Department MSE, for help with thermodynamic calculations and to Dr Tony Chamberlain, Microbiology Department, University of Surrey, for discussions on the fate of sulphur species in solution.

Warmest thanks are reserved for Professor J Castle for knowing precisely when to drop the most useful hints and for encouragement and support throughout the period of this work.

I would also like to thank Dr John Rivière for agreeing to examine this thesis.
Entering the 21st century against a background of rapid technological innovation and the growing importance of pollution control, industry must optimise control of its resources and use technology to its best advantage. Thus, process mechanisms must be known so that consideration may be given, both to the degradation in service or during manufacture, and to the fate of the by-products of the manufacturing process.

Many corrosion problems are associated with the presence of impurities which are able to bring about the destruction of the passive layer on a metal surface. The principal elements associated with such corrosion are chlorine and sulphur. The conditions under which a chlorine concentration may result in damage to passive films, by pitting on stainless steels for example, have been well researched over the years. The important role of sulphur as a corroder has only recently come to light. Sulphur is increasingly present as a pollutant, in coal, oil and gas, as leaner mines and wells are used, and is also found in many metal-bearing ores. From these sources, as well as natural ones such as volcanoes and the oceans, sulphur may enter the atmosphere, the waters and the material goods of the earth by many different routes.

The evidence to date on the role of sulphur in corrosion suggests that it is active at much lower concentrations than chlorine, often at monolayer concentrations. With
current materials developments emphasising the minaturisation of devices, the use of thin films and the control of the interface in composite materials, the importance of research into the action of sulphur cannot be denied.

The work reported in this thesis examines the information and experimental methods that are available to the corrosion scientist interested in the action of sulphur on metal surfaces in very small quantities - of the order of a monolayer.

The work is divided into three main parts:

i) a survey of the literature concerning the role of sulphur in corrosion and the many materials which are subject to accelerated corrosion under the action of sulphur at high temperature, in air, from micro-organisms and in solutions. The survey of the incidence of sulphur-induced corrosion is deliberately wide to emphasise the ubiquitous nature of sulphur's activities in materials degradation. Attention is also drawn to the properties of a monolayer of sulphur adsorbed onto a metal surface and the subsequent consequences for surface passivation and dissolution.

These observations lead into the second half of this chapter which is concerned with the use of experimental analytical techniques for surface characterisation, principally X-ray photoelectron spectroscopy (XPS). The development of methods for estimating the character of
nearest neighbours (to the element under study) from photoelectron line shifts is covered: from Koopman's approximation for electron orbital energy to the incorporation of both inter- and extra-atomic relaxation energy terms. The results from studies on silicon and chlorine are reviewed.

ii) Chapter 2 examines in more detail the experimental results in the literature pertaining to the surface analysis of sulphur, and the characterisation of sulphur in the solid state. The experimental work reported covers the surface analysis of a range of sulphides and sulphates and compares the data with those for sulphur monolayers on CuNi and gaseous and organic sulphur compounds. The correlation of extra-atomic relaxation energy with alternative measures of electron orbital polarizability is investigated.

iii) The third chapter is a study of the mechanism of stimulation of corrosion of CuNi(90,10) in deaerated sea-water. Two contrasting theories of this alloy's corrosion are considered:

1) the acceleration of the cathodic reaction due to the formation of a thicker and more porous oxide film in sulphur polluted waters.

2) the catalytic stimulation of the cathodic reaction by adsorption of sulphur.

The behaviour of the alloy is investigated in solution by introducing H₂S and by using samples with previously

(iv)
adsorbed monolayers of sulphur. Electrochemical characterisation is followed by surface analysis. The results are compared to the data in Chapter 2.

iv) Chapter 4 is a summary of the main findings of this work and includes recommendations for further work.
SPELLING CONVENTIONS

Throughout this work the terms polarization and polarisation are used, but in different contexts.

Polarization refers to changes in electron density as a result of local changes in electric field, such as the approach of a foreign atom, or the creation of a core hole.

Polarisation, however, is used to describe control of the electrical potential of a sample in an electrolyte, with respect to a standard reference electrode.
CHAPTER 1 LITERATURE SURVEY

1:1 THE ROLE OF SULPHUR IN CORROSION

1:1.1 HIGH TEMPERATURE CORROSION

1:1.1.1 CORROSION RESISTANCE AT HIGH TEMPERATURES

In turbines, rocket systems, supersonic aircraft, engines, power stations and in manufacturing, materials have to be exposed to high temperatures. In addition to the dangers of failure by creep, corrosion phenomena cannot be ignored.

At high temperatures the competing reactions of interest are sulphidation, oxidation and diffusion of sulphur and/or hydrogen into the bulk, generally via grain boundaries or dislocations at the surface since these are higher energy sites. In coal fired power stations and the petrochemical industry these reactions are of crucial importance since the difference between an adherent or a flaking oxide/sulphide on a pressure vessel outlet pipe will determine the efficient lifetime of the plant. In general oxides tend to be more stable than the nearest sulphide. However, when sulphide does form beneath an existing oxide, its lower melting point, with respect to the corresponding oxide, will give rise to additional problems such as the sloughing of an outer oxide and liquid metal salt/metal corrosion.

In stainless steels Cr,Al or Si additions are made to
take advantage of their higher free energies of oxidation so that protective films of $\text{Cr}_2\text{O}_3$, $\text{Al}_2\text{O}_3$ or $\text{SiO}_2$ can form. The well known Delhi Pillar of cast iron contains 6% Si which appears to have protected it from corrosion, in a very humid area for hundreds of years.

Developments in coating technology have led to improvements: aluminium can be deposited directly onto nickel turbine blades and heated to form a diffusion bonded oxidised layer which contains fewer impurities than similar layers formed directly by alloy addition, providing greater corrosion protection for a given thickness.

However, these oxide films have disadvantages due to the difference in the thermal expansion coefficients of the oxide film and the metal substrate. When temperature changes result in different thermal expansion, stresses are set up within the oxide film and at the interface between oxide and substrate. These stresses tend to act as nucleation centres for thermal fatigue cracks which eventually propagate into the base alloy causing catastrophic failure if undetected.

1:1.1,2 HIGH TEMPERATURE CORROSION IN SULPHUR CONTAINING ENVIRONMENTS

At certain partial pressures of oxygen a sulphide may become more stable than the corresponding oxide, and the result may be:

- sulphidization: formation of a sulphide;
- sulphidation: formation of a mixed oxy-sulphide;

or - hot corrosion: sulphur attack assisted by deposits.

In petrol refineries in the 1950’s efforts were being made to improve the quality of petrol, entailing reforming under catalytic action. This process required a certain pressure within the reactor to be maintained. Dramatic losses of pressure were traced to the clogging of low Cr steel tubes due to the flaking of iron sulphide scales (1). Current practice recommends the use of austenitic stainless steel, to make use of the protection afforded by a Cr rich layer.

In fluidised-bed combustion of coal for power stations, limestone is commonly used as a sorbent of sulphur, and the calcium sulphate formed can cause corrosion of the metal parts of the bed by sulphidation where the concentration of oxygen is low. Although conversion rates are high so that up to 90% of the sulphur in coal can be removed, the fluidised beds are continuously agitated so the wear resistance of the coating in this environment will determine the lifetime of the boiler tubes.

On Cr and FeCr alloys in molten sulphur or sulphur vapour at 350°C Cr$_2$S$_3$ scale grows with parabolic kinetics, as a diffusion controlled reaction (2). In Cr rich alloys (>40% Cr) the rate limiting step appears to be diffusion of metal cations through the scale to the scale/sulphur interface via scale defects assumed to be cation vacancies. Pure Cr in molten Na$_2$S$_3$ has a linear corrosion rate of
around 100µm/year while duplex coated chromed steel (>70%Cr + Fe,C,Al,N at the surface) has a corrosion rate of 3µm/year in the same solution due to alloying elements reducing the concentration of defects in the Cr₂S₃ film.

Alloys high in nickel may form liquid sulphides; the Ni/Ni₃S₂ eutectic melts at 645°C and is capable of dissolving iron. This might occur when burning sulphur-bearing fuels in air deficient conditions, or when handling H₂S or CS₂. Extreme care must be taken when welding nickel or nickel-base alloys to prevent any sulphur-containing greases or other material decomposing and penetrating the melt.

The important range of NiCrAl alloys, protected by alumina, can suffer catastrophic corrosion due to loss of Cr by sulphide formation below the growing oxide film, in air/sulphur dioxide mixtures. This arises because the ratio of sulphur to oxygen partial pressures at the oxide/metal interface becomes a good deal higher than it was in the bulk of the gas, (the oxygen partial pressure will equal the dissociation pressure of the oxide). The loss of Cr to its sulphide allows nickel to oxidize as a non-protective film. The result is rupture of the alumina film, internal oxidation of Al and Cr and sulphidation at a greater depth. The attack proceeds via grain boundaries. If yttrium additions are made at less than 1% levels corrosion may be reduced and an adherent oxide preserved. The yttrium is assumed to getter the sulphur and trap it in the grain.
boundaries (3).

For Mo in sulphur vapour, linear growth kinetics are found due to cracking at the $\text{MoS}_2$/Mo interface due to compressive stresses in the scale. However at lower temperatures and pressures parabolic growth has been observed, in which case the diffusion of sulphur is thought to be rate controlling. In liquid sulphur a compact and adherent film is formed.

The marketing of battery powered vehicles has been limited for at least the two following reasons: the first is that the capital outlay for an electrical vehicle tends to be high, and although running costs are low, there is short battery lifetime (4 years), fleet owners tend to trade in fleets after 2 years and thus cannot take the long term view while dealers are unlikely to push onto the market vehicles requiring little maintenance; secondly, a nine hour recharge is commonly required, (presumably to give around 7 hours driving time), but at the moment the electricity cheap rate tariff lasts only for 7 hours.

A new NaS battery, having five to six times the energy density of a conventional lead acid battery, has good prospects for commercial vehicles used regularly, and possibly also submersibles, trebling the range and reducing the unladen weight. Regular use is preferred in order to keep the battery at its efficient operating temperature of 270°C, which presents a very corrosive environment to the Cr plated mild steel casing and the aluminium gas-tight
seals. LiS cells are also under development but these require an operating temperature of around 400°C (4). Current cells fail by rupture of the cell walls and research into improving the choice of casement material continues (5).

It is necessary to distinguish between polysulphide melts and molten sulphur since in each case the activity of sulphur will be different and different corrosion products, with different solubilities will be formed. In addition the defect structure is important; sulphides tend to be cation deficient, and the extent of defects in the corrosion products will control the diffusion rates of sulphur anions and metal cations. Similarly to aqueous corrosion (cf: 1.5 Aqueous corrosion), workers have noticed that sulphur in small quantities can be relatively more active than in higher quantities.

This has led to a steadily increasing number of fundamental studies into the precise way in which sulphur is taken up by metals and alloys under well controlled conditions. In order to do this, sophisticated analysis techniques are employed and the work requires a capital investment of not inconsiderable size compared to more simple experiments such as measuring relative weight losses/gains from different alloys/surface treatments in a particular gas atmosphere at a particular temperature. Workers in this field have turned to Low Energy Electron Diffraction (LEED) to measure the structure of adsorbed
molecules of particular gases on single crystal surfaces, followed by calculation of the adsorption isotherms. By introducing other gases the competition for adsorption sites may be estimated and suggestions made for the safe impurity level in a stream of gas for a particular lifetime within a certain temperature regime. Conjoint use of AES and XPS will give semi-quantitative surface analyses and chemical state information which can subsequently be used to investigate field samples from a mechanistic background. The analysis of time dependence requires the analysis of thicker films and also perhaps several microns into the bulk in order to measure diffusion profiles. AES, SIMS and EDXA are used where spatial resolution is required.

In work on sulphur diffusion it has been suggested that hydrogen may catalytically assist the adsorption of sulphur onto nickel surfaces, either when present as $H_2S$ or as hydrogen dissolved in the bulk (6). The presence of sulphur at the surface, either by adsorption or by segregation from the bulk, modifies the surface reactivity. Heat of adsorption measurements indicate a large binding energy for sulphur to transition metal surfaces of around 4 - 5eV/atom for Ni and Fe (7). This gives stability over a large temperature range and the possibility of involvement with other surface reactions. This is often described as "poisoning" of the surface for oxidation.

For example, the diffusion of sulphur through the oxide scale on 304 stainless steel has been studied (8). The
authors found that if the oxide scale had formed initially in the presence of small amounts of $\text{H}_2\text{S}$, in addition to the preferred $\text{CO-CO}_2-\text{N}_2$ mixture, a more porous oxide scale was formed with sulphur concentrated at the oxide metal interface which resulted in a dramatic increase in permeability to sulphur and subsequent internal sulphidation of chromium. This observation may be explained by the finding that sulphur and oxygen islands can form independently on FeNi(60,40) (9). In this case the authors describe how vertical growth of oxide can continue by oxygen dissociation on top of the existing oxide islands, but since diffusion is limited to the island area a polycrystalline oxide containing many more defects than usual is formed. Once a certain thickness has been reached vertical diffusion becomes rate limiting and lateral growth may occur over the sulphide islands.

SUMMARY

Thus, sulphur can have extremely detrimental effects at high temperatures. It is important to discover which particular sulphide may have formed in a high temperature corrosion scale failure, in order that the correct thermodynamic adjustments can be made - i.e. changes in partial gas pressures or improvements to alloying element stability.
1.2 STRESS CORROSION CRACKING (SCC)

1.2.1 STRESS CORROSION CRACKING MECHANISMS

Two models are commonly used to describe stress corrosion cracking and corrosion fatigue:

1) film rupture/slip and anodic dissolution
or
2) hydrogen induced cracking.

1) Film rupture followed by dissolution at the film-free crack tip is a model developed to explain the development of strain assisted crack paths. TEM work has shown that the tip of a crack in an austenitic stainless steel contains many mobile dislocations and that in these regions dissolution of material is accelerated. Although the sides of a crack and the crack tip may subsequently repassivate, the time taken for repassivation will depend on the rate of diffusion of oxygen to the bared surfaces. The stress concentration remains at the passivated crack tip, which under repeated loading will again rupture. The sensitivity of this time dependent crack growth may be described by the equation:

\[ V_t = \frac{M}{nF\rho} \cdot \frac{Q_f}{e_f} \cdot \varepsilon_{ct} \]  

(E 1:1.2,1a)

where \( V_t \) = time dependent crack growth rate due to the environment

- \( M \) = atomic weight for the crack tip metal
- \( \rho \) = density
- \( F \) = Faraday's constant
\[ n = \text{number of electrons/mole involved in the oxidation process} \]
\[ Q_f = \text{the oxidation charge density passed between oxide rupture events} \]
\[ e_r = \text{charge on an electron} \]
\[ \varepsilon_{ct} = \text{the strain rate in the metal matrix at the crack tip} \]

This type of model can be tested experimentally by straining electrodes under the mechanical and electrochemical conditions expected to persist at the crack tip. Good agreement has been found for many environmental and alloy systems (10). However it is obvious that the crack tip strain-rate and the repassivation rate will determine whether mechanical (slip) or chemical (dissolution and repassivation) processes govern the growth of the crack. In addition, the aggressive properties of certain anions may be modelled if it is assumed that a certain concentration of these may be maintained at the crack tip. Once an aggressive environment is introduced the sides of the crack will also undergo dissolution and the ratio of the dissolution rate at the crack tip to the dissolution rate at the crack walls determines whether the crack blunts or propagates (11).

2) The hydrogen-induced cracking model stems from direct fractographic observations of ductile and brittle striations in SCC fractures. The ductile regions appear
similar to air-fatigue failures and are considered to have had no environmental enhancement. Hydrogen is thought to adsorb onto the bare metal at the crack tip and then to diffuse into the bulk ahead of the crack tip. Hydrogen is trapped at inclusions causing mechanical failure at the inclusion bulk matrix and brittle crack growth further into the matrix.

The presence of manganese sulphide inclusions is thought to be very important in this mechanism since the dissolution of a manganese sulphide inclusion at the crack tip provides $\text{H}_2\text{S}$ and $\text{HS}^-$ which are thought to promote hydrogen adsorption by their adsorption on the bare metal surface. Brittle cleavage failures are very often observed to start at the site of a manganese sulphide inclusion. The rate-determining steps for this type of model include the oxide rupture event as outlined above, but the role of hydrogen ahead of the crack tip means that other rate-determining mechanisms need to be considered also.

Mechanisms for hydrogen embrittlement include:

a) Decohesion: hydrogen may donate its electron to a vacancy in a d-band of a metal's orbitals. If this leads to an increase in repulsive forces between adjacent metal atom nuclei, a decrease in the inter-atomic cohesion of the lattice may follow; this may result in crack growth by bond rupture at the crack tip. Additional support for a) is that a surface covered with adsorbed hydrogen has a lower
surface energy than a clean metal surface, and it is further suggested that this lowers the stress level for crack growth according to the Griffith criterion.

Griffith proposed that a surface energy term be included in the equation for unstable crack growth in order to consider the energy required to create the "two" new surfaces of the advancing crack. The validity of this would depend on establishing what is the time dependence of the process. The probable sequence of events is:

- a monolayer of hydrogen is adsorbed,
- electrons are transferred from H to the d-band of the substrate,
- the stress at the crack tip rises to a level required to break the bond between two adjacent metal atoms (one or both having an extra d-band electron), and fresh metal is exposed.

The bond energy for chemisorbed hydrogen on various metals is larger for Cr (74 kcal/mol) than for Fe and Ni (68 and 67 kcal/mol respectively), suggesting that SCC via this model should be faster through the outer Cr rich film in stainless steels than through the Cr poor near-surface layer.

This model has also been used to consider liquid metal embrittlement and anions other than hydrogen. For example hydrogen sulphide is known to inhibit the recombination and evolution of hydrogen from the metal surface which could promote the above reaction. Marsh (12) found that the
diffusion of hydrogen into a furnace grade steel was observed only in the presence of sulphide in the electrolyte. More work obviously needs to be done on the surface energy criterion for metals containing diffusing hydrogen.

b) A hydrogen pressure mechanism for hydrogen embrittlement concerns the build up of hydrogen within the bulk which can aggregate as molecular hydrogen generating voids and exerting internal stress so as to lower the apparent fracture stress. This mechanism is generally not used when considering brittle failure processes since it is thought to be more important for ductile failure via void growth routes. However, this would seem to be rather similar to the hydrogen induced cracking outlined above.

Thus, in both film rupture/anodic dissolution and in hydrogen induced SCC, sulphur can play a harmful role.
Drier visions, worse foreboding
Glare upon me through the gloom,
Britain's smoke-cloud sinks corroding
On the land in noisome fume,
Smilches all its tender bloom
All its gracious verdure dashes
Sweeping low with breadth of bane
Steering sunlight from the plain
Showering down like rain of ashes.

Extract from BRAND by Henrik Ibsen, 1866

1:1.3,1 INTRODUCTION
Since the notorious pea soup fogs of the 19th century, which lasted well into the middle of the 20th century, scientists, politicians and the general public have appreciated the problems that air pollution can cause. In 1872 Robert Angus Smith (13), having coined the term acid rain, and conducted several experiments into the acidity of rain water around Manchester, wrote "When the air has so much acid that two to three grains are found in a gallon of the rain water,..., there is no hope for vegetation...galvanised iron is valueless...stone and bricks of buildings crumble."
The first scientific confirmation of dirty snow claimed to originate from Britain was made in 1881. In the beginning of the 20th century the first effects of acid rain on wildlife were reported as mass deaths of salmon in rivers of southern Norway. However acid rain was not blamed until 1959 when Dannevig (14) made the suggestion which has spurred an increasing amount of research, sponsored by governments and also those accused as culprits. It was not until 1986 that the British government formally admitted that the acidification of the atmosphere had serious pollutant effects.

The precise chemical reactions that occur in the atmosphere of the earth are extremely complex. As different industrial pollutants make their way into the atmosphere, conditions of partial pressures, temperature, light and humidity are constantly changing. The modelling of all possible reactions is desirable, but a huge task. Progress in this field at the current time is focused on atmosphere sampling at altitude from aeroplanes. The data on the concentrations of molecular species together with meteorological details and the locations of known major pollution sources provide the information required to estimate the predominant reactions occurring in the different strata of the atmosphere. Currently we may confidently say that sulphur and nitrogen dioxides are known to react with water vapour to form acid rain, and
that this reaction may be catalysed by the presence of light and ozone.

Some brief details may serve to show how the photochemical smogs are built up. In the lower parts of the atmosphere, below the ozone level, the solar radiation is limited to $\lambda > 290\text{nm}$. In these layers most inorganic gases are converted to stable salts like sulphates and nitrates, while organic components are converted to $\text{CO}_2$, $\text{H}_2\text{O}$, ammonium salts and nitrates. The combustion of metal sulphides, coal, and oil leads to $\text{SO}_2$ and $\text{SO}_3$ emissions which can react with water to form sulphuric acid in an aerosol form. $\text{O}_3$, $\text{NO}_2$ and oxidised organics are released following photochemical reactions with automobile exhaust fumes (15). In addition to these reactions there is an imposed diurnal cycle depending on temperature and solar radiation.

The important consequence for corrosion is that acidic vapours can condense on any surface and locally change the pH.

1:1.3.3 DAMAGE TO MASONRY

The precise nature of the effects of acid rains on building damage has come to light over the past 10 years. The effect on marble of acidic waters is to dissolve it, forming gypsum which may be washed off the objects during restoration or cleaning and obliterating detail. Rheims Cathedral is a recent example, while the Acropolis in
Athens has had several parts replaced with replicas. If not washed off a brittle crust forms which eventually falls off. Polished marble samples exposed on the roof of the Victoria and Albert Museum have been known to lose their polish in this way within four weeks.

Quantitative studies attempting to measure weathering rates (16) have measured the erosion rate on a balustrade in St. Paul's Cathedral, London, as averaging 0.08mm/year over the 1st 250 years its life, while between 1980 and 1985 0.14 → 0.22mm/year has been measured. Laboratory tests (17) on limestone show that it dissolves 75 times faster in a typical modern rain (pH = 4) than in unpolluted rain (pH = 5.25).

There is little information about the resistance of mortars to acid rain, although Peterson (18) has reported that acid rain dissolves brick masonry by attacking the glassy matrix which binds the silica grains together. This evidence supports work by Feenstra (19) who claimed in 1984 that there was a problem affecting stained glass all over Europe. He has shown that acid water leaches potassium and other chemicals from glass into soluble compounds and that the higher the pH of the water the faster the migration to the surface. The loss of brilliance in stained glass windows, for example the blue at Chartres Cathedral, is suspected to be due to acid rain.
1:1.3,4 DAMAGE TO CELLULOSE

Books stored under more acidic environments absorb both sulphur dioxide and nitrogen dioxide, eventually crumbling. The greater part of acidity in books, however, undoubtedly comes from the processing of wood pulp and from the use of the inorganic size, aluminium sulphate, applied to allow the paper to accept ink. Prior to the 1850's gelatine (an alkali) was used for this purpose, but at that time demand for paper was expanding while the supplies of gelatine were not. Modern paper commonly gives a pH of 4 or 5, while the intense chemical processing of the wood pulp results in pick-up of trace elements. The trace elements Cu and Fe are thought to catalyse the oxidation of sulphur dioxide and stimulate sulphuric acid formation.

In recognition of this and other pollution problems affecting the storage of paper some 30 million pounds has been ear-marked for the creation of an unpolluted environment in which to house the British Library collection (20). Other cellulose-containing products and also leather suffer.

1:1.3,5 DAMAGE TO METAL WORK

A detailed investigation of the corrosion rates of various metals in sulphur dioxide/nitrogen dioxide polluted atmospheres has been carried out (21) in atmospheres with $\text{SO}_2$ and $\text{NO}_2$ concentrations from 300-1400$\mu$g/$\text{m}^3$ at 95% relative humidity using weight loss measurements. For zinc,
SO$_2$ was the main cause of corrosion, NO$_2$ showed no inhibiting properties, copper was particularly susceptible to corrosion in high concentration mixed atmospheres, while gold-plated nickel showed little or no corrosion in pure SO$_2$ or NO$_2$, but accelerated corrosion of nickel via pinholes in the plating in the mixture of gases. Neither steel nor aluminium were corroded in the NO$_2$ atmosphere. The mechanisms proposed for a) NO$_2$ and b) SO$_2$ in humid atmospheres are shown below:

a) $3\text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_2 + \text{NO}_3$ \hspace{1cm} (E 1:1.3,5a)

both products of this reaction are known inhibitors for metals forming oxide films such as steel and aluminium but not for copper or zinc.

b) $\text{SO}_2 + \text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \text{NO}$ \hspace{1cm} (E 1:1.3,5b)

The authors suggest that this reaction may be "catalysed" by NO$_2$. They also claim that SO$_2$ can stick to all surfaces while NO$_2$ does not. The results of this work confirm that a serious corrosion problem exists for copper roofing and perhaps a more serious problem exists for galvanised structures which, for best galvanic protection remain unpainted but do not benefit from the inhibiting action of HNO$_2$ and NO$_3$ as does aluminium.

These types of reactions are particularly important for
quality control standards specifying the performance of electronic devices.

Many chips are interconnected by copper contacts, which are nickel and gold plated. When in use these contacts will warm, when switched off, the contacts cool, via heat sinks, and the surrounding atmosphere can condense onto the contact to an extent depending on the dew point. Further problems may be envisaged concerning the role of dust particles settling on surfaces and occluding oxygen from the surface. The mode of failure of electronic contacts is either by corrosion of the nickel and copper developing from pores in the surface gold plating, or by corrosion product creeping around to the unprotected nickel layer and copper substrate. Once the contact has oxidised, contact resistance increases, the voltage required to overcome this resistance increases and power consumption rises, until the voltage cannot overcome the contact resistance, and the device fails.

This type of failure can be controlled by control of the humidity, sulphur dioxide and nitrogen dioxide content of the atmosphere. Svedung (22,23) proposes the same equation as Henriksen (21) above, for the production of $\text{H}_2\text{SO}_4$ on the surface of a gold contact, but finds evidence for the catalysis of this reaction by gold, when compared to the same conditions on a glass specimen. In this electrochemical system the gold functions as an efficient cathode while the bases of the pores in the gold plating
are the anodes. The corrosion product, thought to be copper and zinc sulphates, is transported up the pores and deposited on the gold surface. At lower humidities nitrosonium hydrogen sulphate (NOHSO₄) can form. The amount of attack varied from none in pure SO₂ at a relative humidity of <60%, to heavy attack in NO₂ at r.h. = 40%. When chlorine is added to the atmosphere the gold itself is attacked. A film of acids forms on the surface of the gold contact and diffusion of the reactants through this layer to the gold catalyst becomes rate-controlling.

Svedung (22,23) has reported a study of the action of different gases and mixtures of gases on circuit board contacts. In H₂S alone corrosion was humidity independent, but significant observations of the edge creep of corrosion products was made, and this was thought to be driven by the potential difference between the anodic cut edges and the cathodic gold. The gold areas were thought to become deactivated as they became covered with reaction product and the cathodic reaction moved towards the centre of the sample. Other workers (24) have proposed that some metallic surfaces can photosensitise photochemical reactions for light of long λ.

Across Europe bronze statues have shown signs of damage by atmospheric pollution. Severe pitting has been found beneath soot deposits and copper sulphate detected as corrosion product, the tin apparently having been converted to metastannic acid and washed away by rain. On high leaded
bronzes, white lead sulphate powder is formed and washed away in the same way. The attractive patina formed on bronze is in fact not protective under these conditions, and by being slowly washed away means that the original surface, often cold-worked by the artist, is lost.

**SUMMARY**

Thus the general acidification of the atmosphere has serious consequences for the environment. The action of sulphur in the chain of acidification is probably more damaging than nitrogen. The effect of these pollutants on printed circuit boards will have important consequences for product reliability and manufacturing quality control.
INTRODUCTION

One of the main reasons for corrosion of metals in the sea or buried under the earth, is deterioration due to biological action in that environment. Some microbes have a reproductive cycle of 10 minutes, which under favourable conditions could result in a biomass of several times that of the earth in 24 hours. Happily such favourable conditions of temperature, light, supply of nutrients, water, and absence of predators, etc, are not found in practice. Many workers have emphasised that it is the interactions between different organisms by exchange of nutrients and metabolites that enhance microbiological corrosion processes.

Five general types of organism are commonly encountered:
1) Algae - metabolise by photosynthesis, a nutrient for other microbes.
2) Fungi - not well known, but deposit organic material. Cladosporium resinae is known to cause corrosion problems in jet fuel tanks, ship and other offshore installations; it is also known to colonise stone, producing carboxylic and other organic acids (25).
3) Bacteria - iron oxidising species have been known from the end of the 19th century; they oxidise ferrous iron to ferric iron and their deposits provide slimy, anaerobic conditions where anaerobic species may survive.
4) Sulphate oxidising species - can convert sulphur and sulphide to sulphates in aerobic conditions, and if stagnant conditions exist the pH can fall to around 1. These species can often coexist, not surprisingly, with sulphate reducing bacteria.

5) Sulphate reducing bacteria (SRB) - this species has been extensively studied. They are able to use sulphate as an oxidising agent/electron acceptor to assimilate organic material from organic acids in a reaction catalysed by the enzyme hydrogenase, to release an ester, $\text{C}_2\text{O}_4^{2-}$ and energy. The reduction of sulphate may occur by several steps involving catalysis by one or more enzymes. These bacteria are found in wet anaerobic conditions where cathodic inhibition might be expected to restrain corrosion.

These bacteria are also thought to be involved in the corrosion of reinforced concrete. The corrosion products arising from the infiltration of deicing salts are $\approx 7x$ more voluminous than the original metal and consequently damage may be easily spotted as cracking and surface blisters. The SRB's are thought to follow chloride ingestion, attacking the iron and extending far along the reinforcing bars. Since the corrosion products arising from SRB activity are less voluminous than those from chloride attack, the SRB induced corrosion may proceed undetected.

1:1.4,2 ACTION ON FERROUS MATERIAL

The sulphide produced by the bacteria leads to the
formation of FeS and Fe(OH)$_2$. Observation of samples showed the presence of a black FeS film, which could be detached to reveal a surface which subsequently suffered accelerated corrosion (26). Two depolarisations are feasible:

1) Anodic depolarisation by stimulation of the anodic reaction due to S$^{2-}$ ions, generally thought to be important initially, but of less importance once a sulphide film has formed.

2) Precipitation of ferrous sulphide leading to cathodic stimulation. Ferrous sulphide is cathodic with respect to mild steel forming a galvanic cell.

3) Stimulation of the cathodic reaction by uptake of hydrogen produced at cathodic sites, by the bacteria.

Miller (26) has suggested that 3) is most important.

These reactions also occur on surfaces in seawater under both anaerobic and aerobic conditions, in the latter case in association with oxygen consuming species, where local anaerobic regions can persist and SRBs may metabolise. In this way these bacteria are often associated with localised or pitting corrosion. However the precise mechanisms, and the importance of solid surfaces is still unclear.

The immunity potential may be depressed for iron in sulphide solutions by up to -200mV (27). This is extremely important for buried pipe lines which are protected from corrosion by impressed potential methods, and which are subject to attack by SRBs.

Shannon and Boggs (28) have observed adherent iron
sulphide films formed in high concentration (515 ppm) sulphide/oil/brine solutions. However, at lower concentrations only non-adherent films were formed. The authors point out the importance of the formation of the macinawite phase \((\text{Fe}_x \text{S}_{1-x})\), said to form non-protective films with large surface areas, at high sulphide concentrations in an \(\text{H}_2\text{S/CO}_2/\text{H}_2\text{O/Fe} \) system. The macinawite phase is thought to be the pyrophoric compound implicated in oil-tanker explosions during cleaning with high pressure water jets. The stability of this phase as a true sulphide is disputed, and its position on the iron/sulphur phase diagram is only tentatively assigned by Clark and Clark (29). Macinawite (up to 50% sulphur) has not been synthesised in the absence of water, is thought to be one of the products of SRB metabolism on iron, and is unstable with respect to the trolite form of \(\text{FeS} \). The formation of macinawite is thought to be restricted to a pH range of 6.5-8.8, while outside this range more protective films may be formed. Thus the Pourbaix diagram reported by Bouet and Bennet (30) should be used with care. Additional evidence from Meyer et al. (31) found that the protective scale could be formed in triply-distilled water but not in brines.

The action of sulphide compounds in sour gas environments has been shown to be highly corrosive on mild steel, leading to corrosion rates of between 5 and 300 mm/year. The corrosion rate in the presence of elemental
sulphur, however, was measured as over 1000mm/year. This has led to the recommendation that sulphur suspensions may be used as low hazard etchants.

Since the early 1970's it has been realised that stainless steels are also subject to microbial attack (32). A study of nine stainless steels in three different sulphate reducing bacteria cultures (33) found that ferritic lower alloyed grades were less resistant than austenitic grades. The propagation of pitting induced by these cultures was assumed to be catalysed by the sulphide ions produced by the SRBs according to the following reactions (34,35):

\[
\begin{align*}
\text{Fe} + \text{HS}^- & \rightarrow \text{Fe( HS}^- \text{)_{ads}} \\
\text{Fe( HS}^- \text{)_{ads}} & \rightarrow \text{Fe( HS)_{ads}} + e^- \\
\text{Fe( HS)_{ads}} & \rightarrow \text{Fe( HS)}^+ + e^- \\
\text{Fe( HS)}^+ + \text{H}_3\text{O}^+ & \rightarrow \text{Fe}^{2+} + \text{H}_2\text{S} + \text{H}_2\text{O}
\end{align*}
\]

The continuous regeneration of H$_2$S means that the pitting of a stainless steel surface can continue with very little SRB activity.

The specific case of the microbiological corrosion of the copper-nickel alloys is covered in Chapter 3.
SUMMARY

Thus, the field of microbial corrosion requires the marriage of materials scientists and microbiologists in order to try to characterise those features of a sub-soil or water circulation system capable of providing a haven for a damaging microbial culture. Further work in mechanism specification would be desirable so that predatory strains of microbes may be introduced to consume or slow the metabolism of the damaging microbes. This is particularly important for the SRB strains which produce H$_2$S.

AQUEOUS CORROSION

INTRODUCTION

The development of corrosion and electrochemical experimentation is following a similar path to studies in high temperature corrosion (cf 1:1.1,1). However in aqueous solutions the environment is inherently more conductive, the transport of ions is fast, surface material is dissolved and, at a given temperature reactions tend to happen faster. This makes for an increase in the complexity of mechanistic studies since many ions may exist and react in the solution phase. Several workers have studied the influence of aqueous species in solution and in concentration cells such as cracks or pits with a view to predicting the pH and then the corrosion rate. With respect to the role of anions two main schools of reasoning may be identified:
a) a primary role by participation of the anion in the charge transfer process;
b) a secondary role by complexing with corrosion products and blocking the surface for hydroxide ion adsorption which results in an increase in the active surface area for dissolution.

However, experimentally, it is hard to distinguish between these two processes. In particular it is difficult to determine the order of the reactions with respect to the anion of interest since an increase in salt concentration at constant pH may lead to varying activity factors which should be compensated. This might be done by using an excess of supporting electrolyte but competition for adsorption by the electrolyte anion could mask the action of the anion of principal interest.

1:1.5,2 EXPERIMENTAL TECHNIQUES

As electrochemical techniques developed in the 1960's, experimenters were able to carry out carefully controlled monitoring of

a) sample potential, with respect to some standard potential, such as the calomel reference electrode, and b) the sample current flowing to an inert counter electrode, commonly gold or platinum, with respect to changes in sample surface finish and concentration of ions in solution.

Brasher (36) studied the effect of chloride, nitrate and
sulphate ions on the breakdown of mild steel oxide films formed after 24 hrs at 180°C. This work showed that the relationship between steady-state potential (E) and anion molar concentration (C) could be expressed by:

\[ E = a - b \log C \]  
(E 1:1.5,1a)

where \( a \) and \( b \) are constants,
and the relationship between corrosion rate and anion concentration by:

\[ \frac{dW}{dt} = K C^n \]  
(E 1:1,5,1b)

where \( W \) = weight loss/unit area
\( t \) = time
\( C \) = concentration of adsorbate

\( K \) and \( n \) are constants for the adsorbent and adsorbate at a given temperature.

These expressions describe behaviour in the chloride and nitrate bearing electrolytes for monovalent anions at concentrations up to \( 10^{-1} \)M, with \( b = 0.07V \) and \( n = 0.5 \), and for the divalent sulphate ion the relations held up to lower concentrations of \( 10^{-5} \)M, with \( b = 0.25 \) and \( n = 41.55 \). The term \( n \) was suggested to be equal to the term \( n \) in the Freundlich adsorption isotherm:
\[ A = K C^n \]  

(E 1:1.5,1c)

where \( A \) = the amount of anion adsorbed/unit area or the fraction of the surface area covered with adsorbate if only monolayers are considered.

The higher value of \( n \) for sulphate solutions suggested that the mechanism is not only adsorption. The author went on to point out that one of the problems in this type of experiment is the difficulty of \( pH \) control: the nature of the cathodic reaction is to produce alkali (\( OH^- \) ions) reducing acidity, while in alkaline solutions with bubbling air, \( CO_2 \) will be absorbed reducing the alkalinity.

Brasher (36) found that on abraded and grit blasted surfaces the oxide film failed at any number of weak spots in the oxide, and that this, and the rest potential, was reproducible. Pickled surfaces on the other hand lack many surface imperfections and corrode in a more uniform fashion, but with less reproducible rest potentials. From the above evidence the important variables appear to be:

- sulphate, sulphur and sulphide concentration,
- \( pH \),
- impressed or rest potential,
- surface finish,
- electrolyte conductivity,
- time and temperature.
THE ROLE OF SULPHUR IN STAINLESS STEELS

In studying the behaviour of alloys in solution where sulphide is present (as an impurity) several authors have reported the presence of elemental sulphur on the sample surface (37,38,40). In steels manganese sulphide inclusions (used to stabilise sulphur as MnS and also act as an lubricant when machining) have been studied (39,40,41) in order to confirm their electrochemical behaviour. Wranglen has suggested, for carbon steels, that manganese sulphide inclusions act as local cathodes:

$$2H^+ + 2e^- \rightarrow H_2$$  \hspace{1cm} (E 1:1.5,3a)

A finely divided ppt of MnS surrounds each inclusion, as a result of non-equilibrium cooling and diffusion gradients set up in the melt, and this leads to enhanced activity in the steel, stimulating the anodic reaction:

$$Fe \rightarrow Fe^{2+} + 2e^-$$  \hspace{1cm} (E 1:1.5,3b)

while the surrounding alloy covered with a passive film behaves as the main cathode:

$$20 + 4H^+ + 4e^- \rightarrow 2H_2O$$  \hspace{1cm} (E 1:1.5,3c)

This configuration easily gives rise to pitting corrosion and the danger of perforation or the development
of cracks. Many mechanisms for the local chemistry of pitting have been proposed \((39, 40, 41, 42)\) some backed by AES data \((39, 40)\), others from mechanistic studies based on thermodynamics \((42)\). It is often claimed that the species formed within a pit is a sulphide since \(H_2S\) is evolved from the deposit on contact with dilute \(H_2SO_4\).

Forchammer \((43)\) found that heat treatment of steels could result in sulphide coagulation with the possibility that extremely large and potentially damaging stress raising pits could be formed, while when inclusions were finely dispersed, shallower pits were formed. Other workers have tried to reduce pitting by using different sulphur scavengers in the melt, such as caesium \((44)\) or titanium \((41)\), on the basis that these sulphides have a much lower aqueous solubility. In stainless steels, pitting often develops around a manganese sulphide inclusion that is in close association with a mixed oxide or slag inclusion \((39)\). Ke and Castle \((40)\) have studied the dissolution of manganese sulphide inclusions in sodium chloride solution using AES and EDXA to monitor surface (approximately 10nm) and bulk (<1um deep) changes respectively. They have observed the spreading of sulphur around the inclusion and suggest that the sulphide is dissolved, forming a sulphite in solution which is then back-deposited as elemental sulphur on the metal surrounding the inclusion.

Newman \((45)\) has ranked sulphur species in the following order for increasing pitting propensity for 304 stainless
steel at pH = 4.5 - 6:

\[
S_2O_3^{2-} > H_2S = S_4O_6^{2-} > SCN^- >> SO_3^{2-}
\]

However at concentrations above 0.02N of SCN\(^-\) and \(S_2O_3^{2-}\) pitting could be inhibited. The authors (45) support a theory of preferential electro-migration of sulphur ion species, over HS and chloride species which usually carry a 1\(^-\) charge as opposed to the 2\(^-\) charge on the sulphide ion, into pits. If these species are then combined with hydrogen:

\[
S_2O_3^{2-} + 6H^+ + 4e^- \rightarrow 2S + 3H_2O \quad (E 1:1.5,1f)
\]

then acidification may be reduced, and perhaps the H\(_2\)O will be available for repassivation. Newman proposed that at low concentrations, the result of pitting or repassivation should be related to the amount of a particular species that is required to "poison" the exposed metal of a pit. In this case the variables for the experimenter should include:

- solution conductivity,
- pH,
- alloying elements present at the surface and their propensity to form ions in the electrolyte species,
- any preferential dissolution during pitting,
- solution concentration of each adsorbing species and
- temperature.
THE ROLE OF SULPHUR ON NICKEL

The formation of oxide films on nickel has been extensively studied in line with the importance of nickel super-alloys, and the role of this element in stainless steels. Marcus et al. (46) have shown using radiotracer, electrochemical and XPS monitoring that the passivation of nickel may be "poisoned" by a monolayer of sulphur. Kim and Oriani (47) have shown that sulphur from $\text{SO}_2$ diffuses via grain boundaries in pure nickel and forms a nickel sulphide. Studies by tensile fracture and subsequent Auger analysis show that inter-granular fracture dominates until the amount of sulphur present at the grain boundary falls below 0.03 monolayers.

THE ROLE OF SULPHUR ON BRASS

The de-zincification of brass can result in total failure of the material in certain acidic chloride and sulphate solutions. The role of the anions in this process is thought to be the formation of soluble cuprous sulphates and chlorides which, being metastable in solution may redeposit copper on the metal away from the copper atom's original lattice position, resulting in an opening of the lattice for further dissolution of zinc (48).

THE ACTION OF SULPHUR MONOLAYERS

By carrying out adsorption experiments using radioactive sulphur $^{35}\text{S}$, on different metal substrates, generally
single crystals, (Ag, Cu, Fe, Ni, Pt: references 49, 50, 51, 52, 53, and Ni-Fe alloy 54, 55, 56 respectively), it has been shown that the surface coverage of a monolayer of sulphur on Cu(111) equates roughly to 40ng cm\(^{-2}\); this is equivalent to \( \approx 8 \times 10^{14} \) atoms/cm\(^2\) giving a ratio for the number of sulphur atoms to substrate metal atoms in the 1st atomic plane equal to 0.5. The density of adsorbed atoms is only weakly dependent on orientation. These monolayers are generally stable over a wide range of partial pressure ratios (\( P_{\text{H}_2S}/P_{\text{H}_2} \approx 10^{-3} \rightarrow 10^{-5}\)).

When comparing the heat of adsorption (\( \Delta H_{\text{ads}} \)) and heat of formation (\( \Delta H_f \)) of the three-dimensional sulphide, it is found that the former is generally more exothermic: by 75 kJ/mol for Ni. For the materials studied so far a trend approximating to the following equation may be applied:

\[
\Delta H_{\text{ads}} \approx 1.25 \Delta H_f \quad \text{(E 1:1.5,6a)}
\]

In the case of silver the adsorbed monolayer is known to be stable in nitric acid in which the corresponding sulphide would be dissolved. A complete description requires the evaluation of the following equilibria:

\[
\text{Sulphur segregation in the metal} \quad \overset{\text{segregation}}{\longrightarrow} \quad \text{Sulphur desorption on the surface} \quad \overset{\text{desorption}}{\longrightarrow} \quad H_2S - H_2
\]

\[
\text{Sulphur dissolution in the metal} \quad \overset{\text{dissolution}}{\longrightarrow} \quad \text{Sulphur adsorption on the surface} \quad \overset{\text{adsorption}}{\longrightarrow}
\]
A schematic energy diagram of the sulphur metal interactions is given below:

A further finding is that adsorbed sulphur layers are ordered in two dimensions. By using LEED techniques the symmetry of the diffraction pattern and spot intensities are used to determine the adsorbed atom locations. The sulphur atoms are located at points of high coordination and high symmetry. Danielson and Baer (57) have discussed the way sulphur enhances the dissolution of nickel: results from EXAFS (Extended (X-ray) Absorption Fine Structure) have indicated significant alterations in the interplanar spacing of the first two nickel atom layers. For a clean Ni(011) surface, the outer layer of Ni atoms is contracted towards the second layer by 5-10% from the bulk positions, while when covered with a monolayer of sulphur, the first row Ni atoms are expanded by ≈11% from the bulk.
positions, away from the second layer of Ni atoms. The bonding of the adsorbed S atom has been modelled for a Ni$_4$S cluster, by using Ni valence orbitals consisting of 4s$^1$ and 3d$^9$ (one extra electron in the d orbital) and proposing a bonding pair between S(3p$_y$) and two opposing Ni 4s orbitals. The S(3p$_z$) orbital is given some bonding character with the Ni 4s electron while the S(3p$_x$) orbital is complete and repels the remaining Ni 4s orbitals from the atom not involved in 3p$_y$ bonding. These Ni 4s orbitals are able to participate by bonding with neighbouring sulphur atoms. Some S3s and Ni3d character also contributes to the overall picture.

The predictions from the above model give good agreement with LEED results (on single crystal substrates) for the position of the S atom, to within 0.03Å. The covalent nature of the bond is confirmed also from the sulphur atom radius measurement ($\approx$ 1Å), which agrees closely with Pauling's prediction of 1.04Å. By careful measurement of the work function change with sulphur coverage, the fraction of an electron transferred at each adsorption site can be evaluated as a charge transfer from metal to sulphur.

These characteristics give rise to a well bonded layer with dramatic consequences for the reactivity of the surface.

In electrochemical terms the capacitance of the double-layer is lowered by a factor of 2, corresponding to
the change in work function and also the change in the potential of zero charge.

A saturated layer of adsorbed sulphur is found to inhibit completely hydrogen adsorption on Pt, and while this only corresponds to a S/Pt ratio of only 0.8, the influence is complete. At a third of a monolayer, only $\frac{1}{5}$ of the hydrogen that is adsorbed on a clean surface is in fact taken up (58). This has important consequences for hydrogenation reactions and general catalysis where $H_2$ dissociation may be involved. The hydrogen evolution reaction on pure iron is accelerated in the presence of a monolayer of adsorbed sulphur, but is inhibited on nickel.

Marcus and Oudar (59) and Marcus, Oudar and Olefjord (46) have shown that a monolayer of sulphur on nickel, and also on Ni-25%Fe, catalyses the dissolution reaction. From knowledge of the bonding of adsorbed sulphur on nickel, it can be shown that the Ni 4s - 4s bonds are disrupted and the metal-metal bonding weakened. This means a lower activation energy for dissolution/solvation and a lower electrochemical potential may be recorded in solution, a drop of 60mV for pure Ni and a drop of 100mV for the alloy. The passivation is delayed until a portion of the sulphur has desorbed by oxidation, and is found at a higher potential than the passivation potential for the clean surface. Passivation occurs when two OH$^-$ ions adsorb on adjacent sites and can react by disproportionation:
This explains why inhibition of passivation is found even though some OH$^-$ ions can be adsorbed and detected using XPS.

On iron however, the iron sulphur bond is less stable in an electrolyte than the Ni-S$_{ads}$ bond. The result is an accelerated dissolution, followed by passivation after S desorption is complete, prior to the beginning of the passivation region for iron. On the alloy, passivation is achieved with a higher passivation current than the clean surface, at a coverage 70-80% of a monolayer, which has distorted structure.

In conditions where sulphur is dissolved in the NiFe alloy, sulphur segregates from the bulk to the surface during dissolution. Once the amount of sulphur accumulating at the surface reaches a critical level, passivation is inhibited. The sulphur is found at the metal/oxide interface. The final surface compositions recorded were Ni$_3$S$_2$ for nickel and Ni$_{2.5}$Fe$_{0.5}$S$_2$ for the alloy. These would constitute non-protective films.

Although the above work was reported for single crystals the consequences for real samples are clearly similar. In particular sulphur adsorption will commence at local defects (dislocations and grain boundaries) and can quickly reach a monolayer concentration able to give rise to local pitting attack, intergranular corrosion and hydrogen
adsorption.

However, the crucial point is the conclusive evidence for the action of sulphur in a monolayer, the high stability of that monolayer and the fact that a discrete three-dimensional sulphide is not required before accelerated dissolution or other affects are observed.

Further work (59) has included the development of the Pourbaix diagram to include the region of stability of the sulphur monolayer in aqueous solution. Results for Pt have recently been reported and are reproduced here in Figure 1:1.

Figure 1:1: Equilibrium potential/pH diagram for the system $S_{ads}$-Pt-H$_2$O at 25°C.
Yates et al. (60) have showed from theoretical calculations the variation in valency charge density above an Rh(001) surface with and without a sulphur monolayer. The height of a given valence charge density \((10^{-6} \text{a}^{-3}\text{eV}^{-1})\) varies from \(\approx 5\text{Å}\) on the clean surface, to \(\approx 6.3\text{Å}\) on the sulphur covered surface when considering electrostatic interactions. When including chemical effects a perturbation of the local density of states about the Fermi level results in a lowering of the Fermi level of around 1Å for both nearest and next nearest neighbours. Illustrative diagrams are reproduced in Figure 1:2.

Figure 1:2 : The perturbation to local density of states due to an adsorbed S monolayer on Rh(001) (ref 60). a) Valence charge, b) Fermi level.
SUMMARY

This survey of the role of sulphur in aqueous corrosion forms a basis for the study of the action of sulphur on a clean surface. What is not clearly understood is how sulphur causes passive film breakdown.

It might be assumed that one mechanism is via pores in the passive film, followed by the adsorption of sulphur onto bare metal, thereby changing the dissolution characteristics. However, it is not yet clear how sulphur may have a destructive action on an oxide, it might be supposed that by virtue of being a bigger ion than $\text{O}^{2-}$, the orbitals of the sulphide ion can interact with the metal ion orbitals from beyond the metal/oxygen ion and result in debonding of oxygen, rebonding to sulphur.

1:1.5,7 BENEFICIAL EFFECTS OF SULPHUR

In contrast to the above evidence for the detrimental effects of sulphur there is a significant role for sulphur-containing compounds in the inhibition of corrosion on aluminium (61) and of intergranular corrosion (IGC) on stainless steel (62). The use of organic sulphur-containing compounds such as phenylthiourea and dibenzyl-sulphoxide, is successful in preventing IGC. In these compounds sulphur atoms have an unshared lone pair of electrons and are able to inhibit the hydrogen evolution reaction on the entire surface of AISI 304 stainless steel. In areas where Cr was depleted, anodic dissolution was inhibited, while in areas
of no Cr depletion anodic dissolution was stimulated. This results in a similar corrosion rate at both Cr-depleted and Cr-undepleted areas and IGC is prevented. This appears to be an outstanding example of the use of the versatility of the sulphur atom’s properties. Other inhibitors such as benzotriazole are able to reduce IGC by inhibiting the hydrogen evolution reaction alone.

1:1.6 SURFACE ANALYSIS FOR CORROSION STUDIES

This first part of the literature survey has covered both basic and sophisticated data relating to the role of sulphur in corrosion, as well as trying to show something of the way study techniques have developed.

It has tried to show the many situations and classes of material for which sulphur can stimulate the degradation process. It is of extreme practical importance that more is learnt about the environmental conditions which can facilitate this degradation and how it may be controlled.

The review has also emphasised the importance of surface reactions when sulphur is present in monolayer quantities, such as the generation of surface dipoles and the distortion of Fermi and valence band levels on a metal surface.

The importance of sulphur acting in this way on modern materials prompts the analyst to consider what tools are available to characterise the reactions of sulphur at
surfaces. A brief survey of techniques follows:

1) For single crystal studies LEED was the classical technique for monitoring the position of sulphur atoms adsorbed at a surface.

   The other techniques listed below are not single crystal specific.

2) Scanning Tunnelling Microscopy (STM) measures the changes in potential across a surface with single atom resolution. This technique can provide a 2-d image of the positions of atoms at a surface. Further developments are likely to provide additional depth information.

3) Secondary Ion Mass Spectroscopy (SIMS) may be used on polycrystalline samples for identification of molecular fragments. This technique has excellent depth resolution but is only poorly quantifiable. The developing Secondary Neutral Mass Spectroscopy (SNMS) technique is expected to improve quantification in ion-induced mass spectroscopy studies.

4) Auger Electron Spectroscopy (AES) has excellent spatial resolution, having traditionally been used for grain boundary segregation and embrittlement studies. However quantification is difficult, chemical state resolution is limited and sample damage/contamination may cause problems.

5) Synchrotron and ultra-violet (UPS) sources have strong applications in studying valence band changes. These techniques require support from theoretical modelling for interpretation.
6) XPS is quantifiable, surface sensitive and shows good chemical state resolution. There is also a long history of analysis of sulphur in organic molecules. The probing of both core and valence levels of the atom provides a wealth of useful data for physicists and quantum chemists as well as for the materials scientist. Further discussion of the use of XPS is given in the following, second part of the literature survey.
One of the most interesting aspects of x-ray photoelectron spectroscopy (XPS) is the possibility of deducing, precisely and directly, the binding energy of electron in solids, and very real progress has been made in testing the applicability of theoretical and semi-empirical models for atomic orbital energy calculation.

Shirley (63) has reviewed the use of XPS (X-ray Photoelectron Spectroscopy) in relation to the predictions that could be made by the various models in general use at that time (1974).

One of the fundamental features of XPS is the possibility of resolving differences in binding energy for an element bound to different neighbours and with different valencies. For conductors and semi-conductors, the effects of "screening" can be detected from changes in recorded binding energies, and can be related to the polarization of itinerant conduction and valence band electrons. The initial state information (called the inductive effect by chemists) is the change in binding energy of an electron from that in a free atom to that in a solid or a molecule. It contains three possible contributions: 
a) a Coulomb term, dependent on the electrostatic potential increase at the core, reducing the energy required to remove an electron.

b) An exchange term which contributes to core level splitting in magnetic elements (eg Ni shows ≈0.6eV); however, in general this is not different for different chemical states.

c) The Madelung contribution, which is important in ionic solids where nearest neighbours will carry opposing charge, and the chemical shift will be reduced by this factor.

Other initial state contributions become important for the following additional situations:

- band bending in semi-conductors and interfaces;
- adsorption into a surface electrostatic dipole;
- surface charging;
- surface core-level shifts in pure metals;

and - polarization in molecules.

Final state information relates perceived changes in the relaxation of the atom’s orbitals after photoionisation to its chemical environment and the polarizability of nearest neighbours. The important components of final state shifts are generally the intra-atomic and extra-atomic relaxation energies. The intra-atomic relaxation energy is generally independent of chemical environment for a particular ionisation state.

Much the pioneering work on the elucidation of extra-atomic relaxation energy has been studies of gases
and their adsorption onto solids. For example xenon has been adsorbed onto palladium, and noble gases have been implanted into metals. The advantage of rare gases is that they adsorb weakly and allow the study of almost pure extra-atomic relaxation. For more complex systems the behaviour of monolayers of adsorbed gases can be studied, for example the extra-atomic relaxation energy for a monolayer of Ar on Ni (1.74eV) was found (63a) to be less than that for Ar on CO on Ni (1.84eV) (2 monolayers of gas on the metal), suggesting that the CO could behave like a conductor in this structure.

The use of these experimental data in conjunction with the various theoretical models can assist in defining the range of applicability of a model.

For example the ground-state-potential model (GPM) (64) is used to predict chemical shifts due to initial state properties as a result of the establishment of molecular orbitals and changes in electrostatic potential energy at core orbitals. It is found to work well for 2nd row elements in roughly similar molecules, such as a series of fluorinated methanes and ethanes, where relaxation effects can be neglected. Once the regime of usefulness is established the measured shifts on other compounds can be used to calculate charge distributions (65,66,67).

A second approach is the use of tightly bound valence orbitals in simple solids such as binary III-V and II-VI compounds. Manne (69) suggested that XPS and X-ray emission
spectra together would give useful information about the atomic orbital composition since both techniques have good sensitivity for different parts of the valence band; the results are used with theoretical density of states calculations (70).

When comparing molecules whose structures are different, but contain a common element, it is possible to consider relaxation effects, that is an apparent change in binding energy, with respect to the free atom orbital energy, as outer orbital, valence band and conduction electrons of the ionized and nearest neighbours atoms are "pulled inward" by the action of the positive nucleus on the creation of a core hole. In some cases the initial state or inductive effect may show no shift while the relaxation effect may be quite large. In this case the relaxation potential model (RPM) (71) predicts the shifts fairly accurately and much better than the GPM which predicts shifts in the wrong direction.

Thus it is clear that relaxation effects will need to be considered in theoretical models. A survey of the methods for its estimation from ESCA techniques will be outlined.

1:2.2 METHODS FOR THE ESTIMATION OF RELAXATION ENERGIES

Much of the work towards an awareness of relaxation energies has been carried out Wagner and co-workers (72), most important being the screening of many published papers in order to compile a data bank of peak positions, spectra
and Auger parameters for use as finger-printing tools for
samples of unknown chemistry. These data are available on
floppy disc through the National Bureau of Standards,
Gaithersburg, USA.

Wagner's approach to the estimation of relaxation energy
during photoemission arose following observations of large
chemical shifts associated with Auger lines arising from
core holes. The model used considers first the orbital and
binding energies associated with an isolated atom and
compares the predicted binding energy to the Koopman value.
Then, in order to apply the model to real samples, the case
for both the gas and solid phases is outlined. Koopman's
theorem states that, for an isolated atom the binding
energy of an electron is given by the energy of the
electron shell in the ground state, (\( \epsilon_a \)) : this may be
determined from a Hartree-Fock calculation for a frozen
system, that is the wave functions of the other orbitals
are assumed to remain unchanged after photoemission.

For the isolated atom, the effect of a core hole is to
redistribute the potential of the nucleus among the
remaining electrons in order to balance Coulombic and other
forces and stabilise the atom. This is manifest as an
attractive force on the electron orbitals and causes the
energy barrier for the escape of the core electron to be
lowered. Thus the electron requires less energy to overcome
the potential barrier and the measured binding energy (\( E_B^* \))
of the escaping electron is less than its orbital energy
by an amount called the intra-atomic relaxation energy \( R_{ia} \). This is written below (referenced to the valence band):

\[
E^v_B = h\nu - E^v_K \quad \text{(E 1:2.2a)}
\]

\[
E^v_B = \varepsilon_a - R_{ia} \quad \text{(E 1:2.2b)}
\]

where \( E^v \) is the measured kinetic energy,
and \( h\nu \) is the photon energy,
and subscripts \( b \) and \( a \) refer to binding energy and free atom respectively.

Moving to consider the atom in the gas phase as a molecule there are additional considerations. As the atom joins with another to form a molecule certain molecular orbitals are set up in which the electrons are said to be delocalised about the atom pair. These electrons then have a slightly different orbital energy \((\varepsilon_a - \Delta \varepsilon_g)\) than in the above case. During the ejection of a core electron, the attractive potential of the nucleus on the surrounding electrons will extend beyond the outer orbital of the atom with the core hole and will have a distorting effect on the electron orbitals of the neighbouring atom (this is often called "the screening of the nucleus" or "polarization of nearest neighbours"). The recorded binding energy is then reduced from the orbital energy by an additional amount called the extra-atomic relaxation energy \( R_{ea} \), since it arises from outside the original atom.
The chemical shift is then given by:

\[ \Delta E^v_{B} = \Delta \epsilon - R^{ea}_{g} \]  \hspace{2cm} (E 1:2.2d)

Wagner has clearly assumed here that \( R^{ia}_{g} = R^{ia}_{a} \), and has neglected those electrons in the outer orbitals which are now the bonding orbitals, so that in fact, \( R^{ia}_{g} < R^{ia}_{a} \) by an amount that is not equal to \( R^{ea}_{g} \) due to the competing action of the neighbouring nucleus on the bonding orbitals.

A similar approach is used to give the binding energy in a conducting solid, where the atom is now close packed with several neighbours, either similar to, or different from, itself. The shift from the isolated atom to the conducting solid is analysed as for the gas molecule giving:

\[ \Delta E^v_{B} = \Delta \epsilon - R^{ea}_{e} \]  \hspace{2cm} (E 1:2.2e)

where \( \epsilon \) refers to the elemental conducting solid state.

Classically for a conductor with a dielectric constant \( (k) \) and a minimum screening radius \( (r) \) determined by the size of the atom, the relaxation or polarization energy may be given by (72a):

\[ E'_{B} = \epsilon_{a} - \Delta \epsilon - R^{ia}_{a} - R^{ea}_{q} \]  \hspace{2cm} (E 1:2.2c)
where e is the charge to be screened.

For noble gases implanted in metals, in the absence of any chemical bonding between the gas and the metal, then $\Delta e$ (the change in orbital energy due to initial state effects) is zero, $\Delta E_{b} = \Delta R_{d}^{a}$ and $\Delta R_{d}^{a}$ is indeed proportional to $1/r$. However for non-conductors and cases of imperfect screening, the radius is not easily defined and equation (E 1:2.2f) less easy to apply.

The emission of an Auger electron is treated in a similar way but rather more terms are included in the initial definition of energy reflecting the greater complexity of the Auger emission process. The Auger electron, may be emitted as a result of relaxation following core hole emission. A schematic diagram of the process is shown in Figure 1:3. The energy of emission of the Auger electron from the isolated atom is:

$$E_{K_{e}}^{v} = E_{B}^{v}_{(K+)} - 2E_{B}^{v}_{(L+)} - \delta_{(X)} + R_{a}^{1a}$$  \hspace{1cm} (E 1:2.2g)

where $E_{B}^{v}_{(K+)}$ is the binding energy of the initial core electron emitted,

and $E_{B}^{v}_{(L+)}$ is the binding energy of the electron which fills the core hole,
X-Ray photoemission of Si 1s electron followed by de-excitation through Auger electron emission.

Figure 1.3: Schematic diagram of X-ray stimulated photoelectron and Auger electron emission

$\delta_{(x)}$ = the two hole interaction energy due to coupling of the two holes on Auger emission, and $R_{a(T)}^{1a}$ = the total static intra-atomic relaxation energy,

$$R_{a(T)}^{1a} = R_{a(K+)}^{1a} + 2R_{a(L+)}^{1a} \quad (E \ 1:2.2h)$$

The binding energy of the Auger electron that is emitted can be written as $E_B^{v(L+L+)}$. The additional $L+$ in the subscript shows that the Auger electron is emitted from an $L$ orbital which already has a hole resulting from an
electron dropping down to fill the initial core hole in the \( r \) orbital. \( E_B^V \) cannot be directly measured, so the equation uses \( E_B^V \) as an approximation.

For the atom in the gas molecule, and when both final holes are found in the same orbital, the shift from free atom to molecule is written:

\[
\Delta E_{KE}^V = \Delta c_{g(K)} - 2\Delta c_{g(L)} - R^{ea}_{g(g+)} + R^{ea}_{g(L+L+)} \quad (E \ 1:2.2i)
\]

By assuming that \( \Delta c_{g(K)} = \Delta c_{g(L)} \), since these are considered identical in the charged sphere model the equation simplifies to:

\[
\Delta E_{KE}^V = -\Delta c_{g(L)} + R^{ea}_{g(L+L+)} - R^{ea}_{g(g+)} \quad (E \ 1:2.2j)
\]

For the conducting solid a similar equation can be written:

\[
\Delta E_{KE}^V = \Delta c_{e(K)} - 2\Delta c_{e(L)} - R^{ea}_{e(e+)} + R^{ea}_{e(L+L+)} \quad (E \ 1:2.2k)
\]

Using the assumptions of the Hartree-Fock method, that the chemical shifts for different core level orbital energies are the same, the above equation becomes:

\[
\Delta E_{KE}^V = -\Delta c_{e(L)} - R^{ea}_{e(e+)} + R^{ea}_{e(L+L+)} \quad (E \ 1:2.2m)
\]
Assuming further that the minimum screening radius is the same for the one hole \((k^+\)) and the two hole \((l^+l^+)\) states, and using the classical equation for polarization of a charge \((E 1:2.2e)\), and substituting for the numbers of electrons involved:

\[
\frac{R_{ka}^e}{e_{(k^+)}^e} = \frac{1}{2\pi k} (1-1) \quad \text{(E 1:2.2n)}
\]

\[
\frac{R_{ka}^e}{e_{(l^+l^+)}^e} = \frac{4}{2\pi k} (1-1) \quad \text{(E 1:2.2o)}
\]

this leads to the assumption that \(R_{ka}^e \quad e_{(l^+l^+)}^e = 4R_{ka}^e \quad e_{(k^+)}^e\) and then by substituting for \(R_{ka}^e \quad e_{(l^+l^+)}^e\) in (E 1:2.2k) gives:

\[
\Delta E_{KE}^e = -\Delta e_{(l)}^e + 3R_{ka}^e \quad e_{(k^+)}^e
\quad \text{(E 1:2.2p)}
\]

Wagner goes on to define the Modified Auger Parameter:

\[
\alpha' = BE_{PE} + KE_{AE} \quad \text{(E 1:2.2q)}
\]

the sum of the kinetic energy of the Auger electron plus the binding energy of the photoelectron, a charging- and photon source-independent parameter.

Substituting from E 1:1.2,2e and E 1:2.2n for a \(k\) shell photoelectron and a three step Auger transition as described above:
\[ \Delta \alpha' = \Delta c_{e(K)} - R_{e(K+)}^{oa} - \Delta c_{e(L)} + 3R_{e(K+)}^{oa} \quad (E\ 1:2.2r) \]

and using the assumption that \( \Delta c_{e(K)} = \Delta c_{e(L)} \), this reduces to:

\[ \Delta \alpha' = 2R_{e(K+)}^{oa} \quad (E\ 1:2.2s) \]

The main sources of errors associated with this estimation of extra-atomic relaxation energy are:

1) No account is taken of any changes in the minimum distance for screening (see E:1:2.2n,o), i.e., which type of bonding exists, although for certain simple cases attempts are being made to overcome this problem (Moretti (73) and Veal and Paulikas (74)).

2) The assumption that \( \Delta c_{e(K)} = \Delta c_{e(L)} \) may not be valid. Ley (75) estimated 1 to 2 eV for the difference between these two values, and since the peak positions may be measured to ±0.1eV, then the error bar on an Auger parameter measurement will be ±0.2eV, well within the likely difference. The validity of the equality of the orbital shifts will depend on the degree to which the two orbitals have identical core like character, i.e. the \( l \) orbital is fully localised about the nucleus. This would not be the case for molecular orbitals.

Rivièrè et al (76) have shown that the average value of \( \Delta E_B(j) / \Delta E_B(i) \) is 0.85 ± 0.17 from a survey of data in
the literature, and concentrating on those for which good statistics existed, concluded that accurate extra-atomic relaxation energies could not, therefore, be calculated from $\alpha'$.  

3) To be correct, with respect to the physics of trying to correlate final and initial state information, the photoelectron line used for calculating the Auger parameter should correspond to the initial core hole of the Auger transition. If not, errors will be encountered if the difference $\Delta E_{B(J)} - \Delta E_{B(K)}$ is not equal to zero.

However, the survey of Rivière et al. (76) found the average value of $\Delta \alpha'(BE_i + KE_{k11}) / \Delta \alpha'(BE_k + KE_{k11})$ to be $1.00 \pm 0.05$ for 12 metallic elements. Thus, it seems that within the limits of current experimental accuracy the choice of photoelectron - Auger electron combination is not important, and, for fingerprinting exercises of unknown samples the universality of the Auger parameter should have wide appeal and application.

The useful range of applicability of the Auger parameter covers all elements except Li-F, which lack strict core-type Auger processes while the first series of transition metals and the rare earths show multiplet splitting and shake-up processes, which result in rather more complex Auger line shapes, but, all the more informative if the appropriate theoretical calculations can be made to aid interpretation.
Kowalczyk et al. (79) have studied the effect of the assumption that screening electrons become localised within the conduction bands of the photoionised atom, in order to study how effective the screening is in metals. Under the conditions of complete local screening, a 2-electron interaction would take place between the conduction band screening electron and the electron due to be emitted as the Auger electron. This interaction would give rise to the extra-atomic relaxation energy. The results obtained from this theoretical approach were found to exceed the experimental values, showing that screening was in fact less localised than had been assumed.

Tsang et al. (80) have described a second Auger parameter which they call the energy parameter, $\Delta E$. This is the difference between the experimental Auger energy and the value predicted from experimental values for the orbitals involved, but ignoring the effects of relaxation and core holes:

$$\Delta E = E^B_{(J)} - E^B_{(K)} - E^B_{(L)} - E^K_{(JKL)} \quad (E 1:2,2.1a)$$

This parameter has been used (81) to investigate the degree of "quasi atomic" behaviour shown by Cu and Ni metals which have full 3d shells, during emission of the LMM Auger line series, compared to other transition metals which have unfilled d bands i.e. Cr, V.
Other workers have used parameters based on the above to give more precise estimation of extra-atomic relaxation energy than the Wagner Auger parameter. Hohlneicher et al. (82) have suggested that for samples referenced to the vacuum level (gases generally), precision in specification of energy levels gives:

\[
\Delta \beta_1 = 2 \Delta E_{B_1} - \Delta E_{B_k} + \Delta E_{K_{k11}} \quad (E\ 1:2,2.1b)
\]

\[
= -2\Delta R_1 + \Delta R_{11} \quad (E\ 1:2,2.1c)
\]

Using the classical analysis for Coulombic interactions as in Wagner's analysis:

\[
\Delta \beta_1 = 2\Delta R_1 \quad (E\ 1:2,2.1d)
\]

where \( \beta \) represents the 2p orbital.

Substituting for \( \Delta R_1 \) from the binding energy definition of the photoelectron, gives:

\[
\Delta e_1 = -\left[ \Delta E_{p_1} + \Delta \beta_1 / 2 \right] \quad (E\ 1:2,2.1e)
\]

This gives the initial state contributions to chemical shift. The order of ligand group contributions to initial state chemical shifts was found to be different from that for final state chemical shift. The authors were further able to show that the change in polarizability predicted by
the Wagner Auger parameter for a series of ligands on phosphorus-containing gases followed a slightly different order from that predicted from $\Delta \beta$:

a) ligand group contribution to initial state chemical shift:

$$H = \text{Alkyl} < \text{OCH}_3 < \text{Cl} < \text{F}$$

b) ligand group contribution to final state chemical shift, calculated from $\Delta \beta_{2p} = 2\Delta R_{2p}$ for increasing polarizability:

$$\text{F} < \text{H} < \text{OCH}_3 < \text{CH}_3 < \text{Cl} \approx \text{CF}_3 \approx \text{C}_2\text{H}_5$$

c) ligand group contribution to final state chemical shift, calculated from $\Delta \alpha_{(KLL)} = 2\Delta R_{(2p)}$ for increasing polarizability:

$$H \approx \text{F} < \text{OCH}_3 = \text{CH}_3 < \text{CF}_3 \approx \text{C}_2\text{H}_5 \approx \text{Cl}$$

In recognition of the fact that several relaxation processes occur during photoemission, and in order to resolve the question of the difference in chemical shifts for different core levels, Bechstedt and co workers (83) used the Wagner modified Auger parameter and the Tsang energy parameter to express the dynamic (v) extra-atomic relaxation energy for 1s and 2p ionisations in terms of
these empirical parameters:

\[ \Delta R_{D}^{ea}(1s) = \frac{3\Delta \xi}{2} - \Delta \alpha' \]  
(E 1:2,2.1e)

\[ \Delta R_{D}^{ea}(2p) = \frac{1\Delta \xi}{2} \]  
(E 1:2,2.1f)

where \( \Delta \xi = \Delta E_{(jk)} - \Delta E_{(i)} + 2\Delta E_{(j)} \)  
(E 1:2,2.1g)
taken from ref 83a.

and \( \Delta \alpha' = \Delta E_{(ijk)} - \Delta E_{(j)} \)  
(E 1:2,2.1h)

(NOTE: The use of different symbols in the literature for what is essentially the same expression can lead to confusion. \( \Delta \beta \) (Hohlneicher et al. (82)), \( \Delta E \) (Tsang et al. (80)) and \( \Delta \xi \) (Bechstedt et al. (83), Lang and Williams (83a)) are all equivalent and have been used in this text with the symbols used by the authors. \( \Delta E \) gives a positive value, while \( \Delta \beta \) and \( \Delta \xi \) give negative values. In Chapter 2 of this thesis, the Tsang energy parameter has been used as a proxy for \( \Delta R_{D}^{ea}(1s) \))

These equations have been used to study the polarizability of silicon in tetrahedral configurations (84), and in a series of simple chlorides, (85) and further, the sulphur chemistry in this study.

The drawback of this approach in attempts to correlate the
two parameters $\Delta R_{b}^{ea}(1s)$ and $\Delta R_{b}^{ea}(2p)$ appears to arise from using the same term ($\Delta \xi$) in each one's equation. However it does reveal the fact that the extra-atomic relaxation at a core level is dependent on the core vacancy for low Z values. If it is assumed that this is a consequence of different screening radii, and incomplete localisation of the core levels involved, then the classical approximation, which gives rise to the Wagner Auger parameter no longer holds and the derivations are incomplete, as stated by Rivièr et al. (76).

Nefedov et al. (86) describe a more complex model for the combined determination of atomic charge, extra atomic relaxation energy and Madelung energy. This model uses a Hartree Fock calculation to estimate the ionisation energy of the free ion. The effective charge on the ion is estimated from shifts in the Kα lines of the X-ray spectra, while the extra atomic relaxation energy is found from differences in experimental and theoretical Auger parameters. The authors found that some of the methods currently in use made certain simplifying assumptions, particularly in relation to the charge on the atom and its extra atomic relaxation energy. The model is given below.

The core electron binding energy $E_{i}$ is given by:

$$E_{i} = -e_{i}(q) - R_{i}^{a} + M - R_{(K)}^{ca}$$

(E 1:2, 2.1i)

where $e_{i}$ = the orbital energy
\( q = \) the effective charge
\( R^{la} = \) intra-atomic relaxation
\( M = \) Madelung energy
\( R^{ea} = \) extra-atomic energy

The first two terms on the right hand side of equation (E 1:2,2.1i) represent the ionisation energy \((E^q)_1\) of the charged ion in a given chemical compound, obtained from Hartree Fock calculation. \( q \) is determined from X-ray data using an additive methodology, the contributions from surrounding atoms decreasing in the series:

\[ F > Cl > Br > OH > 1/2O > 1/2S,=O > N > P > C \]

The last two terms account for the effect of the chemical environment of the ion.

The binding energies are expressed as follows:

\[
E_1 = E_1(q) + M - R^{ea}_{(K)} \quad (E 1:2,2.1j)
\]

and for the ion with a double vacancy,

\[
E_{kk} = E_{kk}(q) + 2M - 4R^{ea}_{(K)} \quad (E 1:2,2.1k)
\]

where \( R^{ea}_{(kk)} = 4R^{ea}_{(k)} \) \quad (E 1:2,2.1m)

subtracting \((E 1:2,2.1k)\) from \((E 1:2,2.1j)\) gives:

\[ 1 - 65 \]
This assumes that \( M_i = M_k \) and \( R_{(i)}^{ea} = R_{(k)}^{ea} \), i.e., the \( i \) and \( k \) vacancies are virtually completely localised and can be treated as point charges for the calculation of \( M \) and \( R^{ea} \).

The results obtained by the authors give good agreement for the 2p3/2 orbital, and for the 1s orbital once relativistic corrections are included.

The authors also use the additive method to show that for free molecules extra atomic relaxation energy is dependent on more than nearest neighbours: results from additive calculations were found to be of the order of 1-1.5eV less than experimental results.

1:2.3 THE USE OF HIGH ENERGY XPS FOR A STUDY OF SILICON CHEMISTRY

West and Castle (87) used ZrL series X-rays (\( h \nu \) for \( L\alpha = 2042.4 \) and for \( L\beta = 2124.0\)eV) for the analysis of a series of alumino-silicate minerals. By measuring the Auger parameter, in this case the original un-modified Auger parameter:

\[
\alpha = E_B(1s) + E_{KLL} - h\nu \quad (E\ 1:2.3a)
\]
they were able to show correlation of Auger parameter, for tetrahedral coordinated silicon, with a refractive index, n, using the Lorenz-Lorenz relationship. The Lorenz-Lorenz relationship relates bulk polarizability (p) to refractive index (n) according to the following equation:

\[ p = \frac{3V}{4\pi N} \left[ \frac{n^2 - 1}{n^2 + 2} \right] \]  

(E 1:2.3b)

where \( V \) = molar volume and \( N \) = Avagadro's number.

The unpolarized lattice would be expected to have a refractive index of 1, thus by extrapolation, the Auger parameter \( A_e \) was given as 1407.7eV. By using the equivalent core model of Bergstrom and Hill (88) a similar value was obtained. Being able to calculate \( \Delta A \), and using Kuroda's (89) estimation that the shift in the Auger parameter, \( \Delta A \), was equal to the polarization energy of the surrounding charge, \( E_{pol} \), which could in this case also be equated to a constant \( K \), times the polarizability of the oxygen ion, \( P_{O^{2-}} \), (in these mineral compounds the oxygen ions generally contributed over 90% of the molar or bulk polarizability of the crystal lattices), then

\[ \Delta A = E_{pol} = K P_{O^{2-}} \]  

(E 1:2.3b)

Since the Lorenz-Lorenz relationship describes the bulk polarizability of the medium, the two values, one derived...
from XPS and the other from optical data could be compared. The best fit slope was 1.02, with 99.7% correlation.

Further work by Rivière et al. (87a) showed that the above relationship was better fitted by a curve. A straight line relationship could be obtained by correlation of the Auger parameter with the function \((n^2 - 1) / n^2\), obtained from the Mott-Littleton-Bechstedt theory for polarization energy.

The physical reasons for these changes (87) in oxygen ion polarizability were explained as arising from both structural and chemical features, e.g. the longer the bond length, the larger the value of polarizability. In general the oxygen polarizability recorded for tetrahedral aluminium \((O-Al = 0.175\text{nm})\) was higher than that for tetrahedral silicon \((O-Si = 0.162\text{nm})\). For aluminium in octahedral coordination however the oxygen bonded to aluminium had an approximately constant value, while for identical bond lengths the electronegativity of the charge balancing cation could be correlated with oxygen ion polarizability.

Disadvantages of the ZrL X-ray source are the complexity of the spectra generated (since both ZrL\(\alpha\) and L\(\beta\) are present), the fairly wide X-ray line width \(\approx 1.7\text{eV}\), and a steeply rising background in the vicinity of the Si1s line - see Figure 6 in ref 87.

Yates and West (90) developed a monochromatic AgL\(\alpha\)
source by making use of the second order reflection from a
ground and bent quartz crystal customarily used for the
first order reflection of AlKα X-rays. The range of
accessible 1s photoelectron lines was extended to include
Al, Si, P, S and Cl, while Auger lines from nearly every
element could be excited, and the X-ray line width of 1.3eV
is an improvement over the ZrLα source.

By using the Wagner Auger parameter they were able to
show changes in Auger parameter and oxygen polarizability
for glass and carbon fibres with and without silane surface
treatments. From these changes an increase in the Auger
parameter for silane on sized glass fibres was interpreted
as being due to a strong chemical interaction rather than
to a loosely physisorbed layer. This work may be compared to
a fuller study of the chemistry of tetrahedral silicon
(84). The Auger parameter for silane on sized glass fibres
was found to fall just above SiO₂ (quartz), suggesting that
the silane was bound almost as tightly as Si in quartz, (Si
bonded to four oxygen atoms), lending support to the models
suggested by Yates and West (90).

Streubel et al. (91) used AgLα and AlKα to measure Si1s,
Si2p and SiKLL lines, and an LEG 32 electron gun to record
the SiKLL and SiLVV lines. The authors suggested that the
valence band maximum originates from the 3p orbital of Si
combined with the 2p orbital of any 2nd row element
present, or with the 3d orbitals of any 3d element in the
compound. A nearly linear dependence of chemical shift
versus electronegativity difference \((\Delta N_p)\) was found for SiKLL and SiLVV lines:

\[
\Delta E_{\text{KLL}} = (-4.55 \pm 0.27) \Delta N_p \quad \text{(E 1:2.3c)}
\]

\[
\Delta E_{\text{LVV}} = (-7.94 \pm 0.20) \Delta N_p \quad \text{(E 1:2.3d)}
\]

The difference in constants may be related to the difference in KE of KLL (\(\approx 1610\text{eV}\)) and LVV (\(\approx 80\text{eV}\)) Auger electrons. The LVV Auger electron is excited from only the outer monolayer and represents the special characteristics of that layer which are known to be different from subsequent atom layers (87a).

By plotting the extra-atomic relaxation energy from the Tsang (80) energy parameter against \(\Delta N_p\) a similar nearly linear dependence was found:

\[
\Delta R^{ea} = (-2.96 \pm 0.21) \Delta N_p \quad \text{(E 1:2.3e)}
\]

This was also shown to be linearly related to the bulk dielectric constant as:

\[
\Delta R^{ea} = (13.2 \pm 3.3) \Delta(1-1/\epsilon_o) \quad \text{(E 1:2.3f)}
\]

Their work concluded by studying the dynamic relaxation of Bechstedt et al. (83), finding that this value was the most sensitive to changes in the chemical bond.
Paynter et al. (85) studied changes for a small series of simple chlorides. By calculating the extra-atomic relaxation energies for the Cl1s and Cl2p orbitals according to the method of Bechstedt et al. (83), the possibility of comparing extra-atomic relaxation energies for the 1s and 2p core holes was envisaged. The values predicted by Slater (92) for the change in charge upon hole creation $\Delta q$, were 1 for the loss of a 1s electron and 0.85 on the loss of a 2p electron.

The use of Aitken et al.'s (93) relationship:

$$ R_{D}^{ea} = \alpha \frac{(\Delta q)^2}{2} \quad (E\ 1:2.3g) $$

(where $\alpha$ = the bulk polarizability), relates Slater's $\Delta q$ to the polarizability of the medium. When applied to the data for simple chlorides, the ratio of screening energies gave fair agreement (0.64) with Slater's predictions (0.72).

During similar work on the characterisation of silicon compounds it was noted that the extra-atomic relaxation energy value for a native oxide on silicon was considerably less than the value for a 2000Å thick thermal oxide. The refractive index of thermal oxides prepared at different temperatures is known to fall as the oxidation temperature increases, this is believed to be due to thermal expansion strains between substrate and oxide on cooling.

The results of a series of experiments did not show good correlation between refractive index and $\Delta R_{D}^{ea}$ (referenced
to a clean silicon wafer) due to poor performance of the ellipsometer for the characterisation of thin (<100Å) oxide films; however, when referenced to individual sample substrates an improved relationship was seen (94).

More recent suggestions by Paynter (95) have led to suspicions that the excellent agreement for silicon and chlorine compounds (84,85) may have been fortuitous since random numbers generated within the ranges of the experimental data gave a ratio for $\Delta R_{D}^{ea}(2p)$ to $\Delta R_{D}^{ea}(1s)$ similar to that predicted by Slater. This may be however have been a function of the ranges of data selected and deserves further investigation.

Working with zeolites, containing both aluminium and silicon in tetrahedral network structures, Edgell et al. (96), have shown that the use of modified Wagner Auger parameters can give some indication of changes in polarizability of these network structures by loosely bound charge balancing cations, although precision is hampered considerably by the difficulty of preparing these samples for analysis.
SUMMARY - THE USE OF XPS FOR CORROSION STUDIES

It is now appropriate to link the two parts of this literature survey together to emphasise why XPS is a suitable technique for corrosion and for the characterisation of sulphur in particular.

The first part of the literature survey has stressed the variety of corrosion reactions in which sulphur is implicated, in particular those cases where sulphur is thought to act in low or monolayer concentration. It has also stressed the value of knowing which element in an alloy system reacts with the sulphur causing deterioration.

In the area of fundamental work there is an obvious need to be able to distinguish the dominant chemistry of sulphur in corrosive situations.

Of increasing popularity is the use of radioactive tracers in conjunction with surface analysis techniques. By designing experiments where one anion only is of interest, and using radioactive tracers in solution the amount of anion adsorbed on the surface can be measured at intervals during the corrosion event.

Co-joint use of surface analysis techniques provides information on the location and chemical state of the anion. If the anion becomes bound within a complex of corrosion products it will have a different population of
nearest neighbours than if it were chemisorbed at the surface and in nearest association with a larger proportion of metal atoms.

The second half of the literature survey has shown what potential exists for the determination of the chemical nature of the nearest neighbours to sulphur when studied by XPS. In addition, XPS

- can detect all elements except hydrogen,
- has excellent surface sensitivity the analysis depth being of the order of 50nm,
- can excite both core levels and valence levels
- can resolve peak position shifts which may be used to give information relating to initial and final state chemical shifts. The peaks are also sufficiently well resolved to show satellites and multiplet splitting which can be associated with particular oxidation states (mainly in transition elements).
- is quantifiable to ±10%.

Thus it would appear that XPS is ideally suited to a study of the chemical state, and nearest neighbours in corrosion experiments, where the extent of reaction can be carefully controlled and the first stages of corrosion may be monitored over a few nanometers.
CHAPTER 2 THE USE OF HIGH ENERGY XPS FOR A STUDY OF SULPHUR CHEMISTRY

2:1 THE USE OF HIGH ENERGY XPS FOR A STUDY OF SULPHUR IN CORROSION

2:1.1 RATIONALE

The main reason for the use of X-ray photoelectron spectroscopy for corrosion studies is to take advantage of the surface sensitivity, low sample damage and chemical state resolution capabilities.

As explained above the use of a high energy source able to excite the S1s line, in addition to the S2p, SLMM and SKLL lines, gives access to several methods for the calculation of relaxation energies, and the possibility of specifying the character of nearest neighbours and of bonding.

There are also additional benefits (97):

1) the S1s line is a singlet, and has better energy resolution when generated by monochromated AgLa, than does S2p, an unresolved doublet.

2) The chemical shifts for S2p are smaller than for S1s, making for complex curve fitting for two or more oxidation states, since twice as many peaks require fitting compared with S1s.

3) The S1s photoelectron is emitted from the sample with a
Figure 2:1: S1s and S2p recorded with a) AgLα and b) MgKα (ref 97)
Table 2:1: X-ray Photoelectron Energies and Approximate Inelastic Mean Free Paths

<table>
<thead>
<tr>
<th>Line</th>
<th>X-ray used</th>
<th>Photoelectron Energy (KE eV)</th>
<th>IMFP* Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1s</td>
<td>AgLα₁₂</td>
<td>500</td>
<td>13.4</td>
</tr>
<tr>
<td>S2p</td>
<td>AgLα₁₂</td>
<td>2822</td>
<td>31.9</td>
</tr>
<tr>
<td>S kep</td>
<td>AgLα₁₂</td>
<td>2104</td>
<td>27.5</td>
</tr>
<tr>
<td>S2p</td>
<td>MgKα₁₂</td>
<td>1091</td>
<td>19.8</td>
</tr>
<tr>
<td>S kep</td>
<td>MgKα₁₂</td>
<td>1324</td>
<td>21.8</td>
</tr>
</tbody>
</table>

* the inelastic mean free path = 0.6√KE

lower kinetic energy than the S2p photo- or SKLL Auger electrons giving a more surface sensitive analysis. Inelastic mean free path data are shown in Table 2:1. 4) As previously mentioned the chemical shift associated with the S1s orbital is greater than that associated with the S2s, S2p or SKLL, implying that multiple chemical species will be more easily resolved.

These four benefits may be seen in Figure 2:1 opposite. The sample was potassium sulphide powder which had oxidised to the sulphate form on the surface. The upper spectrum, (a), recorded with AgLα shows the good resolution of the S1s peaks, the large chemical shift and the relatively larger sulphate component, compared to (b), which has a
relatively smaller sulphate component, showing less surface sensitivity, less well resolved separation between the two components and a smaller chemical shift.

As explained in Chapter 1, several corrosion phenomena appear to be stimulated by a monolayer of sulphur at the sample surface, and this presents a need for chemical characterisation on a monolayer scale.

2:2 PREVIOUS STUDIES OF SULPHUR CHEMICAL STATES

2:2.1 X-RAY LINE ENERGIES

By careful design of x-ray detection equipment, sufficiently high resolution can be achieved to distinguish certain sulphur compounds. Sato et al. (98) used a Cr X-ray tube and a sodium chloride analysing crystal, to measure SKα peak positions to an accuracy of 1'. The Kα doublet was not resolved, although with improved instrumentation this may be done. The Kα energy was measured for several samples, the range being from 2307.3eV for CdS to 2308.7eV for the sodium, potassium and ammonium sulphates. Using the equations of Coulson (99) the mean number of valence electrons (N) was calculated, referenced to rhombic sulphur. The authors noted that as the number of valence electrons increased, the accuracy decreased since the shifts, ΔKα, are becoming very small.
Horn and Urch (78) have recorded the S Kβ (3p−1s) lines for several sulphur compounds and found different peak numbers, positions and shapes ranging from a narrow singlet for Li₂S to three components in Na₂SO₃.

2.2.2 LASER SPECTROSCOPY TECHNIQUES

This technique uses a laser beam of a fixed frequency to intercept a stream of negatively charged ions of a pre-selected mass, and then records the kinetic energy distribution of the detached electrons. The reaction may be written:

\[ M^- + h\omega \rightarrow M + e^- \quad (E\ 2:2.2a) \]

The electron affinity of the corresponding neutral is deduced by subtracting the kinetic energy of the detected electron from the photon energy.

Nimlos and Ellison (100) have used an argon laser to study SO₂⁻, S₃⁻ and S₂O⁻ ions. The sulphur oxides are thought to be important as possible intermediates in the oxidation of organo-sulphur compounds, and the related negative ions are important species in solution and solid phase systems. Their results are summarised below:
Table 2.2: Electron Affinity values for sulphur gases derived from Photoelectron Spectroscopy

<table>
<thead>
<tr>
<th>Disulphur Anions</th>
<th>Monosulphur Anions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Species</td>
<td>Electron Affinity (eV)</td>
</tr>
<tr>
<td>$S_2$</td>
<td>1.670 ±0.015</td>
</tr>
<tr>
<td>$HS_2$</td>
<td>1.907 ±0.023</td>
</tr>
<tr>
<td>$DS_2$</td>
<td>1.912 ±0.015</td>
</tr>
<tr>
<td>$CH_3S_2$</td>
<td>1.757 ±0.022</td>
</tr>
<tr>
<td>$CD_3S_2$</td>
<td>1.748 ±0.022</td>
</tr>
</tbody>
</table>

The general conclusions are that the addition of a substituent to a sulphur atom in a pair of sulphur atoms, causes the electron affinity to increase. The substituent is thought to bind to an unpaired electron which would otherwise participate in \( \pi \)-orbital back-bonding. While the addition of a hydrogen atom to a single sulphur makes it more electronegative, similarly, alkyl groups reduce electron affinity for the loan sulphur atom. The HS molecule has a very large stretching frequency, \( \approx 2650-2670 \) cm\(^{-1}\), compared to 750cm\(^{-1}\) for \( CH_3S \), showing how much stronger the 1s-3p bonding is compared to the 2p-3p.

2.2.3 AUGER ELECTRON SPECTROSCOPY

Chemical state determination using Auger spectroscopy is not always easy, since high energy resolution, better than
3%, and good counting statistics are required, two characteristics not normally found together in Auger electron spectrometers. Well known examples showing easily resolvable chemical shifts include elemental silicon, silicon carbide and silicon dioxide, and carbon as contaminant and as a carbide (101).

However there are areas where the chemical determination of sulphur Auger signals has proved possible. Yan (102) has shown how the dissolution of a manganese sulphide \( S_{LMM} \approx 149 \text{eV} \) inclusion next to a mixed oxide inclusion in stainless steel results in the spreading of sulphur over the surrounding surface. The use of scatter diagrams is likely to provide useful information on the correlation of pairs of Auger electron lines in mapping. Yan has been able to distinguish the sulphate and sulphide regions of a map by the correlation of the intensity of sulphur and oxygen signals on a pixel-by-pixel basis. However, the unambiguous determination of different sulphur oxides is likely to be extremely difficult by this technique. The use of this transition \((SKLL)\) excited by x-ray photoelectron spectroscopy is more often used and will be outlined below.

2:2.4 X-RAY PHOTO-ELECTRON SPECTROSCOPY

The pioneering studies of chemical shifts in gaseous sulphur compounds were those of Falman et al. (103),
followed by those in a series of nitroaromatic sulphur compounds (104), when increases in apparent binding energies could be correlated with increased positive charge on the atom. In the early study (103) of chemical shifts involving inorganic sulphur attempts to correlate peak shifts with oxidation number were inadequate when the organic compounds were included. It became obvious that the effective charge on the atom would be more important than the formal charge. This was estimated from Pauling's concept of partial ionic character from a valence-bond model:

\[ q_i = Q_i + \sum_{i \neq j} nI_{ij} \]  \hspace{1cm} (E 2:2.4a)

where \( q_i \) = the charge on the atom in the molecule
\( Q_i \) = the formal charge on the \( i^{th} \) atom
\( I_{ij} \) = the partial ionic character of the bond between atoms \( i \) and \( j \), \( I_{ij} = 1 - e^{-0.25\Delta\chi_{ij}^2} \)
\( \Delta\chi_{ij} \) = the electronegativity difference between \( i \) and \( j \)
\( n \) = average bond number, 1 for a single bond, 2 for a double bond

This model permitted estimates to be made of the location of charge in sulphur-oxygen covalently bonded compounds (105), but not for ionic crystals where the
molecular potential needs to be calculated from the sum over all the ions in the crystal. Figure 2:2 shows the close correlation achieved, with a slope of 5.5eV shift in the S2p peak position for each charge increment.

![Diagram showing correlation of S2p BE with charge](image)

**Figure 2:2 : Correlation of S2p BE with charge**

The use of XPS was suggested (103, 104, 105) for studying:

- the chemical state of sulphur in molecular bonding, by analysis of the valence band;
- of oxidation state;
- bond polarity;
- coordination chemistry;
- charge distribution in molecules;
- substituent effects;
- group shifts;
- neighbouring group shifts
as well as in general analysis.

Suoninen (106) studied gaseous sulphur-containing xanthates (CH$_3$OCS$_2$CH$_3$ and (CH$_3$OCS)$_2$), (key anions for ore refining by flotation to remove sulphide minerals), CS$_2$ and OCS. The binding energies for S1s, S2p and SKLL lines, referenced to the neon carrier gas were recorded for the singly bonded (-S) and doubly bonded sulphur (S=). The shift (=S minus -S) for the S1s peak was larger (1.7eV) than those of the S2p (1.5eV), S2s (1.2eV) and SKLL (-1.3eV). It was suggested that the larger shift for the 1s level was due to stronger valence charge interaction with deep, as opposed to shallow, core levels.

In the gas phase for these molecules the greater part of the chemical shift is assigned to the initial-state charge distribution, and only minor relaxation contributions to final state energy shifts. Orbital calculation, by the relaxation potential method recommended by Shirley (62), predicted relaxation energies of the same sign as measured in this work but of twice the magnitude.

In Keski-Rahkonen and Krause’s study (107) of sulphur gases they were able to include the S1s transition excited by AgLa, and also found the larger chemical shift for the
S1s over the SKLL. The differences between H₂S, SO₂ and SF₆ are shown below:

<table>
<thead>
<tr>
<th>Sample</th>
<th>S1s (eV BE)</th>
<th>ΔS1s</th>
<th>SKLL (eV KE)</th>
<th>ΔSKLL</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂S</td>
<td>2478.5</td>
<td>0.0</td>
<td>2098.7</td>
<td>0.0</td>
</tr>
<tr>
<td>SO₂</td>
<td>2483.7</td>
<td>5.2</td>
<td>2095.5</td>
<td>-3.2</td>
</tr>
<tr>
<td>SF₆</td>
<td>2490.1</td>
<td>11.6</td>
<td>2092.6</td>
<td>-6.1</td>
</tr>
</tbody>
</table>

These authors attempted to estimate the extra-atomic relaxation in the gas phase from the following equations. The binding energy was given by:

\[
E_B = -c^{HF} + \Delta E_{RLX} + \Delta E \quad (E \ 2:2.4b)
\]

where \(-c^{HF}\) is the orbital energy from a Hartree-Fock calculation and \(\Delta E_{RLX}\) is the relaxation energy:

\[
\Delta E_{RLX} = \Delta E_{atom}^{RLX} + \Delta E_{molecule}^{RLX} \quad (E \ 2:2.4c)
\]

and \(\Delta E = \Delta E^{CORR} + \Delta E^{REL} + \Delta E^{ED} \quad (E \ 2:2.4d)\)

(the latter three terms being the correlation, relativistic and quantum electrodynamic energy corrections respectively, calculated as = 7.6eV in total).

The latter energy corrections and the orbital eigen
values were then used to obtain $\Delta E_{RLX}$ for the S1s orbital using equation (E 2:2.4b). Theoretical predictions of $\Delta E_{RLX}$ (-29.5 → -31.0) were less than the empirical results (-31.9eV for $\text{H}_2\text{S}$, -31.7eV for $\text{SO}_2$ and -33.0eV for $\text{SF}_6$) and the difference was assumed to be the molecular relaxation energy. Similarly for the SKLL line 18eV for the theoretical estimate, and 19, 20 and 22eV respectively, for the experimental results, were found.

This method predicts the extra-atomic relaxation in the presence of a double core hole, (SKLL), to be more than double that for the single core hole (S1s).

Comparison of gas phase and solid phase may be made if gas samples can be condensed onto a chilled probe in the spectrometer and analysed without significant warming. Wagner, in a compilation of Auger parameter data (108), reports Auger parameters for condensed $\text{CS}_2'$, $\text{SO}_2$ and $\text{SF}_6'$ and compared the results with gas phase data reported by (107, 109 and 110), see Table 2:3.

From these results the role of the screening energy on condensation is clear: $\text{SF}_6$ acquiring the least, having one sulphur atom bonded to six fluorine atoms, $\text{CS}_2$ acquiring almost twice as much from its peripheral sulphur atoms, while $\text{SO}_2$ is an intermediate case. In Figure 2:5 a Wagner Chemical-State plot shows this and other Auger parameter data.
Table 2:3 : Auger parameters for sulphur gases and solids

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mod. Auger (α' = BE\textsubscript{S2p} + KE\textsubscript{KLL}) (eV)</th>
<th>Δα' (solid-gas)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS\textsubscript{2} (solid)</td>
<td>2275.25</td>
<td></td>
</tr>
<tr>
<td>CS\textsubscript{2} (gas)</td>
<td>2271.43</td>
<td>3.82</td>
</tr>
<tr>
<td>SO\textsubscript{2} (solid)</td>
<td>2273.6</td>
<td></td>
</tr>
<tr>
<td>SO\textsubscript{2} (gas)</td>
<td>2270.25</td>
<td>3.35</td>
</tr>
<tr>
<td>SF\textsubscript{6} (solid)</td>
<td>2274.85</td>
<td></td>
</tr>
<tr>
<td>SF\textsubscript{6} (gas)</td>
<td>2272.9</td>
<td>1.95</td>
</tr>
</tbody>
</table>

Sodhi and Cavell (111,112) measured the S1s, S2p and S\textsubscript{KLL} line shifts for a series of 22 gaseous sulphur compounds, and tried to correlate the values with predictions from theoretical models, viz. the atomic charge plus remote potential, and the central atom potential models. The ratio of ΔE(S2p) to ΔE(S1s) was found to be 0.864, and a slope of 0.88 was recorded for a similar study of phosphorus compounds (113). The fact that the value of the slope is not equal to one shows that the 2p orbital is more effectively shielded from the potential at the nucleus than the 1s. The use of core-valence interaction integrals \(\tilde{\delta}(1s,3p)\) and \(\tilde{\delta}(2p,3p)\) can be used to give a measure of this difference, and although a weighted average of 3p and 3s could have been used, the authors chose to consider that the outermost valence electrons provided the greatest
contribution to relaxation effects. These integrals have
been catalogued by Mann (114), and were ratioed as follows,
giving fair agreement with the experimental results:

\[
\frac{\delta^o(2p,3p)_p + \delta^o(2p,3p)_s}{\delta^o(1s,3p)_p + \delta^o(2p,3p)_s} = 0.902 \text{ for phosphorus}
\]

and

\[
\frac{\delta^o(3s,2p)_s + \delta^o(3s,2p)_{cl}}{\delta^o(3s,1s)_s + \delta^o(3s,1s)_{cl}} = 0.927 \text{ for sulphur}
\]

The theoretical models used were found to predict the
S1s and S2p binding energy shifts with good correlation,
while the Auger shifts were not consistently predicted by
any model.

By using the parameter of (83a):

\[
\xi = E_B(1s) - 2E_B(2p) - E_{\text{AUG}} \quad \text{(E 2:2.4g)}
\]

\[
= \delta_{LL}(1d^2) - R^T_S \quad \text{(E 2:2.4h)}
\]

where

\[
\delta_{LL}(1d^2) \text{ is the two hole interaction parameter } = 56.99\text{eV},
\]

assumed to be environmentally independent,

and

\[
R^T_S \text{ is the total static relaxation energy for the}
\text{adiabatic flow of charge on creation of the second core}
\]
hole in the Auger process.

This term is made up of atomic and extra-atomic terms:

\[ R_S^{T}(LL^*) = R_S^{a}(LL^*) + R_S^{ea}(LL^*) \quad (E \, 2:2.4i) \]

where \( L^* \) signifies an \( L, \) or \( 2p, \) orbital with a hole.

\( R_S^{a}(LL^*) \) was evaluated from a self-consistant field calculation giving 17.14eV. Thus, \( R_S^{ea}(LL^*) \) could be evaluated for each sulphur compound. Strongly electronegative ligands were found to have small \( R_S^{ea}(LL^*) \) values while ligands of low electronegativity had larger values. For compounds with mixed ligand character, the value of \( R_S^{ea}(LL^*) \) was predicted fairly well from the equation:

\[ R_S^{ea}(LL^*) = \frac{1}{n} \sum_{j=1}^{n} R_S^{ea}(j) \quad (E \, 2:2.4j) \]

where \( n = \) number of nearest neighbours.

The authors evaluated the effect on the Wagner Auger parameter, \( (\Delta \alpha' = \Delta E_{\text{AUG}} + \Delta E_L), \) of \( \Delta E_{1s} \neq \Delta E_{2p}, \) by comparing \( \Delta E \) with \( \Delta \alpha'. \) The two values were occasionally equal, but more often \( \Delta \alpha' \) was larger than \( \Delta E, \) sometimes by 20-30%. By substituting for \( \Delta E_{1s} \) in \( (E \, 2:1.4g) \) using the ratio for \( \Delta E_{2p}/\Delta E_{1s} = 0.864, \) \( \Delta E \) was given by the same peak shifts as \( \Delta \alpha' : \)
\[ \Delta E = 0.84 \Delta E_L + \Delta E_{\text{AUG}} \]  

(E 2:2.4k)

The calculation of initial state orbital energy shifts, \( \Delta \epsilon \), was given by the following equation:

\[ \Delta \epsilon_{2p} = 0.8647 \Delta \epsilon_{1s} + 0.0416 \]  

(E 2:2.41)

Binding energy shifts for core holes were found to be dominated by initial state effects in the gas phase in agreement with (106).

The lower energy SLVV Auger transition has been used (115) to study metal d- to sulphur 3p-band interactions. For cases of little interaction one peak or a closely spaced doublet is seen, while for significant interaction, additional peaks occur at lower kinetic energies arising from electrons in more tightly bound orbitals, and at higher kinetic energies from less tightly bound orbitals. The authors identify these changes as a "self-convolution of the valence band density of states, weighted by the amount of 3p character". They also suggest that these lines can be predicted from the sulphur K\( \beta \) X-ray emission spectra.

Nishikida and Ikeda (116) used AlK\( \alpha \) to record S2p lines and CrK\( \alpha_1 \) (5414.7eV) and CrK\( \alpha_2 \) (5405.5eV) to record S1s and SKLL lines for a study of a series of sulphur compounds.
where sulphur had, in general, a positive valency. They also found $\Delta S_{1s} > \Delta S_{2p}$ (referenced to solid sulphur) but declined to use the Wagner Auger parameter for determination of extra-atomic relaxation energies, reasoning that since the shifts on the two core levels associated with the Auger electron emission were not equal, the equation derived for relaxation energy, \((E_{1:2.2,2e})\) would not apply. They used the same approach as Sodhi and Cavell (111), but estimated a different value for the atom-like constants: \(\gamma + R^a_{s}(LL^*) = -55eV \) \((E_{2:2.4g})\).

The shifts for the 1s and 2p orbitals were found to correlate with increasing formal oxidation number, while the shift of the KLL line was found to be largely a function of the final state charge distribution. Noting the problem of distinguishing between atomic relaxation and extra-atomic relaxation energy due to the fact that the bonding electrons play a role in both energies, the 3s and 3p orbitals were considered as contributors to the extra-atomic relaxation energy, together with surrounding atoms. When considering a 6+ ion however, the 3s and 3p orbitals are empty. The 1s,2s and 2p orbitals were considered to comprise the atomic relaxation energy. The results for \(R^a_{s}(LL^*)\) ranged from 24.2eV for rhombic sulphur, through 21.1eV for sulphur surrounded by 4 oxygen atoms in the sulphates and thiosulphates, to 18.8eV in \(\text{NH}_2\text{CSNH}_2\).
The authors used the shifts from the core levels to calculate the X-ray line energy shift \((\text{BE}_{1s} - \text{BE}_{2p})\), which was correlated with the mean number of valence electrons according to two methods of Coulson et al. (99). The results are given in Figure 2:3, while equations for the curves are given by:

A) \[ \Delta E_{K\alpha} = \frac{v(v+3)}{11} \]  

B) \[ \Delta E_{K\alpha} = \frac{v(v+4)}{8} \]

where \(v\) is the oxidation number or degree on ionisation.

Figure 2:3: Shifts in sulphur K\(\alpha\) energy due to various degrees of ionisation. A) Koopmans' theorem, B) Adiabatic model.
The experimental data fitted the adiabatic model over the ionisation range -0.3 to 1.3 examined.

By attributing the change in $K_\alpha$ line energy to the electronic charge on the sulphur atom only, the number of electrons ($n$) in the 3s and 3p orbitals was calculated from the equation ($E \ 2:1.4n$), where $n = 6 - \nu$.

Snyder (118) has found that the contribution to relaxation for a 2p core level hole, from the 3s and 3p orbitals, amounts to 1.09eV/electron in the isolated atom. In the presence of two core holes, ie an Auger electron emission, this value can be doubled to an estimate of 2.2eV/electron. So from the values of $n$ calculated above, Nishikida and Ikeda (116) gave an estimate of the static outer atomic relaxation energy, $R_{e^{a}}(LL^*)$, for the Auger electron emission:

$$R_{e^{a}}(LL^*) = 2.2n \quad (E \ 2:1.4a)$$

By subtracting this value from the value for static extra-atomic relaxation energy $R_{s}^{a}(LL^*)$ the difference was said to be the polarization energy corresponding to relaxation due to surrounding atoms. This term was strongly correlated with the atoms surrounding sulphur:

- by their ionic radii;
and
- by their polarizability and number,
rather than the oxidation state of the sulphur atom or the chemical shifts of binding energies for the core electrons of the sulphur atom.

The largest polarization energy was found for the central S atom of thiosulphate (13.2eV), bonded to three oxygen and one sulphur atom. Sulphate had a lower polarization energy (12.1eV), while a sulphite showed a lower polarization energy (11.0eV) than the sulphate, but in this case the coordination number is lower. A smaller polarization energy was recorded for the terminal S in thiosulphate (8.3eV), bonded only to another S atom, while sulphur bonded to carbon showed a much smaller value (2.3eV).

2:3 THE AIM OF THIS STUDY

Since most previous studies have been carried out on gaseous or organic sulphur compounds, it is of importance and practical relevance to examine sulphur in the solid state with a view to characterising its chemical state in situations of corrosion and catalysis.

The aim of this study was to analyse fully the chemical state of solid sulphur compounds, with particular emphasis on those sulphur compounds associated with corrosion of metals, using the chemical shifts of the 1s,2p and KLL line shifts. The resulting data would then be available for the
examination of field samples.

This approach is the first time that the two photoelectron transitions (1s and 2p) and the Auger transition (KLL) from a series of solid sulphur compounds have been studied using a single high energy XPS source.

2.4 EXPERIMENTAL

2.4.1 SAMPLE PREPARATION

A series of sulphates and sulphides were obtained (details are given in Appendix A at the end of this Chapter). Certain water sensitive samples were obtained in powder form, in nitrogen sealed packets. The containers were opened inside an argon filled glove bag, which was attached to the preparation chamber of a VG Scientific ESCA3 MkII Electron Spectrometer. Each sample was crushed using an agate pestle and mortar, and then dusted onto double sided tape. The samples were loaded into the preparation chamber of the spectrometer, which was rough pumped to $10^{-2}$ Torr and allowed to reach $10^{-8}$-$10^{-9}$ Torr under the action of a diffusion pump overnight.

2.4.2 ANALYSIS

For MgKα analysis the X-ray source was operated at 240W, (12kV,20mA) while for AgLα, 480W power was used.
(12kV, 40mA). The samples were analysed with MgKα X-rays before and after AgLα x-rays in order to monitor any sample degradation. The pass energy used was 50eV for narrow scans, and 4mm slits were used throughout. A base pressure of 1-2x10⁻⁹ Torr was present in the analysis chamber. For charge neutralisation when irradiating with AgLα, a VG LEG51 low energy electron gun was used. The use of the flood gun for charge neutralisation has been documented by Edgell et al. (84), and the main details are outlined here.

During the X-ray photoelectron process electrons are removed from the surface of the sample. If the sample is insulating, then positive charge can build up over time. When using polychromatic X-ray sources the passage of X-rays through an aluminium window, prior to entering the analysis chamber, generates a flux of secondary electrons of energy < 50eV. These electrons arrive at the sample surface and reduce the build up of positive charge so that the photoelectron peaks appear within 5-10eV of the position expected for a conducting sample.

In the case of monochromated XPS sources the X-ray flux is significantly reduced after monochromation and far fewer secondary electrons are generated at the aluminium window. This effect, coupled with the greater distance between the aluminium window and the sample in the VG ESCA3 MkII,
reduces the efficiency of charge neutralisation and consequently large shifts of the order of 100eV may be observed.

The use of a supplementary low energy electron gun aims to counteract this effect. Variable energy and emission current controls (0-14V and 0-0.5mA on the VG LEG 51 gun) are provided so that a reference peak may be brought to its correct position. This method relies on a sufficient flux of electrons reaching the surface. In practice the use of low flood gun accelerating potentials (≤6V), as recommended by the manufacturers, did not give efficient charge neutralisation across the whole of the spectrum (0-3000eV). This was due to perturbation of the flux by the high positive potentials applied to the retarding grid of the analyser, the latter being approximately 1-2cm from the sample surface. The use of flood gun energies >6eV overcomes this problem and efficient charge neutralisation is realised across the whole spectrum.

By recording all three peaks: S1s, S2p and SKLL, under the same analysis conditions, the same conditions of static charge will apply for each of the three peaks.

2.5 RESULTS

2.5.1 CALIBRATION
1) Initial calibration used Cu, Au and Ag foils, sputter cleaned inside the spectrometer, while for higher kinetic energies other methods were employed since reference values for high energy Au peaks, for example, have not yet been agreed. By recording peak positions in AgLa and MgKα radiation, the energy difference of the Auger parameter should equal the photon source energy difference. So for the Cu2p₃ and the CuLMM lines in MgKα and AgLa:

\[-\hbar \nu + KE_{AE} + BE_{PE} = \]
\[-2984.3 + 917.9 + 933.5 = -1132.9 \quad (AgLa = 2984.3\,\text{eV})\]
\[-1253.6 + 918.0 + 933.45 = +597.85 \quad (MgKα = 1253.6\,\text{eV})\]

\[\text{differences} = 1730.75 \quad 1730.7\]

And for the Au4f and AuNOO lines:

\[-\hbar \nu + KE_{AE} + BE_{PE} = \]
\[-2984.3 + 240.2 + 84.7 = -2659.4 \quad (AgLa = 2984.3\,\text{eV})\]
\[-1253.6 + 240.1 + 84.8 = -928.7 \quad (MgKα = 1253.6\,\text{eV})\]

\[\text{differences} = 1730.7 \quad 1730.7\]

By this good agreement across a wide energy window (almost 3000eV) of the spectrometer, good calibration exists for the X-ray lines used.

2) The use of the electron flood gun for charge neutralisation was checked by examining copper, nickel and zinc sulphate samples at various flood gun accelerating
Figure 2.4: Peak position and full-width-half-maximum values vs flood gun accelerating potential for a sample of copper sulphide powder with oxidised surface: a) O1s, b) Cu2p3, c) S2p.
potentials. By plotting peak position versus accelerating potential for lines of different energy, the efficiency of charge neutralisation across the energy spectrum can be monitored, see Figure 2:4. The linearity beyond 8V is good. 3) A third method is by measurement of the difference between the 1s and 2p line energies. This difference is in fact the SKα X-ray line energy, which may also be plotted against accelerating potential. The value from Physical Chemistry Tables (119) for the SKα line is 2306.64eV.

The consistency of the value, shown in Table 2:4, for sulphates at 10eV bias and their excellent agreement with the values of Sato mentioned above (98) (section 2:2.1) is considered to be a good indication of efficient charge neutralisation within the accuracy of peak position measurement (±0.1-0.2eV).
SULFUR

MODIFIED AUGER PARAMETER (eV)

SOLIDS

C S O

Na₂S₂O₃

Na₂SO₃

C S₂

Na₂S₂O₃

C S₂

Na₂S₂O₃

C O₃

S F₆

S O₂

S O₂
Figure 2.5: Wagner plot for sulphur, S2p vs SKLL
Table 2:4 : S1s minus S2p at different flood gun potentials

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bias 2 (V)</th>
<th>S1s - S2p eV</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSO$_4$</td>
<td>2307.75</td>
<td>2307.8</td>
<td>2308.4</td>
<td>2308.55</td>
<td>2308.45</td>
<td></td>
</tr>
<tr>
<td>NiSO$_4$</td>
<td>-</td>
<td>2308.4</td>
<td>2309.0</td>
<td>2309.0</td>
<td>2308.6</td>
<td></td>
</tr>
<tr>
<td>ZnSO$_4$</td>
<td>2309.2</td>
<td>2309.0</td>
<td>2309.7</td>
<td>2309.6</td>
<td>2308.7</td>
<td></td>
</tr>
<tr>
<td>Cu$_2$S</td>
<td>2305.8</td>
<td>2306.9</td>
<td>2307.2</td>
<td>2307.8</td>
<td>2307.5</td>
<td></td>
</tr>
</tbody>
</table>

Table 2:5 Auger parameter data for Sulphur in MgKα

<table>
<thead>
<tr>
<th>Id</th>
<th>Sample</th>
<th>S2p BE (eV)</th>
<th>SKL KE (eV)</th>
<th>$\alpha'$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni$_3$S$_2$</td>
<td>163.2</td>
<td>2115.9</td>
<td>2279.1</td>
</tr>
<tr>
<td>2</td>
<td>Cu$_2$S Tech</td>
<td>166.7</td>
<td>2112.2</td>
<td>2278.9</td>
</tr>
<tr>
<td>3</td>
<td>Ni(100) + S*</td>
<td>163.1</td>
<td>2115.6</td>
<td>2278.7</td>
</tr>
<tr>
<td>4</td>
<td>Cu$_2$S(repolished)</td>
<td>164.2</td>
<td>2115.4</td>
<td>2278.6</td>
</tr>
<tr>
<td>5</td>
<td>Cu(111) + S*</td>
<td>162.7</td>
<td>2115.9</td>
<td>2278.6</td>
</tr>
<tr>
<td>6</td>
<td>CuNi(90,10) pure sulphided</td>
<td>163.2</td>
<td>2115.0</td>
<td>2278.2</td>
</tr>
<tr>
<td>7</td>
<td>Cu$_2$S</td>
<td>162.4</td>
<td>2115.8</td>
<td>2278.2</td>
</tr>
<tr>
<td></td>
<td>MoS$_4$</td>
<td>170.5</td>
<td>2107.7</td>
<td>2278.2</td>
</tr>
<tr>
<td></td>
<td>ZnSO$_4$</td>
<td>175.0</td>
<td>2103.1</td>
<td>2278.1</td>
</tr>
<tr>
<td>8</td>
<td>Rhombic Sulphur</td>
<td>166.9</td>
<td>2110.6</td>
<td>2277.5</td>
</tr>
<tr>
<td>9</td>
<td>CuSO$_4$</td>
<td>175.0</td>
<td>2102.4</td>
<td>2277.4</td>
</tr>
<tr>
<td>10</td>
<td>NiSO$_4$</td>
<td>173.8</td>
<td>2103.2</td>
<td>2277.0</td>
</tr>
<tr>
<td>11</td>
<td>CuNi(90,10) + S* comm</td>
<td>176.3</td>
<td>2100.3</td>
<td>2276.6</td>
</tr>
</tbody>
</table>
2:5.2 AUGER PARAMETER DATA

2:5.2.1 $S_{2p} + SKLL = \alpha'$ with MgKα

The Auger parameters for a small selection of the sulphur compounds analysed are presented in Table 2:5. This gives a range of data from 2279.1 to 2276.6, a spread of 2.5eV. These data are shown in Figure 2:5, with the published Wagner plot overlaid. The data are consistent with Wagner's plot, the more polarizable the bonding of sulphur, the larger the Auger parameter.

2:5.2.2 $S_{2p} + SKLL = \alpha'_3$ with AgLα

The full range of data acquired using the AgLα monochromated X-ray source is given in Table 2:6.

The range of Auger parameter data for the $\alpha'_3$ Auger parameter is from 2274.8eV to 2279.1eV, a total spread of 4.3eV. These data are plotted in Figure 2:6a-c as Wagner chemical state plots turned through 90° clockwise.

Figure 2:6a shows the sulphide data, the outliers 12 and 8 illustrating the difference between samples that are conducting and those that are non-conducting and have their peak positions displaced by an amount approximately equivalent to the flood gun bias (10eV).

The results are in accordance with expectations: a higher Auger parameter for samples with high conductivity and more easily polarizable lattices. The Auger parameters
<table>
<thead>
<tr>
<th>Reaction</th>
<th>2p BE</th>
<th>1s BE</th>
<th>SKLL KE</th>
<th>$\alpha'_2$</th>
<th>$\alpha'_3$</th>
<th>E</th>
<th>$\Delta R^a_{0}(1s)$</th>
<th>$\Delta R^a_{0}(2p)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 Ni$_2$S$_3$</td>
<td>2470.4</td>
<td>164.1</td>
<td>2115.0</td>
<td>4585.4</td>
<td>2279.1</td>
<td>27.2</td>
<td>3.15</td>
<td>1.75</td>
</tr>
<tr>
<td>26 CuNi comm + S*</td>
<td>2459.4</td>
<td>153.1</td>
<td>2124.6</td>
<td>4584.0</td>
<td>2277.7</td>
<td>28.6</td>
<td>2.45</td>
<td>1.05</td>
</tr>
<tr>
<td>11 MoS$_2$</td>
<td>2460.0</td>
<td>152.7</td>
<td>2125.7</td>
<td>4585.7</td>
<td>2278.4</td>
<td>28.9</td>
<td>1.30</td>
<td>0.90</td>
</tr>
<tr>
<td>10 Cr$_2$S$_3$</td>
<td>2459.0</td>
<td>151.9</td>
<td>2125.9</td>
<td>4584.9</td>
<td>2277.8</td>
<td>29.3</td>
<td>1.30</td>
<td>0.70</td>
</tr>
<tr>
<td>8 Cu$_2$S + Cu</td>
<td>2470.1</td>
<td>162.8</td>
<td>2115.3</td>
<td>4585.4</td>
<td>2278.1</td>
<td>29.2</td>
<td>1.15</td>
<td>0.75</td>
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<tr>
<td>7 CuNi sulphided</td>
<td>2458.8</td>
<td>151.5</td>
<td>2126.5</td>
<td>4585.3</td>
<td>2278.0</td>
<td>29.3</td>
<td>1.10</td>
<td>0.70</td>
</tr>
<tr>
<td>9 NH$_4$S</td>
<td>2459.0</td>
<td>151.9</td>
<td>2125.9</td>
<td>4584.9</td>
<td>2277.8</td>
<td>29.3</td>
<td>1.30</td>
<td>0.70</td>
</tr>
<tr>
<td>25 Cu + S*</td>
<td>2468.6</td>
<td>161.1</td>
<td>2116.4</td>
<td>4585.0</td>
<td>2277.5</td>
<td>30.0</td>
<td>0.55</td>
<td>0.35</td>
</tr>
<tr>
<td>17 ZnS</td>
<td>2459.5</td>
<td>152.3</td>
<td>2124.2</td>
<td>4583.7</td>
<td>2276.5</td>
<td>30.7</td>
<td>0.50</td>
<td>0.00</td>
</tr>
<tr>
<td>24 Ni + S*</td>
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<td>150.9</td>
<td>2127.0</td>
<td>4585.7</td>
<td>2277.9</td>
<td>29.9</td>
<td>0.30</td>
<td>0.40</td>
</tr>
<tr>
<td>5 Li$_2$S</td>
<td>2459.4</td>
<td>152.1</td>
<td>2123.8</td>
<td>4583.2</td>
<td>2275.9</td>
<td>31.4</td>
<td>0.05</td>
<td>-0.35</td>
</tr>
<tr>
<td>4 Rhombic Sulphur</td>
<td>2462.0</td>
<td>154.3</td>
<td>2122.7</td>
<td>4584.7</td>
<td>2277.0</td>
<td>30.7</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>3 K$_2$S</td>
<td>2460.5</td>
<td>152.4</td>
<td>2123.6</td>
<td>4584.1</td>
<td>2276.0</td>
<td>32.1</td>
<td>-1.10</td>
<td>-0.70</td>
</tr>
<tr>
<td>21 FeSO$_4$.H$_2$O</td>
<td>2468.6</td>
<td>160.3</td>
<td>2116.3</td>
<td>4584.9</td>
<td>2276.6</td>
<td>31.7</td>
<td>-1.10</td>
<td>-0.50</td>
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<td>20 Cr$_2$SO$_4$.5H$_2$O</td>
<td>2468.0</td>
<td>159.5</td>
<td>2117.3</td>
<td>4585.3</td>
<td>2276.8</td>
<td>31.7</td>
<td>-1.30</td>
<td>-0.50</td>
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<td>2 NaHS</td>
<td>2459.5</td>
<td>151.3</td>
<td>2123.5</td>
<td>4583.0</td>
<td>2274.8</td>
<td>33.4</td>
<td>-1.85</td>
<td>-1.35</td>
</tr>
<tr>
<td>19 Na$_2$SO$_4$</td>
<td>2468.4</td>
<td>159.9</td>
<td>2115.7</td>
<td>4584.1</td>
<td>2275.6</td>
<td>32.9</td>
<td>-1.90</td>
<td>-1.10</td>
</tr>
<tr>
<td>1 Al$_2$S$_3$</td>
<td>2460.5</td>
<td>151.9</td>
<td>2123.7</td>
<td>4584.2</td>
<td>2275.6</td>
<td>33.0</td>
<td>-2.05</td>
<td>-0.65</td>
</tr>
<tr>
<td>18 Cu$_2$SO$_4$</td>
<td>2468.0</td>
<td>159.0</td>
<td>2116.7</td>
<td>4584.7</td>
<td>2275.7</td>
<td>33.3</td>
<td>-2.60</td>
<td>-1.30</td>
</tr>
<tr>
<td>17 ZnSO$_4$</td>
<td>2468.0</td>
<td>159.0</td>
<td>2116.7</td>
<td>4584.7</td>
<td>2275.7</td>
<td>33.3</td>
<td>-2.60</td>
<td>-1.30</td>
</tr>
<tr>
<td>16 Ag$_2$SO$_4$</td>
<td>2468.4</td>
<td>159.0</td>
<td>2117.6</td>
<td>4586.0</td>
<td>2276.6</td>
<td>32.8</td>
<td>-2.75</td>
<td>-1.05</td>
</tr>
<tr>
<td>14 MnSO$_4$</td>
<td>2468.6</td>
<td>159.4</td>
<td>2116.4</td>
<td>4585.0</td>
<td>2275.8</td>
<td>33.4</td>
<td>-2.85</td>
<td>-1.35</td>
</tr>
<tr>
<td>13 Li$_2$SO$_4$</td>
<td>2468.1</td>
<td>159.1</td>
<td>2116.0</td>
<td>4584.1</td>
<td>2275.1</td>
<td>33.9</td>
<td>-2.90</td>
<td>-1.60</td>
</tr>
<tr>
<td>23 SnSO$_4$</td>
<td>2469.2</td>
<td>159.2</td>
<td>2116.7</td>
<td>4585.9</td>
<td>2275.9</td>
<td>34.1</td>
<td>-4.00</td>
<td>-1.70</td>
</tr>
<tr>
<td>28 (NH$_4$)$_2$SO$_4$</td>
<td>2467.7</td>
<td>158.6</td>
<td>2116.8</td>
<td>4585.5</td>
<td>2275.4</td>
<td>34.7</td>
<td>-4.40</td>
<td>-2.00</td>
</tr>
</tbody>
</table>

**Table 2:6**: Peak positions, Auger parameters and extra-atomic relaxation energy values for sulphur compounds recorded with AgLα radiation

\[
\alpha'_2 = \frac{BE_{1s}}{KE_{(KLL)}} + KE_{(KLL)} \\
\alpha'_3 = \frac{BE_{2p}}{KE_{(KLL)}} + KE_{(KLL)} \\
E = \frac{BE_{1s}}{2} - 2BE_{2p} - KE_{(KLL)}
\]

2 - 30
Figure 2:6a: S2p vs SKLL for sulphides recorded with AgLα

Figure 2:6b: S2p vs SKLL for sulphides recorded with AgLα
(expanded portion of Figure 2:6a)
for the sulphides are spread over a larger range than those of the sulphates, due to the high polarizability of oxygen and the extent to which this is moderated by the cations present in the salts. By contrast, the sulphur ion in the sulphide is surrounded by ions of low polarizability – significant relaxation will occur only for those sulphides which show metallic or semi-conductive properties.

Elucidation of cation type from these data would be difficult, the range of sulphide data for $\alpha'_3$ (2274.8 → 2279.1 eV) includes all the sulphate data (2275.1 → 2276.1 eV), and the traditional "finger-printing" approach to chemical state determination would be unreliable.
These results also show the importance of also knowing the spectroscopy of the metal cation photoelectron transitions, since it will not be possible to determine unambiguously which particular metal cation is allied with the sulphur, particularly in the sulphate form. The recording of the cation spectra is particularly important since much information may be obtained from a study of satellite structure related to the oxidation state of the cation. For example, in the copper oxides Cu(I) has a strong satellite following each of the 2p lines while the Cu(II) does not, while in a series of transition metal chlorides, Saniman and Castle (120) have found variations in multiplet splitting in addition to changes in satellite intensity, across the Periodic Table.

2:5.2,3 $S_{1s} + SKLL = \alpha'_2$ with AgLa

This Auger parameter is that which is more physically correct since the binding energy included refers to the initial photoelectron (1s) of the Auger electron transition (KLL).

Wagner chemical state plots (turned through 90°) are shown in Figure 2:7. The spread of data, shown in Table 2:6, is from 4586.0 to 4583.0eV, a range of 3.0eV, consistent with, although smaller than, the variations of $\alpha'_3$ from the same set of data.
Figure 2:7a : S1s vs SKLL for sulphides (AgLα)
Figure 2:7c : S1s vs SKLL for sulphates (AgLa)

From this it would be reasonable to assume that the Auger parameter shift is not dependent on the use of the 1s initial core level rather than the 2p. However, closer inspection shows that the order of the shifts is different. From $\alpha'_2$, silver sulphate would appear to be most polarizable, with nickel sulphide 6th in the list, but from the $\alpha'_3$ results, nickel sulphide is most polarizable and silver sulphate comes 10th in the list. Similar differences are evident at the low polarizability end.
At this point it is useful to compare the Auger parameter data $\alpha'_2$ and $\alpha'_3$ for sulphides and sulphates with the same cations, see Table 2:7.

On consideration of the polarizability of the ligands the Auger parameter of the sulphate should be larger than the Auger parameter of the sulphide (ion polarizability values $O^{2-}=0.5-3.3$, $Cu^+=1.6$, $Zn^{2+}=0.8$ and $Li^+=0.03$ $\text{Å}^3$ (121)). This is indeed found to be so for $\alpha'_2(1s+KLL)$, for all compounds in Table 2:7 except for the conductor $Cu_2S$. $Cu_2S$ has metallic bonding and can facilitate complete screening of any core hole by conduction electrons. The

Table 2:7 Comparison of $\alpha'_2$ and $\alpha'_3$ Auger parameter (AP) results for sulphur salts with common cations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\alpha'_2$</th>
<th>$\alpha'_3$</th>
<th>AP of sulphide lower than sulphate (difference)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr$_2$S$_3$</td>
<td>4584.9</td>
<td>2277.8</td>
<td>Y (0.4)</td>
</tr>
<tr>
<td>Cr$_2$SO$_4$.H$_2$O</td>
<td>4585.3</td>
<td>2276.8</td>
<td></td>
</tr>
<tr>
<td>Cu$_2$S</td>
<td>4585.4</td>
<td>2278.1</td>
<td>N (0.7)</td>
</tr>
<tr>
<td>CuSO$_4$</td>
<td>4584.7</td>
<td>2275.7</td>
<td></td>
</tr>
<tr>
<td>(NH$_4$)$_2$S</td>
<td>4584.9</td>
<td>2277.8</td>
<td>Y (0.6)</td>
</tr>
<tr>
<td>(NH$_4$)$_2$SO$_4$</td>
<td>4585.5</td>
<td>2275.4</td>
<td></td>
</tr>
<tr>
<td>ZnS</td>
<td>4583.7</td>
<td>2276.5</td>
<td>Y (1.0)</td>
</tr>
<tr>
<td>ZnSO$_4$</td>
<td>4584.7</td>
<td>2275.7</td>
<td></td>
</tr>
<tr>
<td>Li$_2$S</td>
<td>4583.2</td>
<td>2275.9</td>
<td>Y (0.9)</td>
</tr>
<tr>
<td>Li$_2$SO</td>
<td>4584.1</td>
<td>2275.1</td>
<td></td>
</tr>
</tbody>
</table>
shows the reverse, the values for the sulphides are larger than those of the sulphates. To explain this it is necessary to consider the constraints imposed by bonding in sulphates and sulphides.

In the sulphate ion the bonding is covalent and (crudely) \( sp^3 \) hybridization of the sulphur 3s and 3p electrons with the oxygen 2p electrons results in 4\( \sigma \) and 2\( \pi \) molecular orbitals, with the 2 extra electrons being involved in the ionic bonding of the metal cation. In sulphides ionic bonding predominates (except where metallic or semi-conducting bonding exists). The \( S^{2-} \) ion has a higher polarizability (4.8-5.9) than the \( O^{2-} \) ion, and it may be presumed that the polarizability of the (assumed) \( S^{2+} \) ion in the sulphate tetrahedron is low.

Screening efficiency is proportional to polarizability. The data suggest that the screening efficiency for an S2p hole in a sulphate is less than in the corresponding sulphide, while the screening efficiency for an S1s hole in a sulphate is larger than in the corresponding sulphide. The S1s hole will be screened by S2s, S2p, S3s, and S3p electrons, while the S2p hole can be screened only by the S3s and S3p electrons, (the S1s and S2s electrons play a negligible part in screening the S2p core hole). In the sulphate the S3s and S3p electrons in molecular orbitals are the only electrons, within the ion, which provide
screening for an S2p core hole. For the S1s hole, both S2s and S2p electrons in atomic orbitals can provide efficient screening, in addition to that from the forementioned S3s and S3p molecular orbitals. By contrast, in the sulphide, ionic bonds exist and bring two additional electrons to the sulphur atom which will, in addition to the absence of any molecular orbitals, permit more efficient screening of the S2p core hole.

Thus it appears that S1s core holes are generally fully screened, whether the charge on the ion is $2^-$ or $2^+$, while the S2p core hole may not always be fully screened by the time the 2p electron is ejected from the atom. This conclusion will be reinforced later when extra-atomic relaxation energies are considered.

The results for this selection of sulphur compounds may be compared with those of Sodhi and Cavell, for gaseous sulphur compounds, as reviewed by Rivière et al. (76), where two slopes were found for a plot of $\alpha'_3/\alpha'_2$, of 0.81 for sulphur bonded to one or two oxygen atoms/halogen atoms, and 1.01 for sulphur bonded to hydrogen, carbon or phosphorus. In this work a slope in the region of 1.1 (although the correlation is poor = 0.8%) is found for the sulphides and monolayers of sulphur on metal substrates, but not for the sulphates which showed a scatter, as shown in Figure 2:8.
Considering conductivity, \( \text{Cu}_2\text{S} \) and \( \text{ZnS} \) are known semi-conductors with smaller band-gaps (1.7 and 3.54eV respectively) than insulators. Thus they would be expected to exhibit more efficient screening than the corresponding non-conducting sulphates. More efficient screening is indeed seen for \( \text{Cu}_2\text{S} \) in both Auger parameters, while for \( \text{ZnS} \), only for \( \alpha'_3 \).

![Diagram](image)

**Figure 2.8**: Correlation of \( \alpha'_2 \) and \( \alpha'_3 \)
2.5.3 RELAXATION ENERGY DATA

The extra-atomic relaxation energies are evaluated for both 1s and 2p core holes using the methodology of Bechstedt (83) previously used for a study of silicon compounds in this laboratory (84). The basic equations are given below:

\[ \Delta R^{ea}_D(1s) = 1.5(\Delta \xi) - \Delta \alpha'_3 \]  
\[ \Delta R^{ea}_D(2p) = 0.5(\Delta \xi) \]

where \[ \Delta \xi = \Delta K_{\text{KLL}} - \Delta B \varepsilon^{1s} + 2 \Delta B \varepsilon^{2p} \]  
\[ = - \Delta E \] the Tsang energy parameter (80)

and \[ \Delta \alpha'_3 = \Delta K_{\text{KLL}} + \Delta B \varepsilon^{2p} \]

All data have been referenced to rhombic sulphur.

These data are plotted in Figure 2.9a (sulphides) and 2.9b (sulphates). They show a large spread of data, particularly for the 1s orbital: from 3.15eV \(-\rightarrow\) -4.40eV. In addition, the ordering of the data corresponds very closely to the order of data for the Tsang energy parameter (80), \( E \), see Table 2.6. For simplicity, this parameter is used in the rest of this work in correlations with other parameters, and it is to be understood that correlation with \( \Delta E \) implies correlation with \( \Delta R^{ea}_D(1s) \).
Figure 2.9: a) $\Delta R_{D}^{ea}(2p)$ vs $\Delta R_{D}^{ea}(1s)$ for sulphides

b) $\Delta R_{D}^{ea}(2p)$ vs $\Delta R_{D}^{ea}(1s)$ for sulphates
Figure 2:10a: Partial ionic character vs Tsang energy parameter

2:10b: Partial ionic character with stoichiometric adjustment vs Tsang energy parameter
In this work the spread for the Tsang parameter is larger than for the Wagner Auger parameters, in contrast to the results for the gaseous samples of Sodhi and Cavell (111).

The gradient of the linear regression line \( [\Delta R_{D}^{ea}(2p)/\Delta R_{D}^{ea}(1s)] \) is 0.56 ±0.05 for the sulphides and 0.44 ±0.05 for the sulphates, suggesting that the relaxation energy associated with the 1s orbital is generally larger than that with the 2p, and that this effect is more pronounced for the sulphates than the sulphides. This endorses the conclusions drawn earlier for the Auger parameters. The correlation coefficient is greater than 0.96 in both cases.

It may be shown, by manipulation of the equations above, that under circumstances where \( 2\Delta R_{D}^{ea}(2p) = \Delta R_{D}^{ea}(1s) \), then D  D  D  D \( \Delta \alpha' = 0 \). This observation goes some way to explaining why the Auger parameter shifts are small in comparison to core level peak shifts.

While it is obvious that any method aimed at estimating extra-atomic relaxation energies will have to make some compromises, unless a fairly sophisticated computer model (eg CNDO techniques) is available, it is nevertheless useful to compare the obtained empirical data with parameters reflecting alternative estimates of polarizability. One of the simplest is to consider the
electronegativity (defined as the electron withdrawing power of the atom) of the surrounding ions in the molecule; although it is agreed that electronegativity differences are not strictly applicable to ionic systems without the consideration of the Madelung factor, within the same crystal structure the electronegativity difference may be used qualitatively (105).

At the same time as CNDO-type calculations were becoming routine, the possibility of making rigorous calculations for electronegativity, based on quantum mechanics, gave rise to a resurgence of interest in the topic (122). However the stock of data currently in the literature has been primarily developed for organic molecules. Inorganic molecules, especially those containing the transition elements, have been less well covered.

Thus for the purposes of this investigation it is sufficient to show what agreement exists using traditional (Pauling Np) electronegativity values and the derived values for partial ionic character $= 1 - e^{0.25 \Delta \chi^2}$, where $\Delta \chi$ is electronegativity difference.

Figure 2:10a shows the partial ionic character plotted against the Tsang energy parameter, E. The data are spread around a regression line of slope -0.054, with a poor correlation coefficient of -0.659. This measure of ionic character does not take account of stoichiometry, however.
A simple approach might be to estimate an averaging of the electronegativity difference ($\Delta \chi$) from the following equation:

$$
\Delta \chi = \frac{y(N_{ps}) - x(N_{px})}{y}
$$

(E 2:5.3e)

where the chemical formula of the sample is $MxSy$, and $N_{p}$ is Pauling's electronegativity number (which equals 2.5 for sulphur).

The resulting graphical output is given in Figure 2:10b and shows fair correlation for 5 of the samples ($r = 0.975$). Of the two outlying points, 1, $Al_2S_3$ can be discounted due to being in a state of continuous decomposition, and unlikely to present a stoichiometric surface to the spectrometer. To date no good reason for the displacement of $Ni_3S_2$ has been found.

2.5.4 FURTHER POSSIBILITIES FOR CORRELATION OF RELAXATION ENERGIES

The following avenues were considered worthy of further investigation for the ranking of the chemistry of solid sulphur:

i) Refractive Index Data.

The traditional route for the determination of ion
polarizability is to fit refractive index data to the Clausius-Mossotti or Lorenz-Lorenz relationship (123), or to the Mott-Littleton-Bechstedt expression for polarization energy (87a). By this former method values for ion polarizability were obtained for cubic systems and it was then assumed that these values held good regardless of the chemical environment of the ion. Mahan (124) was able to show that while this was true for a series of cations, it was not so for the accompanying anions. The polarizability of the anion was found to depend on the lattice constant, or unit cell volume.

Refractive index data were successfully employed by West and Castle (125) to examine the shifts in $\Delta \alpha'_\text{Si}$ and $\Delta \alpha'_\text{Al}$ for a series of minerals. By evaluating the oxygen polarizability from the Lorenz-Lorenz relationship, and plotting this against the polarizability derived from the Auger parameter, a slope of 1.02 with a correlation coefficient of 0.997 was found.

Few measurements of refractive index for solid sulphur compounds have been made. More values are available for sulphates with high levels of water of crystallization, but since samples for this study were chosen in order to minimise the amount of water of crystallization (known to reduce $\alpha'$ values due to the polar nature of the water molecule) almost no data was found, and this method could
not be used.

From the studies of Tessman et al., (121), Mayer and Mayer (126) and Mahan (124), the polarizabilities of ions in crystals have been calculated from the Lorenz-Lorenz equation with a view to estimating molar or bulk polarizability on an additive basis. The results for a selection of the sulphur compounds for which sufficient data were available are shown in Figure 2:11 as a plot of molar polarizability vs E. An approximate slope (excluding the point 28 for ammonium sulphate) shows correlation of increasing molar polarizability with increasing Tsang energy parameter for sulphides. The limited range of sulphate ions, on the other hand, seem to show a roughly constant value of E with respect to molar polarizability.

In the West and Castle study (125) oxygen ion polarizability, deduced from the Auger parameter, for tetrahedrally bonded Al varied in a systematic way with refractive index, while that for octahedrally bonded Al was constant. The explanation given was that the screening charge in an aluminate ion comes from the oxygen ions alone, while in the case of tetrahedrally bonded aluminium (Al$^{3+}$ bonded to three oxygen ions), the charge balancing cations also participate in the screening process. A similar explanation will apply in the case of the sulphate ions, where four oxygen ions screen the sulphur ion.
ii) Hard and Soft Acids and Bases.

Pearson (127) studied the tendency of different ions to dissociate in solution and produced a ranking, by equilibrium, or dissociation constant, for ions on the basis of their relative acidity or basicity. This ranking depends on the other ions present in solution, so that samples can only be ranked in a relative fashion for a particular solvent.

Applying the generalised ranking of cations as hard, borderline or soft acids to the relaxation energy data, we
are able to consider the extension of HSAB theory to relaxation energy in XPS.

For the sulphides, most of the hard acids are found with negative relaxation energy values relative to rhombic sulphur, while soft and borderline acid cation sulphides have positive relaxation energy values (although there are exceptions). For the sulphates no such ordering is apparent.

iii) Inter-ionic Distance

Crystallographic data have been used to evaluate inter-ionic (sulphur to nearest cation in this case) distances in the crystal. The basic idea behind this approach is that both ΔE and ΔR_D^sa (1s or 2p) are measurements of the efficiency of core hole screening at the sulphur atom. The larger the value, in the case of ΔR_D^sa, the more efficient the screening.

The use of inter-ionic distance as a comparable measure of screening efficiency is anticipated to include, in a simple and empirical way, all the contributions that govern ions in solids: e.g. electronegativity, polarization, molecular orbitals, coordination and ionic radii. It was also hoped that this approach could be applied to sulphide and sulphate data alike.

The data were obtained from existing references
(128,129,130) and evaluated by computer (131). The resulting data — inter-ionic distance versus the Tsang energy parameter —, for a selection of the samples is shown in Figure 2:12. The correlation coefficient is 0.92 (excluding the following outliers). The three outliers are $\text{Al}_2\text{S}_3$, which, as was mentioned above, was decomposing and unfortunately no data for the structure of aluminium sulphate were to hand, and 20 and 21, the iron and chromium sulphates which hold 1 and 5 waters of crystallization respectively. The polarization in this case is dominated by the waters of crystallization.

Figure 2:12: Inter-ionic distance versus the Tsang energy parameter.
A similar linear dependence has also been found for the 01s and F1s binding energies in a series of simple metal oxides and fluorides by Nefedov et al. (132). In these cases, where the metals are the nearest neighbours of the oxygen ions, an increase in the separation shows a linear correlation with decreasing binding energy.

The intercept for inter-ionic distance (iid) at infinity (1/iid = 0) is at E = 39.5eV for the sulphur data in this work, i.e. the value for the free ion. Nefedov suggests that this approach is only valid for the negative ion (i.e. O\(^-\), F\(^-\) and S\(^{2-}\)). However from Figure 2:12 we may see that the sulphate data points lie on the same line as the sulphides. The sulphates are clustered around an inter-ionic distance of 3.3±0.3\(\AA\) and show a variation in E of 2.4eV. Several authors have considered the phenomenon of the sulphur-metal distance being shorter than the corresponding oxide-metal distance, thought to arise from increased overlap between metal d and sulphur p orbitals (133). This may explain the alignment of sulphate data with those of the sulphides in this work, in that the overlap of oxygen orbitals with metal orbitals brings the metal orbitals close to the sulphur atoms.
2.5.5 RELAXATION ENERGIES FOR SULPHUR MONOLAYERS

Monolayers of sulphur on copper, nickel and the cupro-nickel alloy (90,10) were prepared at the University of Pierre and Marie Curie at Paris (134). The sulphur used was a Cu$_2$S source containing $^{35}\text{S}$ as an active $\beta$ emitter with a half life of 88 days. This enabled the quantification of the amount of sulphur to be made before and after electrochemical experiments.

The goal behind the preparation of these samples was to ascertain to what degree the bonding of the sulphur monolayer differed from that in the simple sulphide. The heat of adsorption of S monolayers is known to be higher than the heat of formation of the corresponding sulphide (135), and as an adsorbed monolayer the sulphur can act as a catalyst for the electrochemical reduction of oxygen in a iron-nickel alloy giving rise to accelerated dissolution of nickel. The adsorption of negative ions may generate a dipole which might assist the passage of metal ions into solution, this is envisaged, for example, as a reversal of the Mott driving force for oxidation.

This action of sulphur as a monolayer is suspected in many corrosion pathways but is not well characterised, most corrosion studies allowing thick corrosion products to build up and as a consequence commonly conclude, on stoichiometric evidence from EDX analyses, or from S2p
binding energy values, that a sulphide is present. It has been found (136) that for sulphur present either as a monolayer or as the corresponding sulphide, that the S2p binding energy values are identical.

If it could be shown that significant differences are measurable then a prospective tool for corrosion science experiments could be put to good use.

The electronic environment of sulphur as a monolayer should give relatively high relaxation energies since the 2-D layer is effectively seated on top of a sea of electrons present in the conduction bands of the transition metal. These would be able to flow towards the contracting sulphur orbitals (in the event of core hole generation) with no hindrance, compared to the sulphide where conduction band electrons are also valence band electrons participating in bonding and as such are less free to move. These differences should be reflected as a larger $\Delta R_{D}^{ea}$ (extra atomic relaxation energy shift) for the monolayer where the outer orbitals of the sulphur atom can collapse fully in the presence of a core hole, and a smaller $\Delta R_{D}^{ea}$ for the sulphide where the bonding electrons are polarized to some degree by the cations. However from the results we see precisely the reverse: the relaxation energy shifts are larger for the two sulphides ($\text{Cu}_2\text{S}$ at $1.15\text{eV}$ ($\Delta R_{D}^{ea}1s$) and $0.75\text{eV}$ ($\Delta R_{D}^{ea}2p$), $\text{Ni}_3\text{S}_2$ at $3.15\text{eV}$ ($\Delta R_{D}^{ea}1s$) and $1.75\text{eV}$}
(ΔE_{2p}^{S}) than for the two sulphur monolayers (Cu +S* at 0.55eV (ΔE_{1s}^{Cu}) and 0.35eV (ΔE_{2p}^{Cu}), Ni +S* at 0.3eV (ΔE_{1s}^{Ni}) and 0.4eV (ΔE_{2p}^{Ni})).

From LEED results (137) it is known that the coordination of sulphur in a monolayer is not the same as in the corresponding sulphide, the first atom layer of any substrate being more "loosely" bound than subsequent close-packed layers (138). Synchrotron sources for XPS are also able to detect this layer as an additional photoelectron line at a slightly higher binding energy than the signal from the substrate.

The looser top surface layer could give rise to reduced relaxation energy values for the sulphur monolayer. In this layer the sulphur is tightly bound and the separation of the first metal layer from the bulk of the sample could prevent much participation of the sea of conduction electrons in the relaxation processes. The high energy of adsorption of the sulphur monolayer might indicate the fullest possible occupation of its orbitals, and an absence of orbitals for conduction band electrons to move into during the relaxation process. In the plot of inter-ionic distance versus the Tsang energy parameter (Figure 2:12), good alignment of the nickel sulphide and sulphur monolayer on nickel along the linear regression line supports the concept of the "looser" surface layer.
Wertheim (139) has used a Born-Haber cycle approach to show that the location of screening charge for adsorbates depends on the relative magnitudes of the substrate work function ($\varnothing$) and the ionization potential (IP) of the element one atomic number higher in the periodic table than the adsorbate. If $\varnothing$ is smaller than $IP_{z+1}$ the screening charge is said to reside on the outer orbitals of the adsorbate atom, below the Fermi level. If $\varnothing$ is larger than $IP_{z+1}$ screening occurs by charge tunneling from the substrate. The values for Cu, Ni and Cl are as follows: $\varnothing_{Cu} = 4.65eV$, $\varnothing_{Ni} = 5.15eV$ and $IP_{Cl} = 12.96eV$. Thus the prediction for S on Cu and Ni is that screening charge resides in the outer orbitals of the adsorbate atom. If these are the orbitals strongly binding the S to the substrate, then screening may be restricted from these strongly bonding orbitals. This could also help to explain the relative values for S on Cu and Ni, since the energy of adsorption for S on Ni (\(\approx 230kJ\)) is greater than that for Cu (\(\approx 175kJ\)) (134), giving rise to stronger bonding of S to Ni than to Cu and consequently less efficient screening. Further work is anticipated in this area by the segregation of sulphur onto other transition metals.
In the introduction to this study and in the experimental part of the work it has been shown that the three peaks, S1s, S2p and SKLL, may be used to evaluate estimates of the extra-atomic relaxation energies accompanying each transition. In the following section the previously published data and the results from this work are assembled together for the purpose of showing what additional information may be obtained from this much fuller data set.

Table 2:8, at the end of this section, shows the collated data. Columns 1 to 3 give the raw peak position data, columns 4 to 6 give the Auger parameters (labelled $A'$...) and the Tsang energy parameter (labelled $\Delta E$), columns 7 to 8 give the extra-atomic relaxation energies for the 1s and 2p transitions respectively. The extra-atomic relaxation energy values for the KLL transition may be obtained from column 6 by adding 39.85eV ($111,112$).

In order for the data to be compared together it was necessary to chose a common reference as a standard. Either rhombic sulphur or $H_2S$ would suffice, in this case the results from Sodhi and Cavell (111) for $H_2S$ have been
chosen. The data of Keski-Rahkonen (107) for $H_2S$ was obtained on two different samples, and with slightly different Ne 1s line reference (less than ref 111 by 0.15eV), therefore this data is thought to be less reliable. This use of $H_2S$ as a standard rather than $S_8$ as in the experimental work reported above results in different absolute values for $\Delta R_{D}^{\text{ea}}(1s)$ and $\Delta R_{D}^{\text{ea}}(2p)$, the relative values are the same.

The data have been plotted graphically in order to show the trends in relaxation energy shifts with formal oxidation number, the figures will be found at the end of this section. Figure 2:13 shows $\Delta R_{D}^{\text{ea}}(1s)$ versus $\Delta R_{D}^{\text{ea}}(2p)$ for all the samples, while Figures 2:14 to 2:18 show selections of the data based on valence and nearest neighbour type: $S^{2-}$ gas phase (Figure 2:14), $S^{2-}$ solid phase (Figure 2:15), $S^{x+}$ bonded to oxygen/chlorine (Figure 2:16), $S^{x+}$ bonded to oxygen/fluorine (Figure 2:17) and $S^{x+}$ in solid sulphates (Figure 2:18). The gradient of the line is marked on the plot in where applicable.

Thus, these plots show how the raw data may be used together with a suitable standard to obtain an estimate of the valency of sulphur in an unknown compound by evaluating $\Delta R_{D}^{\text{ea}}(1s)$ and $\Delta R_{D}^{\text{ea}}(2p)$ and determining the ratio of $\Delta R_{D}^{\text{ea}}(2p)/\Delta R_{D}^{\text{ea}}(1s)$: for a gas phase sulphur compound the ratio is 0.86, for solid sulphide the ratio = 0.72, while
for a sulphate the ratio = 0.43.

The absolute values of $\Delta R_D^{\text{oxa}}(1\text{s})$ and $\Delta R_D^{\text{oxa}}(2\text{p})$ may be further used to distinguish oxy/fluoro bonding: the oxy/fluoro data in Figure 2:17 generally has $\Delta R_D^{\text{oxa}}(2\text{p})$ larger than $\Delta R_D^{\text{oxa}}(1\text{s})$ with $\Delta R_D^{\text{oxa}}(1\text{s})$ negative and approximately constant at -0.5.

The data in Figure 2:15 for $S^{2-}$ may also be fitted to a curve of exponential associative form according to the equation: $y = A(1-e^{-Bx}) + C(1-e^{-Dx}) + E$, where $A = 8.72$, $B = 0.258$, $C = -1.0 \times 10^{-8}$, $D = -1.001 \times 10^{-8}$ and $E = -2$.

The distinction of the oxy/chloro bonding from the sulphate would not be possible by ratio value since the oxy/chloro data lie very close to the gradient for the sulphates, however the absolute values are smaller: $\Delta R_D^{\text{oxa}}(1\text{s}) < 1\text{eV}$ and $\Delta R_D^{\text{oxa}}(2\text{p}) < 2\text{eV}$.

In general the following distinctions are found for core level extra-atomic relaxation energies for sulphur compounds and may be confidently applied to data from unknown samples.
<table>
<thead>
<tr>
<th>Bonding</th>
<th>Gradient</th>
<th>$\Delta R_D^{ea}(1s) &gt; \Delta R_D^{ea}(2p)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S^{2-}$ gas</td>
<td>0.82</td>
<td>&gt; 5 exceptions out of 16 compounds*</td>
</tr>
<tr>
<td>$S^{2-}$ solid</td>
<td>0.72</td>
<td>&gt; except NaHS where $\Delta R_D^{ea}(2p) = \Delta R_D^{ea}(1s)$</td>
</tr>
<tr>
<td>$S^x(O/Cl)$</td>
<td>-</td>
<td>&lt; $\Delta R_D^{ea}(1s)$ is -ve</td>
</tr>
<tr>
<td>$S^x(O/F)$</td>
<td>-</td>
<td>&lt; 1 exception $Na_2SO_3$</td>
</tr>
<tr>
<td>$SO_4^{2-}$ solid</td>
<td>0.43</td>
<td></td>
</tr>
</tbody>
</table>

* both xanthates, $(CF_3S)_2$ having competing influence of the three fluorine atoms, $SPCl_2(OCH_3)$ having similar competing influence of the two chlorine atoms, and $H_2S$ of ref (106) considered to be less reliable data.
Table 2.8 Extra-atomic relaxation energy data for sulphur - compilation from literature
<table>
<thead>
<tr>
<th>Compound</th>
<th>Weight (g)</th>
<th>Temperature (°C)</th>
<th>Density (g/cm³)</th>
<th>Heat of Transition (kJ/mol)</th>
<th>Weight Loss (%)</th>
<th>Density Change (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr₂(SO₄)₂·SH₂O</td>
<td>2468</td>
<td>2117.3</td>
<td>159.5</td>
<td>2276.8</td>
<td>4585.3</td>
<td>31.7</td>
</tr>
<tr>
<td>NaHS</td>
<td>2459.5</td>
<td>2123.5</td>
<td>151.3</td>
<td>2274.8</td>
<td>4583</td>
<td>33.4</td>
</tr>
<tr>
<td>Na₂SO₄</td>
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<td>2115.7</td>
<td>159.9</td>
<td>2275.6</td>
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<td>32.9</td>
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<tr>
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<td>151.9</td>
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<td>4584.2</td>
<td>33</td>
</tr>
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<td>4584.7</td>
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<tr>
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<td>2116.7</td>
<td>159.2</td>
<td>2275.9</td>
<td>4585.9</td>
<td>34.1</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>2467.7</td>
<td>2116.8</td>
<td>158.6</td>
<td>2275.4</td>
<td>4584.5</td>
<td>33.7</td>
</tr>
</tbody>
</table>
Figures 2:13 to 2:15: $\Delta R^{ea}_D(2p)$ versus $\Delta R^{ea}_S(1s)$ referenced to $H_2S$
Figures 2:16 to 2:18: $\Delta R_{D}^{oa}(2p)$ versus $\Delta R_{S}^{oa}(1s)$ referenced to $H_2S$. 

Gradient = 0.43
2.7 CONCLUSIONS

1) In addition to the advantages of surface sensitivity and the quantitative nature of X-ray Photoelectron Spectroscopy, the ability to excite core, intermediate and valence levels and thereby to measure the energy of the relaxation of the excited atom, provides unrivaled information for both the chemist and the physicist.

2) A data bank of sulphide and sulphate photoelectron peak shifts has been prepared including Auger parameters and relaxation energies.

3) Several methods for the estimation of relaxation energies have been used in the past. The larger chemical shifts for the 1s compared to the 2p core electron is shown to restrict the applicability of the Wagner Auger parameter for polarization energy determination of solid samples.

4) Differences between sulphides and sulphates have been observed as follows:
   i) sulphates show a narrower range of chemical shift compared to sulphides due to the constraints of the highly electronegative oxygen atoms.
ii) for the same metal cation the sulphides have higher $\alpha'_3 (BE_{2p} + KE_{KLL})$ and lower $\alpha'_2 (BE_{1s} + KE_{KLL})$ Auger parameters than the sulphates reflecting the complete screening of the 1s hole and incomplete screening of the 2p hole at the time the 2p electron leaves the sulphate atom.

iii) the range of relaxation energy for sulphides is larger than that for sulphates, for the same reason as (i).

iv) the relative screening of 1s and 2p holes suggests a larger than expected screening for the 1s orbital for sulphur in contrast to previous results obtained for chlorides (140).

5) A range of extra-atomic relaxation energy shifts from $3.15 \rightarrow -4.4\text{eV}$ was recorded providing good possibilities for sample finger-printing with greater precision than using the Wagner Auger parameters for which a smaller range of values were found ($2274.8 \rightarrow 2279.1\text{eV}$ for $\alpha'_3 = BE_{2p} + KE_{KLL}$ $4583.0 \rightarrow 4586.0\text{eV}$ for $\alpha'_2 = BE_{1s} + KE_{KLL}$).

6) The relaxation energy shifts were found to correlate independently, with inter-ionic distance; percentage ionic character, stoichiometrically adjusted; and molar or bulk
7) In a compilation of data from the literature with the results obtained in this work, the ratioing of core hole extra-atomic relaxation energies shows good chemical state information, with respect to the formal valency of sulphur and certain types of nearest neighbour.
# APPENDIX A : SULPHUR COMPOUNDS - QUALITY AND SOURCE

<table>
<thead>
<tr>
<th>Compound</th>
<th>Source, Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_2$S$_3$</td>
<td>University Pierre et Marie Curie, 99.99%</td>
</tr>
<tr>
<td>CuNicomm + S*</td>
<td>CuNicomm from Yorkshire Metals UK, annealed under H$_2$, 800°C, 8hrs.</td>
</tr>
<tr>
<td>Cu$_2$S + Cu</td>
<td>University Pierre et Marie Curie, 99.99%</td>
</tr>
<tr>
<td>CuNi sulphided</td>
<td>University Pierre et Marie Curie, 99.99%</td>
</tr>
<tr>
<td>Cu + S*</td>
<td>University Pierre et Marie Curie, 99.99%</td>
</tr>
<tr>
<td>Ni + S*</td>
<td>University Pierre et Marie Curie, 99.99%</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>Ventron Alfa, W Germany, 97%</td>
</tr>
<tr>
<td>Cr$_2$S$_3$</td>
<td>Ventron Alfa, W Germany, 99%</td>
</tr>
<tr>
<td>NH$_4$S</td>
<td>BDH, Poole, UK, Analar</td>
</tr>
<tr>
<td>ZnS</td>
<td>Ventron Alfa, W Germany, 99.9%</td>
</tr>
<tr>
<td>Li$_2$S</td>
<td>Ventron Alfa, W Germany, 97%</td>
</tr>
<tr>
<td>Rhombic Sulphur</td>
<td>BDH, Poole, UK, Analar</td>
</tr>
<tr>
<td>K$_2$S</td>
<td>Ventron Alfa, W Germany, 97%</td>
</tr>
<tr>
<td>FeSO$_4$·H$_2$O</td>
<td>BDH</td>
</tr>
<tr>
<td>Cr$_2$SO$_4$·H$_2$O</td>
<td>BDH</td>
</tr>
<tr>
<td>NaHS</td>
<td>Ventron Alfa, W Germany, 97%</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>BDH, Analar</td>
</tr>
<tr>
<td>Al$_2$S$_3$</td>
<td>Ventron Alfa, W Germany,</td>
</tr>
<tr>
<td>CuSO$_4$</td>
<td>BDH</td>
</tr>
<tr>
<td>ZnSO$_4$</td>
<td>BDH, Analar</td>
</tr>
<tr>
<td>Ag$_2$SO$_4$</td>
<td>BDH, Analar</td>
</tr>
<tr>
<td>MnSO$_4$</td>
<td>BDH, Analar</td>
</tr>
<tr>
<td>Li$_2$SO$_4$</td>
<td>BDH, Analar</td>
</tr>
<tr>
<td>SnSO$_4$</td>
<td>BDH, Analar</td>
</tr>
<tr>
<td>(NH$_4$)$_2$SO$_4$</td>
<td>BDH, Analar</td>
</tr>
</tbody>
</table>

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CHAPTER 3 INVESTIGATION INTO THE STIMULATION OF CORROSION OF CuNiFe (90,8.5,1.5) IN MARINE ENVIRONMENTS

3:1 INTRODUCTION

3:1.1 THE USE OF CuNiFe

The CuNi(90,10) alloy was developed between 1920 and the beginning of the 2nd World War for use in marine engineering applications, replacing admiralty brass, CuSnZn(70,1,bal), which was subject to de-zincification and erosion at flow rates exceeding 1.5m/s. The addition of small amounts (usually between 1 and 2%) of Fe improved the erosion corrosion properties of CuNi allowing flow rates up to 3.5m/s to be used without apparent problems. The iron acts to help form an erosion resistant layer at the boundary between lower corrosion products and the electrolyte (141). This alloy is the only suitable material for use in a marine environment where corrosion, erosion and bio-fouling resistances are required.

Efird (142) has supplied details of the Pourbaix diagram for this alloy in sea water and points out that the formation of the Cu$_2$O part of the passive layer is by initial dissolution of Cu:

$$2\text{Cu} + 2\text{Cl}^2^- \rightarrow \text{Cu}_2\text{Cl}_2^{2^-} + 2\text{e}^-$$  (E 3:1.1a)

This is an electrochemical reaction, dependent on potential and the concentration of ionic species, and is followed by the precipitation from solution of the solid Cu$_2$O, forming
a non-adherent film:

$$2Cu_2Cl_2^{2-} + 2H_2O \rightarrow 2CuO + 4Cl^- + 2H_2 \quad (E\, 3:1.1b)$$

which is pH and potential dependent above pH 8.5. Below this pH, potential determines whether cupric, $Cu^{2+}$, or cuprous, $Cu^+$, ions or compounds form. The normal pH of sea water lies in the range 7.8 - 8.1, this being within the general corrosion region for CuNiFe at potentials positive with respect to -280mV (SCE) (see Figure 3.1).

![Simplified Pourbaix diagram for 90-10 CuNi in clean and polluted (containing dissolved H₂S) sea-water at 25°C (after Macdonald et al. 143)](image-url)

Figure 3:1 : Simplified Pourbaix diagram for 90-10 CuNi in clean and polluted (containing dissolved H₂S) sea-water at 25°C (after Macdonald et al. 143)

Only states of copper are shown.

3:1.2 THE ROLE OF IRON AND NICKEL

The evidence for the origin of the good corrosion properties of this alloy come from Scorchelletti et al. (144). They found nickel enrichment in sodium chloride
solutions. Efird (142) noticed that the change in slope of polarisation resistance of CuNiFe(bal,10,1.5) with time compared to that for CuNi(70,30) was due to a change in kinetics which could be explained by surface enrichment with nickel and an extension of the passive range for this new composition.

Efird (145) also studied the role of iron in the properties of the passivating film and found that a synergistic effect existed between iron and nickel. That is, the addition of iron allowed the passivating effect of nickel to become apparent at lower concentrations than in the absence of iron. The lowest corrosion rate without iron was found with 25 - 30% nickel. On the addition of iron these rates could be achieved with an alloy containing only 10% nickel. The atomic adsorption analysis of the corrosion films found the Cu$_2$O films enriched in metallic nickel in those alloys holding iron in solid solution. This effect was accompanied by a change in the film colour from black or green/black to brown. The precise mechanism by which iron enhanced the role of nickel was not known.

In terms of the metallurgy of the system the iron may be present in a metastable solid solution (if the alloy has been water quenched from 900°C), and this is the preferred microstructure. If annealed between 600 and 700°C, a continuous or discontinuous precipitate of $\alpha$ Fe-Ni or Ni$_{17}$Fe$_{30}$Cu$_{53}$ will be present at the grain boundaries. The continuity of the precipitate obviously depends on temperature and time of anneal and Fe concentration. The
precipitated phase may be magnetic.

Drolenga et al. (146) found that the microstructure had important consequences for the corrosion behaviour which outweighed the influence of varying Fe content: the homogenous and continuously precipitated alloy showed good corrosion resistance while the presence of discontinuous precipitates was associated with poorer corrosion properties and a corrosion film ten times thicker.

The corrosion products under the outer iron-rich film are associated with a high resistance to electronic and ionic conduction. The corrosion resistance is associated with inhibition of the predominant cathodic reaction, the reduction of oxygen in near neutral solutions:

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad (E \ 3:1.2b)
\]

This inhibition may be seen in the changes to the Tafel slopes in electrochemical experiments (147).

3:1.3 THE CORROSION OF CUNIFE

This alloy has traditionally performed extremely well in service in marine environments where water is oxygenated and flowing. A slow dissolution of Cu\textsuperscript{2+} ions is thought to confer the anti-fouling properties of this alloy in shallow marine waters. However, problems are continually coming to light in cases where the alloy has been exposed to stagnant, polluted or mud-line environments, with failure by pitting corrosion.
The first reports of premature failure of this alloy were announced by Stover (148). He reported an instance of corrosion of a CuNiFe identity tag from a mud-line site at a rate of 5g/m²/day instead of the expected 0.07g/m²/day. Black corrosion products were identified as the sulphides of the alloyed metals, and the sample was found to be magnetic.

Further work by Efird (149) in putrefied sea water solutions found that a sharp drop in rest potential occurred within one or two days of immersion, from around -200mV (SCE) to around -600 to -700mV (SCE). No dramatic change in pH occurred, (8 to 7), but the subsequent exposure of these samples to fresh aerated sea water, after 25 days in an increasingly putrid solution, resulted in a doubling or trebling of the corrosion index, (a relative measure of corrosiveness derived from polarisation resistance values). This work has spurred studies into the role of sulphide, its concentration and chemistry in sea water (143).

The half life of H₂S in aerated sea water was found to be 20 minutes (150), with elemental sulphur, sulphite (S₂O₃²⁻), sulphate (SO₄²⁻) and thiosulphate (S₂O₃²⁻) as reaction products in addition to the polysulphide ions Sₙ²⁻ and polythionate ions (O₃S-Sₙ-SO₃)²⁻. The oxidation of sulphur to the oxyanions was found to be slow (151), and may be catalysed by UV (152).

A concentration of sulphide of less than 0.85mg/litre was sufficient to cause loss of polarisation resistance by
a factor of 8 (143). (This effect was independent of sulphide concentration above 0.85mg/l.) By cyclic voltammograms the authors showed that peaks commonly associated with the formation and reduction of oxide/hydroxide phases were no longer apparent. The black, loosely adherent corrosion film was identified as orthorhombic chalcocite \((\text{Cu}_2\text{S})\), cubic \((\text{Cu}_2\text{S})\) and further sub-stoichiometric phases, by X-ray diffraction.

Consultation of the Pourbaix diagrams for copper in sulphide polluted waters (143 and 153), suggests that in the presence of dissolved sulphide, the rest potential of the alloy falls below the hydrogen evolution line \((\approx -750\text{mV vs SCE at } \text{pH } = 8)\), requiring the cathodic reaction to be that of hydrogen evolution, resulting in loss of immunity (due to lack of \(\text{OH}^2-\) ions). The reaction may be written as

\[
2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\uparrow \quad (E\text{ 3:1.3a})
\]

and was thought to involve the adsorption of \(\text{H}^+\) onto the metal in an intermediate stage. However, this did not fully explain the acceleration of corrosion in aerated waters observed by Efird (145).

Sanchez and Schiffrin (154) proposed that the role of sulphur was to contaminate the passive film making it a suitable catalyst for the electrochemical reduction of oxygen. Aluminium brass, aluminium bronze and CuNiFe(bal,10,1.5) after 90 minutes in natural sea water, (containing \(\text{Na}_2\text{S}\) additions at a rate of 1ppm), showed an
increase in the cathodic reaction by a factor of 10. The rate of the anodic reaction remained unaltered with a shift in corrosion potential to a value approximately 50mV more positive.

The work of Kato et al. (155) discussed the precise nature of the corrosion films forming on CuNiFe(bal,10,1.5) and found that an inner closely adherent film forming beneath the more porous Cu$_2$O layer was the site of the dissociation of water, and that the rate of oxygen reduction was then controlled by the transport of electrons across the inner layer due to low electronic conductivity. The rate of thickening of the inner layer was found to be parabolic.

A second study (156) on the effect of sulphide contamination of the solution in conjunction with SEM and XPS analysis, found behaviour similar to that found in Efird’s experiments (149). In addition Kato et al. (156) were also able to show that thicker porous films (70µm vs 10µm) formed in the polluted environments. These films appeared to comprise three rather than two distinct layers: an outer highly porous layer growing perpendicular to the alloy surface, a middle slightly less porous series of layers lying parallel to the alloy surface and then the thin inner highly adherent layer.

The samples were exposed to a deaerated, 5-8ppm sulphide solution for up to 10 days and were then removed to an aerated 3.4% NaCl solution in an electrochemical cell. A higher $E_{corr}$ (-140mV vs SCE compared to the clean samples
at $E = -240 \text{mV vs SCE}$) and a 100-fold increase in the corrosion rate ($2 \mu\text{A/cm}^2 \rightarrow 150 \mu\text{A/cm}^2$) were recorded. The outer loosely adherent films were black; $\text{Cu}_2\text{S}$ and $\text{Cu}_2(\text{OH})_3\text{Cl}$ and possibly also $\text{Cu}_2\text{O}$ were identified by X-ray diffraction. XPS examination showed that the sulphur appeared to be concentrated in the outer layer of corrosion product as a sulphide.

By showing that the corrosion rate typical of the clean alloy surface could be regained when the contaminated porous layer was stripped away, the increased corrosion rate was identified as due to the catalysis of oxygen reduction at the porous, outer layer of the sample tarnish. Deposition of Pt onto the inner tarnish layer, a well known catalyst for oxygen reduction, resulted in an increase in the cathodic reaction similar to that for a sample exposed to sulphide solution for 5 days.

The authors went on to suggest that there may be some evidence to support the catalysis hypothesis from the known behaviour of a mixed iron/nickel sulphide, $\text{Fe}_{0.5}\text{Ni}_{0.5}\text{S}_2$ (157), which is 40 times more active than $\text{Fe}_2\text{S}_3$ for oxygen reduction. Since Fe and Ni were found in relatively high concentration, (with respect to their concentrations in the bulk alloy), on the surface of the inner adherent layer, together with medium levels of sulphur, it is not unreasonable to suggest that a similar compound may come into loose co-existence in these conditions.

An alternative hypothesis is that the highly porous...
nature of the thicker corrosion product is responsible for the increase in the cathodic reaction by providing a much larger surface area for the adsorption of oxygen from the electrolyte.

The work of Castle and Parvizi (158) has revealed the link between mud-line attack and the environment. By careful control of fresh filtered sea water, the Tafel slopes from potentiodynamic polarisation experiments could be measured in fresh and deaerated solutions, (Figure 3.2).

![Figure 3:2: Polarisation behaviour of the pre-exposed samples in: A - sea water, B - 3.4% NaCl solution](image-url)
Figure 3.3: AlKα survey scans of sample surfaces after polarisation at -320mV (vs SCE) in sea-water and 3.4% NaCl solution.

The accelerated cathodic reaction in sea-water, shown in Figure 3.2A, is accompanied by pick-up of sulphur, magnesium and calcium, as seen in the XPS surface analysis results (Figure 3.3). The positive ions are picked up while the sample surface undergoes a high rate of cathodic reaction. The surface has a negative potential and these positively charged species are attracted to it. In this case the $E_{corr}$ of the sample was found to drop to a more negative value (-220mV vs SCE $\rightarrow$ -260mV vs SCE).

The presence of sulphur is not thought to be due to the
sample surface negative potential and could arise from the adsorption of a monolayer of sulphur onto the clean surface prior to the acceleration of the cathodic reaction at the specimen. The source of the sulphur is most likely to be the decomposition of marine organisms and the metabolic products of sulphate reducing bacteria.

Parvizi (147) used AC Impedance to study the changes in electrical characteristics of the alloy film as the aerated sea water was exchanged for deaerated sea water and found a small drop in resistance.

3:1.4 MECHANISMS PROPOSED FOR THE ROLE OF SULPHUR IN CUNIFER CORROSION.

The role of sulphur has been discussed by several authors, and the proposed mechanisms are summarised here:

1) A shift in $E_{\text{corr}}$ to allow a high rate of hydrogen reduction, caused by a reduction in Cu$^{+}$ ion concentration in the water surrounding the metal as Cu$_{2}$S is precipitated (143).

2) Catalysis of the oxygen reduction reaction by sulphides in the corrosion product (154).

3) The increased volume of porous oxide providing a larger surface area for the cathodic reduction reaction (156).

4) The formation of a mixed iron-nickel sulphide, i.e. Fe$_{0.5}$Ni$_{0.5}$S$_{2}$, a highly active catalyst for oxygen reduction (156).

5) Stimulation of electron transport through the protective
inner tarnish by incorporation of sulphide ions arising from the decomposition of organic material (158).

The first mechanism was investigated by de Sanchez and Schifferin (154) who declared that the hydrogen reaction was significant only at potentials more negative than -1.2V, a very low potential for this alloy. This mechanism has consequently received little attention.

The other four mechanisms are not exclusive and probably amount to different aspects of the same mechanism. However, it is fairly clear from the latter four mechanisms that sulphur has a significant role to play in stimulating the cathodic reaction at the outer porous corrosion layers. However, it is not clear how the balancing anodic reaction is also stimulated without some change to the characteristics of the original high resistance film.

3.2 THE AIM OF THIS STUDY

In the light of the above evidence, the aim of this study has been to investigate the action of sulphur on clean and slightly tarnished alloy surfaces. The experimental technique chosen consists of:

- depositing a monolayer of S onto the surface of CuNi(90,10) alloy;
- carrying out electrochemical experiments in aerated and deaerated solutions;
- quantifying the amount of sulphur present on the
surface before and after the electrochemical experiments;
- monitoring the chemical state of sulphur with high energy XPS.

If the corrosion of CuNi(90,10), with or without iron addition, could be shown to be due to the action of sulphur in association with iron and nickel, and the catalytic properties confirmed (mechanism 4 above), then the rational for using the iron-containing alloy might be questioned in applications where fast water flow rates are not envisaged.

3.3 THE USE OF INORGANIC SOURCES OF SULPHUR IN SOLUTION

The use of inorganic sources of S to investigate the corrosion of CuNi has been chosen for this work because organic sources are always accompanied by C and N from the adsorbed layers of bio-proteins. XPS studies of the adsorption of bio-proteins onto CuNi and the subsequent colonisation by algae and other marine species has been studied by Garner (159). The presence of these bio-masses makes the interpretation of XPS spectra very complex.

The aim behind the use of inorganic sources of sulphur was to examine:
- the first stages of sulphur-pickup by the alloy;
- whether a compound or a sulphur monolayer might be identified as the stable form;
- determination of the degree to which the electrochemical reactions might be related to the amount of sulphur on the surface.
In order to have a datum base line with which to compare the experiments with sulphur monolayers, the following experiments were carried out on CuNi (90:10; commercially pure) alloy material in clean and later H₂S purged solutions of 3.4% NaCl.

Initially, experiments were attempted using enough Na₂S to give between 10 and 20ppm of sulphur in the electrochemical cell. This concentration has been used successfully in the past by other workers, but, to work well, requires a continuous flow of dosed solution past the sample, and is commonly used for long term exposure tests, or in the monitoring of changes in O₂ concentration (160). The Na₂S addition was made at a level sufficient for there to be enough sulphur (assuming equilibrium dispersal in the cell electrolyte) in the double layer at the sample to form two monolayers (at 40ng/cm²). Additions of the Na₂S, dissolved in ≈ 5ml of the electrolyte, were made to the electrochemical cells and polarisation curves run shortly afterwards. Results were irreproducible.

It is thought that these small additions of S may start to polymerise during solvation, prior to addition to the cell and as they diffuse through the electrolyte, leaving insufficient S²⁻ ions to affect the sample surface in any significant way.

In alkaline solution the reaction of Na₂S is thought to
be as follows:

\[
Na_2S + 2H_2O \rightarrow 2NaOH + H_2S \quad (E\ 3:2a)
\]

\(H_2S\) is then oxidised to produce \(S^0\) which can recombine with \(Na_2S\) to form stable \(Na_2S_x\) compounds.

\(H_2S\), on the other hand, when added directly to the solution is ionised to \(HS^-\). This may then form thiosulphate and/or an elemental colloidal sulphur, but is not thought to polymerise.

\[
2HS^- + H_2O \rightarrow S_2O_3^- + 4H_2\uparrow \quad (E\ 3:2b)
\]

It was therefore decided to use \(H_2S\) added directly to the electrochemical cell from a gas cylinder. This would ensure the minimum polymerisation of sulphur and a continuous supply of \(HS^-\) in the solution. For safety, the experiments were carried out inside a glove bag within a fume cupboard. Lead acetate scrubbers were used on the gas exit piping from the cell.

3.3.2 METHOD

The cathodic reaction at \(-300\)mV vs SCE was monitored for clean and filmed samples in fresh, oxygenated 3.4\% NaCl solution over a range of pHs. The filmed samples were prepared by anodic exposure at \(-100\)mV vs SCE for up to 24 hours. The tarnish produced was of a uniform brown colour.

The potentiostatic curves of current density vs time at
pH = 8 are shown in Figure 3:4, while Table 3:1 tabulates the results for various pHs.

Subsequent experiments with H$_2$S (experimental details are given in Appendix C) were carried out by holding the sample at -300mV vs SCE for 20 minutes, turning the O$_2$ supply off, the H$_2$S supply on and monitoring the current density.

Figure 3:4: Cathodic current density vs time for clean and tarnished samples in 3.4% NaCl at pH = 8
Table 3:1: Results from potentiostatic exposure of clean and filmed samples in 3.4% NaCl

<table>
<thead>
<tr>
<th>Clean</th>
<th>Cathodic Current Density (µA/cm²)</th>
<th>no of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>after 80 160 240 500 mins</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>73 69 59 50</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>29 32 41 38</td>
<td>3</td>
</tr>
<tr>
<td>7</td>
<td>49 45 44 31</td>
<td>3</td>
</tr>
<tr>
<td>8</td>
<td>89 77 61 47</td>
<td>3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Tarnished</th>
<th>Time at -100mV Cathodic Current Density (µA/cm²)</th>
<th>(mins) after 80 160 240 500 mins</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>480</td>
<td>3.7 3.4 3.2 2.8</td>
</tr>
<tr>
<td></td>
<td>980</td>
<td>5.6 6.6 6.6 6.6</td>
</tr>
<tr>
<td>8</td>
<td>1300</td>
<td>2.6 3.0 3.3 3.3</td>
</tr>
<tr>
<td></td>
<td>1300</td>
<td>3.3 3.4 3.5 3.6</td>
</tr>
</tbody>
</table>

3:3.3 RESULTS

3:3.3.1 ELECTROCHEMISTRY

Typical plots are shown in Figure 3:5 for clean and filmed samples, and specific data values shown in Table 3:2.

The H₂S was bubbled for up to 15 minutes, turned off and O₂ reintroduced. After the introduction of the H₂S a short induction period (1-3 minutes) was followed by a sharp increase in the cathodic current density. Shortly afterwards, a matter of seconds, the current changed sense (from cathodic to anodic) and a significantly lower corrosion potential was recorded. When a steady state had been reached a quick (20mV/min) polarisation scan was run from the anodic side, through the corrosion potential and
Figure 3.5: Cathodic current density vs time for clean and tarnished samples exposed to \( \text{H}_2\text{S} \)

Table 3.2: Data values for clean and tarnished samples exposed to \( \text{H}_2\text{S} \) (see Figure 3.5) (CD: Current Density)

<table>
<thead>
<tr>
<th>Event</th>
<th>Clean</th>
<th>Tarnished</th>
<th>units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current Density at -300mV</td>
<td>-111</td>
<td>-4.2</td>
<td>( \mu\text{A/cm}^2 )</td>
</tr>
<tr>
<td>Time between ( \text{H}_2\text{S} ) addition and rise in cathodic CD</td>
<td>2</td>
<td>3</td>
<td>mins</td>
</tr>
<tr>
<td>Cathodic CD peak</td>
<td>-181</td>
<td>-54</td>
<td>( \mu\text{A/cm}^2 )</td>
</tr>
<tr>
<td>Anodic CD peak</td>
<td>+340</td>
<td>+205</td>
<td>( \mu\text{A/cm}^2 )</td>
</tr>
<tr>
<td>( E_{\text{corr}} ) of scan</td>
<td>-630</td>
<td>-390</td>
<td>mV vs SCE</td>
</tr>
<tr>
<td>Cathodic CD after scan</td>
<td>-55</td>
<td>-180</td>
<td>( \mu\text{A/cm}^2 )</td>
</tr>
<tr>
<td>50mV below ( E_{\text{corr}} )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time of ( \text{H}_2\text{S} ) exposure</td>
<td>6</td>
<td>15</td>
<td>mins</td>
</tr>
</tbody>
</table>
into the cathodic region.

From Table 3:2 the following points are important to note:
1) the time before the cathodic rise is longer for the tarnished sample than for the clean sample;
2) the \( E_{\text{corr}} \) for the tarnished sample is higher than for the clean sample;
3) the final cathodic current density on the tarnished sample is considerably higher than on the clean sample, presumably due to an increase in the surface area.

By this time both of them had turned black, presumably due to the formation of Cu\(_2\)S.

These results do lend support to the idea that the constituents of the passive film are more important than the alloy composition itself for the corrosion of this alloy.

3.3.3.2 SURFACE ANALYSIS

A sample was removed from the H\(_2\)S experiment as soon as the cathodic current was seen to rise, rinsed with propanol, edge dried with tissue and loaded into the spectrometer within 2 minutes. The spectrometer and glove box were connected together as shown in Figure 3:6.

When a suitable vacuum was established within the analysis chamber of the spectrometer ( \( \leq 10^{-9} \) Torr) a semi-quantitative analysis was recorded with AlK\(\alpha\) radiation, this was followed by analysis with AgL\(\alpha\).
Figure 3.6: Glove box connected to VG ESCA3 MkII electron spectrometer for H₂S electrochemical experiments
Table 3:3: Semi-quantitative analyses of CuNi samples in AlKα radiation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atomic percentage (minus carbon)</th>
<th>Stoichiometric ratios</th>
<th>S/Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>Ni</td>
<td>Cl</td>
</tr>
<tr>
<td>CuNipure + S*</td>
<td>14.7</td>
<td>5.7</td>
<td>-</td>
</tr>
<tr>
<td>(30.6)</td>
<td>(11.8)</td>
<td>(51.8)</td>
<td>(5.9)</td>
</tr>
<tr>
<td>CuNicomm + S*</td>
<td>10.8</td>
<td>4.7</td>
<td>-</td>
</tr>
<tr>
<td>(25.2)</td>
<td>(10.9)</td>
<td>(58.7)</td>
<td>(4.1)</td>
</tr>
<tr>
<td>CuNipure + S* 300mV</td>
<td>9.3</td>
<td>7.7</td>
<td>3.0</td>
</tr>
<tr>
<td>(15.3)</td>
<td>(12.7)</td>
<td>(67.0)</td>
<td>(3.1)</td>
</tr>
<tr>
<td>CuNicomm + S* 300mV</td>
<td>5.9</td>
<td>4.7</td>
<td>8.6</td>
</tr>
<tr>
<td>(11.9)</td>
<td>(9.4)</td>
<td>(61.4)</td>
<td>(17.3)</td>
</tr>
<tr>
<td>CuNicomm + H2S 300mV, 45°TOA</td>
<td>7.5</td>
<td>2.1</td>
<td>2.0</td>
</tr>
<tr>
<td>(-300mV) 30°TOA</td>
<td>(25.4)</td>
<td>(7.0)</td>
<td>(6.7)</td>
</tr>
<tr>
<td>CuNipure -270mV 1.6As</td>
<td>8.0</td>
<td>-</td>
<td>9.0</td>
</tr>
<tr>
<td>(15.8)</td>
<td>(16.0)</td>
<td>(68.0)</td>
<td>(6.5)</td>
</tr>
</tbody>
</table>

radiation for S1s, S2p and SKLL line positions for comparison with data in Chapter 2. A summary of semi-quantitative XPS data is given in Table 3:3, in which atomic percentages with and without carbon and stoichiometric ratios are shown, while peak position data are given in Table 3:4.

The data in Table 3:3 contain the surface analysis results for the two CuNi alloys with adsorbed monolayers of sulphur (preparation details follow, section 3:4). The third and fourth entries are for the two CuNi alloys with adsorbed monolayers exposed to 3.4% NaCl solution at -300mV
for 3 hours. The fifth entry, labelled CuNi + H₂S, is for the experiment described above. The sixth entry, labelled CuNiFe, is taken from ref 158, and is for the ternary alloy exposed at -270 in 3.4% NaCl after the a charge of 1.6As had been passed. (This would correspond to about 15 hours in the case of the third and fourth samples mentioned above.)

The Cu/Ni ratio shows enrichment by nickel, varying from 3.6 for the H₂S experiment, through ≈ 2.5 for the S monolayer standards to 1.3 for the samples with sulphur monolayers exposed at -300mV vs SCE. The ratio from EDX data is 9, for the sample bulk.

The concentration of sulphur on the sample exposed to H₂S is slightly higher ([Cu+Ni]/S = 4.6) than that on the standards ([Cu+Ni]/S = 8.7); the ratio for a bulk sulphide would be 2. The result for the sample exposed to H₂S is considered to be of the order of a monolayer once an allowance is made for the difference in the experimental conditions: the surface area of the sample in the H₂S experiment must be larger than that of the standards. The standards underwent thermal etching during annealing prior to monolayer adsorption and consequently had a more uniform surface.

XPS data for the H₂S experiment were recorded at two take-off angles, the take-off angle being reduced to 30° to show any depth variation of concentration, in particular for sulphur. The Cu/Ni ratio remained constant at 3.6, while the ratios of Cu+Ni to O, Cl and S all increased.
Table 3:4 : AgLα and AlKα peak position data (eV) for CuNi sample exposed to H₂S.

<table>
<thead>
<tr>
<th>S1s</th>
<th>S2p</th>
<th>SKLL</th>
<th>α'₁</th>
<th>α'₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgLα</td>
<td>2458.1</td>
<td>2125.6</td>
<td>4583.7</td>
<td>(flood gun used, 10eV accelerating potential)</td>
</tr>
<tr>
<td>AlKα</td>
<td>-</td>
<td>169.1 2109.1</td>
<td>-2278.2 (approx 8eV charging C1s at 291.7eV)</td>
<td></td>
</tr>
</tbody>
</table>

slightly for the more surface sensitive analysis. The S/Cl ratio was unchanged.

The Auger parameter results correspond to the values recorded for sulphides in the standards work, while the amount of sulphur present is very close to that recorded for a monolayer of sulphur in the standards work.

The Auger parameter result recorded with AgLα is similar to that for ZnS (4583.7eV) from the standards list (Table 2:8), while that recorded with AlKα is similar to that for Cu₂S + Cu (2278.1eV), MoS₂ (2278.4eV) and CuNi sulphided at 2278.0eV. The values of the Auger parameters for monolayers of sulphur are ≈ 0.5eV (MgKα data : S2p + SKLL) and 1.5 – 2eV (AgLα : S1s + SKLL) higher than the values recorded for the CuNi sample exposed to H₂S in solution.

The sample was returned to the glove box and introduced into a cleaned electrochemical cell (3.4% NaCl, O₂ gas flowing) at -300 mV vs SCE. The cathodic current density was monitored to see if the cathodic current would continue to rise. The cathodic current on insertion into the cell
was 110µA/cm², and it is assumed that this represents the diffusion limited cathodic current density under these conditions. Although higher cathodic currents, ≈ 180µA/cm², were recorded with H₂S was flowing, the gas flow rate was too low for the available meters to measure, and it is thought that a difference in the gas flow rates for oxygen and hydrogen sulphide would account for these differences.

3:3.4 DISCUSSION

The results of these experiments will be discussed more fully in the final discussion section, in the light of the results for the electrochemistry of the sulphur monolayers on CuNi.

It will be sufficient to note here that the cathodic reaction for both clean and tarnished samples has been reproducibly measured and that conditions giving rise to accelerated corrosion of CuNi established, with reproducible effects.

3:4 PILOT STUDY FOR SULPHUR MONOLAYER DEPOSITION

The aim of the pilot study was:

- to investigate the feasibility of monolayer deposition onto CuNi(90,10) alloy, using thermodynamic principles to estimate suitable starting conditions;
- to prepare a series of standard sulphides and sulphur monolayers, on different substrates, for use as standards for XPS analysis;
and to study the electrochemical behaviour of the alloy in deaerated and aerated NaCl solutions, with and without sulphur monolayers.

3:4.1 THE PREPARATION OF SULPHUR MONOLAYERS

The following samples were prepared for adsorption experiments:

- Cu(111) as a standard;
- a high purity, fully equilibrated polycrystalline sample of CuNi(90,10) prepared at the University Pierre et Marie Curie (UPMC) (denoted CuNi\textsuperscript{pure});

and - a nominally pure CuNi(90,10) polycrystalline alloy prepared by Yorkshire Metals, UK (denoted CuNi\textsuperscript{comm}).

An energy dispersive X-ray analysis (EDX) was made of the latter alloy with the result:

Ni 10.6%
Cu 89.3%

In addition both nickel and silicon were detected at separate inclusion sites. The nickel was present as nickel oxide, the and silicon was presumably left over from the de-oxidising flux used.

From previous work (49) in Paris it was known that a monolayer of sulphur deposited onto Cu(111) corresponds to a coverage of 40 ±2 ng/cm\textsuperscript{2}. This was then the reference to which coverage on alloy samples was compared for each experiment. The activity of the \textsuperscript{35}S was monitored by referencing the activity count of each sample to a prepared
Figure 3:7: Schematic diagram of monolayer adsorption rig

STANDARD, a high purity copper sample containing dissolved S* to a level between 18.5 and 19ppm.

S* denotes sulphur consisting mainly of $^{32}\text{S}$ but which has been irradiated with neutrons to form $^{35}\text{S}$. The specific activity of the freshly prepared sulphur was quoted as 1mCi/mg (Amersham, France). The standard notation for the production of the $^{35}\text{S}$ nuclide is $^{34}\text{S}(n,\gamma)$, the energy of the decay by emission of a beta particle being 0.167MeV.

A schematic diagram of the apparatus for the deposition
of S monolayers is shown in Figure 3.7. It consisted of a vacuum pumping system (diffusion and backing pump), a hydrogen purification system (Johnson Matthey palladium membrane furnace), a circuit for the preparation of the \( \text{H}_2\text{S}^* \) atmosphere containing \( \text{CuS}^* \) in a small silica boat and a similar section for the sample. The apparatus was made of pyrex with rubber O-rings used as sealing gaskets.

Polished (0.25\( \mu \text{m} \) diamond or electropolished), cleaned and dried samples were inserted into a pyrex glass tube which was clamped onto the apparatus using a Viton O-ring and a sprung metal clamp. The sample side of the apparatus was evacuated to \( 10^{-5} \) Torr and pure hydrogen gas was introduced. The sample was annealed in flowing hydrogen at 800°C for several hours.

The \( \text{H}_2\text{S}^* \) was prepared according to the equilibrium:

\[
\text{Cu}_2\text{S}^* + \text{H}_2 \leftrightarrow \text{Cu} + \text{H}_2\text{S}^* \quad (E \, 3:4.1a)
\]

and the partial pressure ratio \( \frac{\text{P}_{\text{H}_2\text{S}^*}}{\text{P}_{\text{H}_2}} \) was controlled by the furnace temperature (see Appendix A for partial pressure calculation). The total pressure in this section was 250 mbar.

Initially the sample was held at 600°C for adsorption, but this resulted in the formation of small sulphide crystallites, and subsequent experiments were carried out at 500°C. The most successful quenching method was found to be evacuation, furnace removal, followed by an iced water
Dousing.

The coverage was measured using a Geiger counter which was calibrated daily for a copper sample containing no S, called the blank, and for the standard containing 18.75ppm dissolved sulphur. The method of calculation of coverage is given in Appendix B.

3:4.2 ELECTROCHEMISTRY

Electrochemical measurements were carried out on the CuNi(90,10) + S samples in a gas tight cell using a gold wire counter electrode and a calomel reference electrode. Potentiodynamic scans were controlled by an EG&G 273 model potentiostat interfaced to an Apple computer. The electrolyte was 3.4% NaCl in distilled and deionised water, and the pH was adjusted to pH = 8 with NaOH and HCl. Both aerated (O₂) and deaerated (N₂) experiments were carried out. The deaerated experiment was carried out inside a glove box containing a nitrogen blanket, and the electrolyte was deaerated for 12 hours prior to the experiment. Scans were started in the cathodic region and the potential was changed at a rate of 10mV/min.

3:4.3 MgKα INDUCED XPS

XPS analysis of S monolayers and S sulphided samples was carried out in the VG MkII ESCALAB using MgKα X-rays (20mA, 12kV) at 50eV pass energy using 15x6mm slits, (5x2mm sample analysis area).
3:4.4 MONOCHROMATIC AGLα INDUCED XPS

The reader is referred to Chapter 2 where the experimental conditions and results of AgLα monochromated XPS are covered.

3:4.5 RESULTS

The adsorption results are shown in Table 3.5, surface analysis results in Tables 3.6, and 3.7, and the electrochemical polarisation curves are plotted in Figures 3:5a-f.

3:4.5.1 ADSORPTION OF SULPHUR MONOLAYERS - RESULTS

The results of the adsorption experiments are given in Table 3:3 below. The first result was an obvious sulphidation, as mentioned above, due to insufficiently fast cooling of the specimens. Subsequent experiments showed improvements as lower values were recorded. The value for a monolayer on an electropolished Cu(111) sample is given as 40ng/cm² ± 4ng/cm². With this goal in mind it may be assumed that the last two experiments were successful within the bounds of experimental error.

It should be noted here that the CuNi<sub>comm</sub> sample was not electropolished and its surface will have been rougher than that of the original standard. Although attempts have been made to model the effect of surface roughness on Geiger count rate, no successful model has yet been found and so there was no possibility of making corrections for surface roughness.
Table 3:5 : Results of Adsorption Studies

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp oC</th>
<th>( P(H_2) ) ( P(H_2) )</th>
<th>Intensity ( \text{Geiger Count} )</th>
<th>Coverage ( \tau(\text{ng/cm2}) )</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuNipure</td>
<td>600</td>
<td>2x10^{-4}</td>
<td>17634</td>
<td>117.6</td>
<td>Water quench</td>
</tr>
<tr>
<td>Blank</td>
<td>-</td>
<td>-</td>
<td>1058</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Standard</td>
<td>-</td>
<td>-</td>
<td>10879</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>CuNipure</td>
<td>600</td>
<td>1x10^{-4}</td>
<td>9106</td>
<td>57.31</td>
<td>Vacuum and</td>
</tr>
<tr>
<td>Blank</td>
<td>-</td>
<td>-</td>
<td>1075</td>
<td>-</td>
<td>iced water</td>
</tr>
<tr>
<td>Standard</td>
<td>-</td>
<td>-</td>
<td>10841</td>
<td>-</td>
<td>quench</td>
</tr>
<tr>
<td>CuNipure</td>
<td>500</td>
<td>8x10^{-5}</td>
<td>f 6349</td>
<td>38.6</td>
<td>Vacuum and</td>
</tr>
<tr>
<td>Cu(111)</td>
<td></td>
<td>m 6453</td>
<td>6104</td>
<td>46.44</td>
<td>iced water</td>
</tr>
<tr>
<td>Blank</td>
<td>-</td>
<td>-</td>
<td>1031</td>
<td>-</td>
<td>quench</td>
</tr>
<tr>
<td>Standard</td>
<td>-</td>
<td>-</td>
<td>10639</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>CuNipure</td>
<td>500</td>
<td>8x10^{-5}</td>
<td>m 6295</td>
<td>39.0+</td>
<td>Vacuum and</td>
</tr>
<tr>
<td>Cu(111)</td>
<td></td>
<td>m 6136</td>
<td>6136</td>
<td>37.8</td>
<td>iced water</td>
</tr>
<tr>
<td>CuNicomm</td>
<td></td>
<td></td>
<td>7296</td>
<td>46.44</td>
<td>quench</td>
</tr>
<tr>
<td>Blank</td>
<td>-</td>
<td>-</td>
<td>1065</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Standard</td>
<td>-</td>
<td>-</td>
<td>10415</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Notes: * Different grain sizes: CuNipure 600μm, CuNicomm 80μm

\( f \) Experiment to investigate the influence of electropolishing pits on the intensity of the giga counter reading by selecting regions on the sample with few(f) and many(m) pits; little difference in coverage was detected.

The influence of pits due to electropolishing appears to be negligible (< 1ng/cm² - from one experimental result). However, the relative proportion of grain to grain boundary does appear to influence the detected coverage. Some thermal etching occurred during annealing or during adsorption, which increased the surface area giving the profile as shown below (dimensions estimated from optical microscope using a graticule and dial gauge).
3:4.5.2 SURFACE ANALYSIS - RESULTS

Analyses of surface composition were made in the VG ESCALAB Mk II and in the VG ESCA3 MK II. In both cases the dessicator holding the samples was opened, and samples mounted up, within an Ar filled glove box or bag. The data of May 1988 were acquired on the VG ESCALAB MkII, while those of Sept 1988 were acquired using the VG ESCA3 MkII. The semi-quantitative results are presented in Table 3:6.

Sulphided Samples

From the MgKα data a rough estimate of stoichiometry for the sulphides gives the Cu₂S sample as Cu₂.₄S, Ni₃S₂ as Ni₁.₅S and CuNi_{pure} (90,10) sulphided as Cu₁Ni₁.₃S₂₂. The analyses of the nickel and alloy sulphides are in excellent agreement with the desired stoichiometry. The poor agreement for Cu₂S was due to S diffusion from the sulphide skin into the Cu-rich bulk in the centre of the sample, this sample being thicker than the others. The alloy shows a strong enrichment of nickel at the surface, the stoichiometry suggesting a sulphide similar to Cu₂S, but with every other Cu atom replaced by a nickel atom.

The stoichiometric ratios have been calculated from peak
Table 3:6 : ESCALAB Data: semi quantitative analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Date</th>
<th>Element and Line, Atomic %</th>
<th>S2p</th>
<th>Cu2p3</th>
<th>Ni2p3</th>
<th>O1s</th>
<th>C1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu₂S</td>
<td>May/88</td>
<td>15.3 36.0 - - 48.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni₃S₂</td>
<td>May/88</td>
<td>8.6 - 12.7 20.6 58.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuNi</td>
<td>May/88</td>
<td>49.4 22.4 28.2 - -</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(111)</td>
<td>May/88</td>
<td>1.5 15.4 - 18.9 64.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(100)</td>
<td>May/88</td>
<td>6.5 - 18.3 21.6 53.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuNi</td>
<td>Sept/88</td>
<td>0.98 - 0.65 3.6 94.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuNi</td>
<td>May/88</td>
<td>2.9 14.7 5.7 24.9 51.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuNi</td>
<td>Sept/88</td>
<td>2.4 2.6 0.1 2.7 92.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuNi</td>
<td>May/88</td>
<td>1.8 10.8 4.7 25.6 57.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuNi</td>
<td>Sept/88</td>
<td>11.2 11.0 1.7 10.9 65.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

areas with Shirley background subtraction and using Wagner sensitivity factors. For samples where sulphur was present as a monolayer a surface sensitivity (S') factor was used. A surface sensitivity factor is the conventional sensitivity factor (S) divided by a factor related to the inelastic mean free path (161) :

\[
S' = S \left[ \frac{KE(F1s)}{KE(x)} \right]^{0.66}
\]

(E 3:4.5,2a)

where x is the photoelectron line sampled.

The sulphided alloy sample was analysed three times in the ESCALAB, copper diffusion resulting in changes to the copper/sulphur and nickel/copper ratios : Cu/S = 0.43, 1.16, 1.21, Ni/Cu = 0.21, 0.05, 0.02, and consequently the

3 - 32
nickel/sulphur ratio also fell: Ni/S = 0.09, 0.06, 0.03. The sample was observed to change colour from the blue/black of the sulphide to a paler hue, with Cu metal colour visible under the optical microscope. This is presumably the diffusion of copper from the centre of the sample where the sulphur concentration was lower than at the surface. Stoichiometric values are given in Table 3:7.

Table 3:7 Stoichiometric ratios for selected samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Date</th>
<th>Cu/S</th>
<th>Ni/S</th>
<th>Ni/Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu + S*</td>
<td>May/88</td>
<td>10.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sept/88</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni + S*</td>
<td>May/88</td>
<td>2.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sept/88</td>
<td>0.66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuNi</td>
<td>May/88</td>
<td>5.1</td>
<td>2.0</td>
<td>0.4</td>
</tr>
<tr>
<td>pure + S*</td>
<td>Sept/88</td>
<td>1.1</td>
<td>0.04</td>
<td>0.04</td>
</tr>
</tbody>
</table>

The gross increase in carbon signal (Table 3:6) is presumed to be from diffusion pump oil vapours and contamination during transit between the laboratories and between the two instruments. The inelastic mean free path of C1s photoelectrons from MgKα excitation at 45° take-off-angle may be given as $\approx \sin 45 \left(0.6\sqrt{970\text{eV}}\right) = 13.2\text{Å}$, which suggests a layer of carbon contamination of some 40Å, (using the estimate that 95% of the XPS signal comes from a depth of $3\lambda\sin\theta$ from the surface (162)). Fortunately the S2p and SKLL lines have higher kinetic
energies than the C1s line and it was still possible to detect their signals.

**Samples with monolayers of sulphur**

For the monolayer samples the metal signals are masked to a greater extent than the sulphur signals. This is due to the difference in analysis depth for the lines used for the different elements, see below. The greater attenuation of low kinetic energy electrons by any overlayers results in lower metal/sulphur ratios than for the initial runs in the ESCALAB.

<table>
<thead>
<tr>
<th>Element, line</th>
<th>KE with MgKα X-rays (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2p</td>
<td>1083</td>
</tr>
<tr>
<td>C1s</td>
<td>966</td>
</tr>
<tr>
<td>O1s</td>
<td>722</td>
</tr>
<tr>
<td>Ni2p</td>
<td>398</td>
</tr>
<tr>
<td>Cu2p</td>
<td>323</td>
</tr>
</tbody>
</table>

It is known that the transmission function for the ESCALAB is not the same as for the ESCA3 (162). Although the equations for evaluating this are complicated, an empirical approach by comparing the ratio of heights of the Cu2p/Cu3p peaks taken from a cleaned copper stub analysed in each instrument will suffice in this case. The ratio for the ESCA3 is less than for the ESCALAB, which suggests that the low KE end of the spectrum is transmitted more efficiently in the ESCALAB than in the ESCA3. The implication for this work is, ceteris paribus, that the ratio Cu/S would be higher in the ESCALAB than in the ESCA3. This may account for some part of the discrepancy
between the results for the two instruments.

The alloy sample CuNi\textsubscript{pure} +S* also showed a decrease in the nickel/copper ratio between the two instruments. This cannot be explained by inelastic mean free path considerations or by transmission function variation, and leads to the supposition that on quenching from the adsorption temperature the alloy was left with a surface that was unstable in air. The Ni/Cu ratio is initially higher than expected (0.4 recorded, 0.1 expected) as recorded in the ESCALAB (5/88), but four months later it was lower than expected (0.04) as analysed in the ESCA 3.

The CuNi\textsubscript{cohm} + S* sample was found to contain nickel oxide inclusions. It is thought that the 8 hour anneal under hydrogen prior to adsorption removed oxygen from the outer surface of the sample, leaving the surface alloy lattice slightly richer in nickel. It is assumed that this diffused into the bulk of the sample with time.

3:4.5.3 ELECTROCHEMISTRY - RESULTS

The electrochemistry results for potentiodynamic scans for clean, tarnished samples and samples with monolayers of sulphur are collated in Table 3:8, and the potentiodynamic scans are shown in Figure 3:8.

The result of controlled exposure to sodium chloride solution for several days is clearly seen by a change in Tafel slope and a reduction in the corrosion current (I\textsubscript{c}) in Table 3:8. The results are shown graphically in Figure 3:8, and can be seen by comparing Figure 3:8a with Figure
Figure 3.8: Potentiodynamic scans of CuNi(90,10) in 3.4% NaCl
Figure 3.8: Potentiodynamic scans of CuNi(90,10) in 3.4% NaCl

Table 3.8: Tafel plot data for CuNi (90,10) in 3.4% NaCl and exposure conditions (as received samples equilibrated for 20 mins at Ecorr prior to scan).

<table>
<thead>
<tr>
<th>Exposure</th>
<th>Aged Scan start</th>
<th>Activity</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deaerated Scan start</td>
<td>Deaerated Scan start</td>
<td>Before After</td>
<td>Before After</td>
</tr>
<tr>
<td>CuNiFe (bal,10,1.5)</td>
<td>CuNiFe (bal,10,1.5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>467</td>
<td>58</td>
<td>25</td>
</tr>
<tr>
<td>f</td>
<td>491</td>
<td>50</td>
<td>5.5</td>
</tr>
</tbody>
</table>

θ after starting the experiment in the cathodic region. In the case of f the cathodic (forward) and anodic (reverse) scans were identical.
3:8b, and Figure 3:8c with Figure 3:8d. The effect of starting a polarisation scan in the anodic region is a suppression of the cathodic reaction as a result of the surface layers built up.

The negative value of BC for the cathodic slope on the reverse scan of sample (f) is a result of a reduction reaction occurring on the sample, the experiment was not run far enough into the cathodic region to obtain a slope value for the true cathodic reaction.

Samples (e) and (f), possessing a monolayer of sulphur, showed no significant loss of sulphur after these experiments. This is evidence for the strong adsorption of sulphur as a monolayer even after excursion to a high anodic current density (0.1A/cm² at \( \approx -40\text{mV} \) vs SCE) in a potential range where the alloy is usually forming \( \text{Cu}_2\text{O} \).

In earlier experiments it became apparent that computer control was not always ideal. Specifically the setting of potentiodynamic scans could leave interesting regions unscanned if the rest potential changed between starting the forward and the reverse sweeps (see below). In addition a delay period existed between connecting the cell to the potentiostat and commanding the computer to begin the experiment, and the experiment actually beginning. During this delay time the sample was not under potential control and would be freely corroding. Therefore the later work was manually controlled using a chart recorder for data output.

3:4.6 DISCUSSION
Table 3:5 shows that reproducible adsorption results can be obtained so long as the vacuum and ice quench is used.

In the case of adsorbed S*, Ni was present as an hydroxide (856.2eV) as well as the metal form (852.9eV). Copper was consistent on all samples as the metallic form (932.2eV). For the S* monolayers on CuNi there appeared to be an excess of nickel (0.11 expected).

The electrochemical curves in Figure 3:8 (a,b and c,d) clearly show the change in Tafel slope for the cathodic reaction on the sample once a protective film of copper oxide-chloride complexes had built up over a period of several days, the anodic reaction remaining approximately the same.

The samples possessing S* monolayers (Figure 3:8e and f) were potentiodynamically cycled about the rest potential. In the aerated experiment (f), the reverse scan cathodic slope is almost negative indicating that two reactions are taking place. It should be noted that the reverse scan (anodic to cathodic) in the aerated experiment has a higher rest potential than the forward (cathodic to anodic) run. As a result of the way the Apple computer was programmed and because the rest potential of the sample must have changed during the forward scan, the reverse scan started at a potential about 100mV more positive than the end of the forward scan. This more anodic starting potential forced the specimen into a region of the Pourbaix diagram where Cu^{+} ions would be expected. It is thought that this reaction resulted in the precipitation of a thin
film of a copper (II) compound (probably CuO) on the surface which was subsequently reduced on entering the cathodic region. The cathodic curve then fell to meet the original cathodic curve, to turn to a positive slope at -300mV (vs SCE). This is also in accordance with the Pourbaix diagram, -300mV vs SCE represents the onset of immunity of copper (Figure 3:1)

In the deaerated scan the rest potential is significantly more negative than either of the aerated scans (60mV) and the corrosion current is a factor of 10 less. In neither case was any $S^*$ lost from the surface during the experiments. The deaerated sample (CuNi$_{pure}$ (90,10)) had been conditioned at the rest potential for 12 hours in the deaerated electrolyte. This confirms that hydrogen reduction was not a significant reaction under these conditions.

3:4.7 PRELIMINARY CONCLUSIONS

1) The deposition of a monolayer of sulphur on CuNi (90,10) alloy appears to have been achieved using conditions similar to that required for $S$ adsorption on Cu(111).

2) The change in the cathodic reaction on the build up of the protective tarnish is confirmed for the experimental conditions used.

3) The electrochemical behaviour of the CuNi alloy with an adsorbed sulphur monolayer under aerated conditions shows no accelerated cathodic reaction, but in fact the reverse: a Tafel slope value typical of a highly inhibited reaction.
4) Under deaerated conditions the CuNi alloy with an adsorbed monolayer of sulphur shows no evidence of a stimulation of the hydrogen reaction.

3:5 EXTENDED STUDY

In the light of these interesting results confirmation was necessary, in particular for the electrochemical results. A second series of experiments were devised to test reproducibility and to estimate experimental error bars.

This extended study covers further adsorption experiments, a series of cyclic potentiodynamic scans and potentiostatic scans monitoring the cathodic reaction with time.

3:5.1 MONOLAYER DEPOSITION

The preparation of samples for deposition of monolayers of \( S^* \) and the deposition of monolayers of \( S^* \) was carried out as described in the pilot study.

3:5.2 ELECTROCHEMISTRY

3:5.2.1 CYCLIC POTENTIODYNAMIC SCANS

Cyclic electrochemistry was carried out using a three electrode system: sample, calomel and gold counter electrodes, in solutions of 3.4\% NaCl, at a pH of 7 - 7.5 and aerated by bubbling oxygen. Samples were introduced to and removed from the cell with potential applied.
Experiments were started in the cathodic region and were swept to and from the anodic region at 1mV/s. Up to ten such scans could be recorded in roughly 2 hours. The aim of this technique was to monitor the development of any steady state, and the change of Tafel slopes with time.

Initially a sample of clean CuNi_{\text{pure}}, freshly annealed at 800°C under H_2 overnight, was cycled, followed by runs on CuNi_{\text{pure}} and CuNi_{\text{comm}} each covered with a monolayer of S^*.

Samples were mounted in PTFE sample holders, with viton O-ring seals and stainless steel sprung contacts backing the rear of the sample. After each experiment the sample area that had tarnished was measured using an optical microscope. Tafel slopes BC and BA, the rest potential Ec, and the corrosion current Ic were estimated manually where possible from the straight line portions of the potential/current density curves, at least 70mV from the rest potential.

3:5.2,2 POTENTIOSTATIC SCANS

Potentiostatic experiments were undertaken in the same conditions, by holding the sample potential at -300mV vs SCE, and recording the current passing from the sample to the counter electrode.

In both experiments the potential was controlled by a Tacussel PRT10-0,5 potentiostat, and current versus time was recorded on a chart recorder.
3:5.3 RESULTS
The results of the adsorption study are shown in Table 3:9, and the electrochemical data in Table 3:10.

3:5.3.1 ADSORPTION - RESULTS
This set of adsorption experiments was not as successful as the previous set. Using the same conditions as above, the coverage was continually lower than expected. Although the sulphur was by now at a much lower activity than earlier, this was not thought to be the cause of the lack of coverage.

A second standard was prepared over three days to ensure equilibrium conditions throughout the Cu sample, but no improvement in the figures was achieved.

In an attempt to check if slow kinetics of the reaction were the cause of the low coverage, the ratio of partial pressures was increased, but this also had no effect. It was assumed that a calibration problem did exist, but its precise nature was not immediately obvious. Therefore in order to continue with electrochemical experiments, it was considered fair to assume that monolayers were present on the sample surface, and that the calibration problem would be solved at a later date.
Table 3.9: Results of Adsorption Studies

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp °C</th>
<th>P$<em>{H_2}$ / P$</em>{H_2}$</th>
<th>Intensity*</th>
<th>Coverage* (ng/cm$^2$)</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuNi(111)</td>
<td>500</td>
<td>8x10$^{-5}$</td>
<td>380</td>
<td>30.7</td>
<td>11-2-89</td>
</tr>
<tr>
<td>CuNi$_{pure}$</td>
<td></td>
<td></td>
<td>401</td>
<td>33.0</td>
<td>2.5 hours</td>
</tr>
<tr>
<td>CuNi$_{comm}$</td>
<td></td>
<td></td>
<td>435</td>
<td>36.7</td>
<td></td>
</tr>
<tr>
<td>CuNi$_{comm}$</td>
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<td>395</td>
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<td>-</td>
<td>761</td>
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<tr>
<td>CuNi$_{pure}$</td>
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<td></td>
<td>411</td>
<td>34.5</td>
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</tr>
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<td>CuNi$_{comm}$</td>
<td></td>
<td></td>
<td>337</td>
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<td>741</td>
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<td>CuNi$_{comm}$</td>
<td></td>
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</tr>
<tr>
<td>CuNi$_{comm}$</td>
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<td></td>
<td>394</td>
<td>33.7</td>
<td>2 hours</td>
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<td>-</td>
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<td>-</td>
<td>736</td>
<td>-</td>
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</tr>
</tbody>
</table>

* Notes

The Geiger counter used was the "glove box" model, and the readings are the average of 3x5 minutes.

† The standard was prepared in February. When compared to saturated monolayers on Cu(100), for which τ = 38.5ng/cm$^2$ and Cu(111), for which τ = 39ng/cm$^2$, the activity of the sample was equivalent to 19.9 ppm of dissolved sulphur.

* The coverage was calculated using the equation:

$$\tau = \left( \frac{I_{\text{sample}} - I_{\text{blank}}}{I_{\text{standard}} - I_{\text{blank}}} \right) \times \left( \frac{\text{ppm}_{\text{standard}} \times \text{density}}{\text{ppm}_{\text{standard}} \times \text{density}} \right) \times \text{Adsorption coefficient}$$

where the density of the alloy = 8.95 g/cm$^2$

ppm of dissolved sulphur in the standard = 19.9

adsorption coefficient = (0.9 x 0.24) + (0.1 x 0.295) for CuNi(90,10)
Table 3:10: Results of Electrochemical Experiments

<table>
<thead>
<tr>
<th>Expt ID</th>
<th>Cycle</th>
<th>Potential</th>
<th>Range</th>
<th>$mV/\text{decade}$</th>
<th>$Ec$ vs SCE</th>
<th>Sample Change in Coverage of $S^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S589A</td>
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<td>46</td>
<td>95</td>
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<td>90</td>
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</tr>
<tr>
<td>E</td>
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<td>467</td>
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<td>-230</td>
<td>CuNipure</td>
<td>+$O_2$</td>
</tr>
<tr>
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<td>491</td>
<td>50</td>
<td>-285</td>
<td>CuNicomm</td>
<td>+$N_2$</td>
</tr>
</tbody>
</table>

* $Ec$ too close to the beginning or end of the scan for a straight line portion to be measured.
The results from the cyclic polarisation are given in Table 3:10. The earlier results have been inserted at the bottom of the table for easy comparison. Potentiostatic curves of current density vs time are shown in Figure 3:6.

On the clean, uncontaminated CuNi sample, the value of BC shows an initial decrease and then an increase after 10 scans. This is in accordance with the electrochemical reduction of a small amount of air formed oxide followed by the passivation of the alloy. The increase in the anodic slope is unexpected, possibly a result of the fast scan rate used. The corrosion potential is initially fairly anodic and falls after 10 scans to around -200mV in accordance with previous work (158).

The samples covered with a monolayer of sulphur show different behaviour. The first three experiments (S594a, S599a and S5106a) were conducted over the potential range -300 to 0mV (vs SCE). They initially show a fairly high Bc value in accordance with experiments in the pilot study (see section 3:2.2.3); the Tafel slope subsequently shows a degree of activation of the cathodic slope, as a decrease in the slope from 212 to 157 and 257 to 171 (mV/decade) for two of the experiments. The third is less conclusive, but the change in rest potential is consistent, increasing in the anodic direction, suggesting a small degree of activation of the cathodic reaction. This could also be interpreted as a fall in the rate of the anodic reaction.
In each case a fall in the measured coverage was recorded. This is thought to be due to attenuation by surface films, (see surface analysis results below).

When the potential range scanned was reduced on the anodic side by 40mV (S5112a, -300 to -40mV vs SCE), the corrosion potential was found to move in the opposite direction (-244mV → -282mV vs SCE) suggesting a decrease in the cathodic reaction. In this case there was no "loss" of surface coverage by sulphur. This could be due to one of two reasons:

1) The loss of sulphur in previous experiments was by slow oxidation at the anodic end of the scan, rather than by attenuation due to surface films. When restricting the anodic excursion to -40mV this no longer happened.

2) No corrosion products were back-deposited onto the alloy surface when the anodic excursion was limited to -40mV vs SCE.

The final experiment (S5112b) was designed to study the behaviour of the alloy by maintaining a predominantly cathodic cycle. The results of this experiment show no loss of sulphur, and in contrast to the penultimate experiment (S5112a) a large shift in the corrosion potential in the anodic direction.

**POTENTIOSTATIC SCANS**

The result of the potentiostatic polarisation at -300 mV (vs SCE) was a steady current density of 31μA/cm² after 3 hours, not particularly high and lower than that recorded
for the H$_2$S experiment (section 3:3.3,1). The calculated surface coverage was 35.6ng/cm$^2$ before, and 27.5ng/cm$^2$ after the experiment, a loss of $\approx$ 23%. Figure 3:6 shows how these results compare with the curves for clean and tarnished films.

It would appear that the two S covered samples reach a lower cathodic current density earlier than the clean alloy. However, the shapes of the curves are different. The cathodic current density on the clean sample will continue to fall as the passive film builds up, as a result of the small anodic currents being passed at the sample at this potential. The samples covered with S appear to have

Figure 3:6: Comparison of Cathodic current density recorded for clean, tarnished and sulphur covered samples at -300mV vs SCE.
reached a limiting current density, which, from their shape, might not be expected to decrease.

3:5.3.3 SURFACE ANALYSIS - RESULTS

XPS analysis of the sample exposed potentiostatically, (using AlKα X-rays at 10kV,20mA, and 90° take-off-angle) showed that a film had formed over the top of the sulphur, through which no sulphur could be detected, suggesting a film thickness greater than 3x the IMFP for S2p in AlKα = 6.5nm. Sulphur could however still be detected from those areas of the sample which had not been exposed to the electrolyte.

The quantification of the area exposed to the electrolyte showed a surface enrichment by nickel, (7.7, and 4.7%), over copper, (9.3 and 5.9%). This is a greater surface enrichment than observed on the samples prior to electrochemical exposure (see Table 3:3 : Ni = 5.7% and 4.7%, Cu = 14.7% and 10.8% for pure and commercial samples respectively).

We may be certain that in this experiment none of the apparent loss of sulphur could be due to oxidation, since the potential used was well into the cathodic region. The signal must, in fact, have been attenuated by the surface layer, mostly nickel hydroxide.
3.5.4 DISCUSSION

Corrosion of CuNi by $H_2S$

The use of $H_2S$ to promote corrosion of the alloy was found to be a suitable method for the addition of sulphur, although improvements to the design would probably include probes for hydrogen evolution and dissolved sulphur.

The results support those of Efird (142) in relation to the corrosion potential shift and the increase in corrosion rate.

These experiments probably represent a relatively high level of sulphur exposure. Notwithstanding this, it has been possible to show that the initial rise in cathodic current density, on introduction of $H_2S$, results in the adsorption of an amount of sulphur which corresponds closely to that for monolayers of sulphur on clean pure metal substrates.

The Increase in the Cathodic Reaction

The normal cathodic reactions involve the consumption of electrons released from the metal atoms going into solution/oxide films:

Oxygen reduction: $O_2 + 4e^{-} + 2H_2O \rightarrow 4OH^- \ (E \ 3:5.4a)$

Hydrogen evolution: $2H^+ + 2e^{-} \rightarrow H_2 \uparrow \ (E \ 3:5.4b)$

For the clean sample the rise happened over approximately 2 minutes, the current density changing from
-111 to -181 \( \mu A/cm^2 \). For the tarnished alloy the rise, from -4.2 to -54 \( \mu A/cm^2 \), was recorded over 30 seconds, (data from Table 3:2). These data can be used to obtain an approximate figure for charge consumed using the cathodic current density (CD) rise:

\[
\frac{1}{2} \left( \text{Maximum CD} - \text{Minimum CD} \right) \times \text{time} =
\]

4200 \( \mu A/cm^2 \) for the clean sample; and 750 \( \mu A/cm^2 \) for the tarnished sample.

It is important to decide what may cause the increase in the cathodic reaction. If it is assumed that the \( H_2S \) is dissolved into solution according to the following reaction

\[
2H_2S \longrightarrow 2HS^- + H_2^+ \quad (E \ 3:5.4c)
\]

then the \( HS^- \) ion may adsorb on the metal surface. As a monolayer of sulphur is formed, the \( H^+ \) ions are released into solution and may form water molecules by the following reaction:

\[
HS^- + Cu + OH^- \longrightarrow (Cu + S_{ads}^0) + H_2O + 2e^- \quad (E \ 3:5.4d)
\]

As the partial pressures of \( HS^- \) and \( H_2S \) increase in solution, the sulphur monolayer converts to a sulphide:

\[
HS^- + 2Cu + OH^- \longrightarrow Cu_2S + H_2O \quad (E \ 3:5.4e)
\]
Other reactions to be considered at the surface are the conversion of copper chloride and copper oxide to the sulphur monolayer:

\[
\text{HS}^- + \text{CuCl} + \text{OH}^- \rightarrow \text{Cu} + \text{S}_{\text{ads}} + \text{H}_2\text{O} + \text{Cl}^- \quad (\text{E 3:5.4f})
\]

\[
\text{HS}^- + \text{Cu}_2\text{O} + \text{OH}^- \rightarrow \text{Cu} + \text{S}_{\text{ads}} + \text{H}_2\text{O} \quad (\text{E 3:5.4g})
\]

The release of hydrogen is not favoured at the working potential and is not thought to be a significant reaction in this case.

Thus none of the reactions listed above are electrochemical, that is, no electrons are taken up from the sample surface during the reactions, so the increase in the cathodic current does not arise from the take up of sulphur onto the surface. In the absence of further data and on the basis of the experimental data reported here, it appears that the increase in the cathodic current density must be a stimulation of the cathodic reduction of oxygen as a result of sulphur adsorption onto the cathodic surface, prior to the formation of the sulphide, seen as sample blackening.

The surface analysis data for this experiment gave in depth information by the use of two different take-off angles. The important information is that:

1) The sulphur/chlorine ratio remains unchanged suggesting that these two elements are intimately mixed.
2) The \([\text{Cu+Ni}] / [\text{O, Cl or S}]\) showed a slight increase in each case for the more surface sensitive analysis suggesting that the metal-oxy-chloro compound, formed prior to introduction of the \(\text{H}_2\text{S}\), extended below the analysis depth of the \(30°\) TOA analysis. The increase in metal content might suggest that the adsorption of the sulphur results in displacement of Cl and O. The low absolute amount of oxygen in comparison to the other samples in Table 3:3 supports this idea. However, these results are only representative of a single sample. Although the electrochemistry was repeated several times the surface analysis was not.

The use of the Radio-tracer \(^{35}\text{S}\)

The use of radioactive sulphur and the ability to make controlled depositions of monolayers of sulphur has made an enormous contribution to this work.

The preparation of standards has provided the information required to make the above deductions for the corrosion sample in \(\text{H}_2\text{S}\). Without this technique, complex iterative programs would have had to be run for XPS data taken at different take-off angles.

This technique has also shown that the presence of a monolayer alone on a clean alloy surface is insufficient to stimulate a dramatic increase in the corrosion of the alloy. The sulphur monolayer becomes buried beneath a thin passive film growing at \(-300\text{mV VS SCE}\).

The use of monolayer standards in conjunction
with prepared sulphides showed useful differences in Auger parameter (Chapter 2). These have been used to identify tentatively the initial adsorption state of sulphur on the CuNi (90,10) alloy surface as a sulphide.
3:5.5 CONCLUSIONS

1) The method for preparation of adsorbed monolayers on CuNi (90,10) has been established.

2) As a monolayer S is exceptionally stable on the CuNi alloy, resisting oxidation by quite high anodic currents.

3) The catalytic action of S as a monolayer does not cause accelerated corrosion when in contact with the pure alloy on the first scan. However the cyclic scan experiments appear to show a gradual activation of the cathodic reaction, although the dramatic results characteristic of deaerated sea-water or H₂S addition are not found.

4) Hydrogen evolution was not a significant cathodic reaction at the potentials studied. The increase in the cathodic reaction for CuNi (90,10) exposed to H₂S is thought to arise from stimulation of the oxygen reduction reaction.

5) The use of AlKα and AgLα XPS both suggest that a sulphide is formed when H₂S is introduced to CuNi in aerated 3.4% NaCl. Only a trace amount, approximately a monolayer, appears to be required to activate the cathodic reaction.
6) The acceleration of corrosion which occurs in polluted seawater cannot be reproduced by deposition of sulphur from the gas phase, at high temperature, onto the clean alloy surface. However, this work gives guidance on the composition of the active sulphur deposited from solution.
APPENDIX A  THERMODYNAMIC METHOD FOR THE CALCULATION OF
H₂S/H₂ PARTIAL PRESSURE REQUIRED FOR THE ADSORPTION OF AN
S* MONOLAYER

The following three reactions are considered:

1) 2Cu + ½ S₂ ⇌ Cu₂S  \[ \Delta G_1^\circ = -31410 + 7.34 \ T \]  ...A1
2) 2H₂ + S₂ ⇌ 2H₂S  \[ \Delta G_2^\circ = -43160 + 23.61 \ T \]  ...A2
3) ½ Ni + ½ S₂ ⇌ ½ Ni₃S₂  \[ \Delta G_3^\circ = -39600 + 19.5 \ T \]  ...A3

For the deposition of an adsorbed layer the following sulphidation equilibriums must not become established:

A) 2Cu + H₂S ⇌ Cu₂S + H₂  \[ \Delta G_1^\circ - \Delta G_2^\circ \]  ...A4
B) 3Ni + 2H₂S ⇌ Ni₃S₂ + 2H₂  \[ 2\Delta G_3^\circ - \Delta G_2^\circ \]  ...A5

The Van't Hoff equation for each of these equilibria yields the partial pressure ratios for A and B at which the equilibrium is established. Once this is known a partial pressure ratio slightly lower than the calculated value may be chosen for the adsorption experiments.

The Van't Hoff equation:

\[ \Delta G = -RT \ln k \]  ...A6

where \( k = \frac{a(\text{products})}{a(\text{reactants})} \)

where \( a = \text{activity} \)

for A:

\[ \frac{\Delta G_1^\circ - \Delta G_2^\circ}{2} = -RT \ln \left( \frac{a_{Cu₂S} / a_{Cu₂}} {a_{H₂} / a_{H₂S*}} \right) \]  ...A7

for B:

\[ 2\Delta G_3^\circ - \Delta G_2^\circ = -RT \ln[ \left( \frac{a_{Ni₃S₂} / a_{Ni₃}} {a_{H₂} / a_{H₂S*}} \right) \]  ...A8

3 - 57
where \( a_{Cu}^2 = a_{Ni}^2 = 1 \) since they are solids. In an ideal solution \( a_{Ni} \) and \( a_{Cu} \) would equal 0.1 and 0.9 respectively, however \( a_{Cu} = 0.908 \) and \( a_{Ni} = 0.277 \) for this alloy at 973K (163), showing that Cu is behaving almost ideally but Ni shows positive deviation from ideality.

The partial chemical potential (\( \mu \)) is related to activity as shown below:

\[
\mu = RT \ln a \quad \ldots A9
\]

which is expanded for the Cu-Ni alloy system by the Redlich-Kister polynomial expression for \( \Delta G(fcc) \) referred to fcc(Cu) and fcc(Ni):

\[
\mu_{Cu} = RT \ln X_{Cu} + a_0 X_{Ni}^2 + a_1 \left[ X_{Ni}^2 \left( 3X_{Cu} - X_{Ni} \right) \right] \quad \ldots A10
\]

and

\[
\mu_{Ni} = RT \ln X_{Ni} + a_0 X_{Cu}^2 + a_1 \left[ X_{Cu}^2 \left( X_{Cu} - 3X_{Ni} \right) \right] \quad \ldots A11
\]

where \( a_0 = 8137.8 + 3.008 T \)

and \( a_1 = 2535.5 - 0.8284 T \).

Using the above expressions (A10 and A11) and substituting values of \( a_{Cu} \) and \( a_{Ni} \) into A7 and A8 we obtain \( p_{H_2} / p_{H_2}^{*} \) at various temperatures as shown in Table 3:A;1.
Table 3:A:1: Hydrogen sulphide/hydrogen partial pressure ratios for CuNi(90,10)

<table>
<thead>
<tr>
<th></th>
<th>Temp K (°C)</th>
<th>773 (500)</th>
<th>873 (600)</th>
<th>973 (700)</th>
<th>1073 (800)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta G^o_1 (\text{Cu}_2\text{S})^e$</td>
<td></td>
<td>-25736</td>
<td>-25002</td>
<td>-24268</td>
<td>-23534</td>
</tr>
<tr>
<td>$\Delta G^o_2 (\text{H}_2\text{S})^e$</td>
<td></td>
<td>-24909</td>
<td>-22548</td>
<td>-20187</td>
<td>-17826</td>
</tr>
<tr>
<td>$2\Delta G^o_3 (\text{Ni}_3\text{S}_2)^e$</td>
<td></td>
<td>-49053</td>
<td>-45153</td>
<td>-41253</td>
<td>-37353</td>
</tr>
<tr>
<td>$a_{\text{Cu}}^e$</td>
<td></td>
<td>0.921</td>
<td>0.919</td>
<td>0.917</td>
<td>0.916</td>
</tr>
<tr>
<td>$a_{\text{Ni}}^e$</td>
<td></td>
<td>0.432</td>
<td>0.376</td>
<td>0.336</td>
<td>0.307</td>
</tr>
<tr>
<td>$P_{\text{H}<em>2}\text{S}/P</em>{\text{H}_2} (\times 10^{-4})$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu pure</td>
<td></td>
<td>1.86</td>
<td>3.85</td>
<td>6.87</td>
<td>11.0</td>
</tr>
<tr>
<td>Ni pure</td>
<td></td>
<td>4.06</td>
<td>15.40</td>
<td>44.6</td>
<td>106</td>
</tr>
<tr>
<td>Cu in the alloy</td>
<td></td>
<td>2.19</td>
<td>15.40</td>
<td>8.17</td>
<td>13.1</td>
</tr>
<tr>
<td>Ni in the alloy</td>
<td></td>
<td>14.3</td>
<td>4.56</td>
<td>229</td>
<td>622</td>
</tr>
</tbody>
</table>

CALCULATIONS FOR THE TERNARY ALLOY: CUNIFE

The calculation of the partial pressure conditions for the ternary alloy is not simple. The following data were calculated using a database developed in the Transcalc Unit, Department of Materials Science and Engineering, University of Surrey and data taken from 'A Thermodynamic Evaluation of the Cu-Ni-Fe System' by Åke Jansson (Materials Research Centre, The Royal Institute of Technology, S 10044 Stockholm 70. TRITA-MAC-0340 April 1987)

The thermodynamic calculation predicts the mole fraction of Fe as 1.62% BCC phase at equilibrium (at a weight
percentage of 1.5%). The existence of Fe dissolved in the FCC lattice of the Cu-Ni system is regarded as metastable. Due to the above the activities calculated for Fe in this system are unrealistically high. Further work with the database would be required to improve the calculation.

Equilibrium free energies for FeS at selected temperatures were calculated as:

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>$\Delta G_{FeS}$ (cal/mol)</th>
<th>(Joules)</th>
</tr>
</thead>
<tbody>
<tr>
<td>673</td>
<td>-13812</td>
<td>-57789</td>
</tr>
<tr>
<td>773</td>
<td>-13737</td>
<td>-57475.6</td>
</tr>
<tr>
<td>873</td>
<td>-13661</td>
<td>-57157.6</td>
</tr>
</tbody>
</table>

the equilibrium considered is:

$$Fe + H_2S = FeS + H_2 \quad \Delta G_{FeS} = \Delta G_4 - \Delta G_3/2$$

where the reaction considered is:

$$Fe + \frac{1}{2}S_2 = FeS \quad \Delta G_4 = -35900 + 12.56T$$

$\Delta G_3$ is defined above.

From the equation $\Delta G = -RT \ln k$

where $k = \frac{a(products)}{a(reactants)}$, ($a =$ activity), $R = 8.314$,

$k$ was calculated as:

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>$k$(FeS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>673</td>
<td>30579.7</td>
</tr>
<tr>
<td>773</td>
<td>7655.8</td>
</tr>
<tr>
<td>873</td>
<td>2630.6</td>
</tr>
</tbody>
</table>

The activities (not activity coefficient) calculated using the Transcalc database for the alloy components are given
below. The values obtained for Fe are rather higher than might be expected, reflecting the low solubility of BCC Fe in the FCC CuNi lattice.

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>FCC only</th>
<th>FCC and BCC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>Ni</td>
</tr>
<tr>
<td>673</td>
<td>0.926</td>
<td>0.225</td>
</tr>
<tr>
<td>773</td>
<td>0.921</td>
<td>0.213</td>
</tr>
<tr>
<td>873</td>
<td>0.918</td>
<td>0.204</td>
</tr>
</tbody>
</table>

This data was then used to calculated partial pressure ratios \( \frac{P_{H_2S}}{P_{H_2}} \) for the CuNiFe system.

### Table 3A;2: Hydrogen sulphide/hydrogen partial pressure ratios for CuNiFe (90,8.5,1.5)

<table>
<thead>
<tr>
<th>Temp (K(°C))</th>
<th>673 (400)</th>
<th>773 (500)</th>
<th>873 (600)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta G^o_1 (CuS)^e )</td>
<td>-25736</td>
<td>-25002</td>
<td>-24268</td>
</tr>
<tr>
<td>( \Delta G^o_2 (H_2S)^e )</td>
<td>-24909</td>
<td>-22548</td>
<td>-20187</td>
</tr>
<tr>
<td>( 2\Delta G^o_3 (Ni_3S_2)^e )</td>
<td>-49053</td>
<td>-45153</td>
<td>-41253</td>
</tr>
<tr>
<td>( a_{Cu} )</td>
<td>0.921</td>
<td>0.919</td>
<td>0.917</td>
</tr>
<tr>
<td>( a_{Ni} )</td>
<td>0.432</td>
<td>0.376</td>
<td>0.336</td>
</tr>
<tr>
<td>( \frac{P_{H_2S}}{P_{H_2}} (\times 10^{-5}) )</td>
<td>Cu pure</td>
<td>6.79</td>
<td>17.7</td>
</tr>
<tr>
<td></td>
<td>Ni pure</td>
<td>6.76</td>
<td>38.6</td>
</tr>
<tr>
<td></td>
<td>Fe pure</td>
<td>3.27</td>
<td>13.1</td>
</tr>
<tr>
<td></td>
<td>Cu in the alloy</td>
<td>7.90</td>
<td>20.7</td>
</tr>
<tr>
<td></td>
<td>Ni in the alloy</td>
<td>63.3</td>
<td>392.0</td>
</tr>
<tr>
<td></td>
<td>Fe in the alloy</td>
<td>21.0</td>
<td>25.0</td>
</tr>
<tr>
<td></td>
<td>Cu in the alloy</td>
<td>8.17</td>
<td>21.4</td>
</tr>
<tr>
<td></td>
<td>Ni in the alloy</td>
<td>39.9</td>
<td>276.0</td>
</tr>
<tr>
<td></td>
<td>Fe in the alloy</td>
<td>6.1</td>
<td>20.3</td>
</tr>
</tbody>
</table>
We consider a planar sample doped with radioactive sulphur, so that it contains $^{32}\text{S}$ and in a known proportion $\theta$, which changes with time. The $^{35}\text{S}^*$ atoms are $\beta$ emitters and we assume that those rays emitted perpendicular to the surface are detected. The detected intensity is given by $i_d$

$$i_d = i_0 e^{-\mu x}$$

$i_0$ = intensity of $\beta$ ray on emission from one atom
$e^{-\mu x}$ = adsorption factor, $\mu = 1/\lambda$ (the mean free path of the electron)
$\mu = 0.24 \times 10^{-6} \text{m}^{-1}$ for Cu
$x =$ the depth in the sample of the emitting atom.

The total detected intensity is given by

$$I_d = \Sigma i_d$$

$$= \Sigma i_0 e^{-\mu x}$$

Now $I = \Sigma i_0$

$$= n_s i_0$$

where $n_s =$ the number of atoms of $^{35}\text{S}$ in a slice of volume $\delta x \ A$, where $A$ is the acceptance aperture of the detector.

The mass of that volume $M \ \delta x = \rho \ A \ \delta x$

where $\rho =$ density,

the mass of sulphur in that volume $M_s = S \ \rho \ A \ \delta x$

where $S =$ the solubility of $^{32}\text{S}$ in the metal

thus $n_s = NA@S\rho \delta x / M_s$

where $N = \text{Avagadro's no}$

$\theta = \text{no of } ^{35}\text{S atoms} / \text{no of } ^{32}\text{S atoms}$
This gives \( I_d(x) = \sum i_d \)
\[ = n_s i_0 e^{-\mu x} \]
\[ = K^{32}S \rho \int i_0 e^{-\mu x} \, dx \]
where \( K = \frac{N A \Theta}{M_s} \).
This expression is then integrated from \( x = 0 \) to \( x = D \) to give:
\[ I_d \text{ total} = K^{32}S \rho i_0 \left[ -e^{-\mu x} / \mu \right]^{x=D}_{x=0} \]
when \( x = 0, \ e^{-\mu x} = 1 \)
when \( x = D = \infty \) wrt lambda, then \( e^{-\mu x} = 0 \)
and \( I_d \) (total) = \( K i_0^{32}S \rho / \mu \).
Thus \( ^{32}S \) can be calculated for the standard sample.

To calculate the coverage when monolayers are considered is significantly more simple:
For a monolayer \( x = 0 \)
the intensity detected from an adsorbed layer (\( I_{\text{ads}} \))
\[ I_{\text{ads}} = \sum n_s i_0 \]
where \( n_s' = \frac{N T_{35} A}{M_s} \)
\( T_{35} \) coverage (g/cm2)
thus \( I_{\text{ads}} = K T_{35} i_0 \)
where \( K = \frac{N A \Theta}{M_s} \) \( (\Theta T_{35} = T_{32}) \)
and \( I_{\text{ads}} / I_{\text{dissolved}} = T_{32} \mu / S \rho \)
where \( S = \) solubility of sulphur in the standard
\( \rho = \) density of the standard
Thus \( T_{32} \) can be calculated.
The use of H$_2$S is not to be undertaken lightly. The toxic effects of this gas are well known and its effects can be sudden. Although it is generally detected by the human nose at $\approx 6$ppm, as exposure time increases, sensitivity decreases.

However, not withstanding the above problem the apparatus was set up as shown in the following diagram.

The experimental set-up worked passably well and O$_2$ and H$_2$S could be introduced into the cell separately and without pressurising any joints between the cylinder and the electrochemical cell. The bottles A and B were installed to prevent pressurising the tap valve, and were used to maintain atmospheric pressure in the gas lines, the over-pressure outlets feeding directly into the main wash bottle system (C), a chain of 5 lead acetate bottles of between 1/2 to 1 litre capacity, followed by a water wash bottle and a final lead acetate indicator bottle.

When gas was passed into the cell, lead acetate solution from the first wash bottle in the chain (C) was prevented from entering the glove box by maintaining a small over pressure of argon gas inside the glove box.

The glove box was flushed with argon gas several times before the experiment began. When the H$_2$S gas had been passed and the experiment completed, the cell and glove box were flushed with oxygen and argon respectively to try to
remove any undissolved $\text{H}_2\text{S}$. Any dissolved sulphide species in the electrolyte were precipitated with lead acetate solution inside the electrochemical cell. This deposit was later removed from the cell, and in particular from the gas frit which separated the gas from the electrolyte, by dissolving in sulphuric acid in a fume cupboard. All glass ware was cleaned by soaking in hot solutions of Micro (a surfactant type cleaner) for several hours and rinsed thoroughly.
The purpose of this final chapter is to tie together the salient points of the preceding chapters, and to make suggestions for further work.

The first chapter surveyed the role of sulphur in corrosion and showed how both basic and sophisticated analytical techniques are used, ranging from a simple test of acid droplets onto an unknown corrosion product - $\text{H}_2\text{S}$ will be released if a sulphide is present - to the more complex modelling of the changes in valence band energy levels on adsorption of a sulphur atom onto a single crystal.

The study of the role of sulphur in corrosion is pertinent to its role as a monolayer, and the important consequences the latter can have for corrosion mechanisms. In particular, emphasis was laid on the need to characterise the action of sulphur in a monolayer with a view to anticipating potential problems in new semi-conductor and magnetic devices and also in the developing field of metal matrix composites. In these cases the interfaces are of critical importance for the materials' performance. Even trace amounts of sulphur in an environment can give rise to a monolayer at an interface.

In order to characterise the sulphur in its various chemical compounds and as a monolayer, the surface analytical technique X-ray Photoelectron Spectroscopy (XPS)
was used.

Chapter 2 shows how a monochromated silver X-ray source may be used in this regard. The principle behind the characterisation was that of monitoring changes in extra-atomic relaxation energy for a series of sulphur compounds with the same formal valency, in this case - sulphides and sulphates. The data were also compared with other data from the literature for gaseous and organic sulphur compounds, the latter showing generally positive formal valencies for sulphur. This has enabled a set of criteria to be established for the use of extra-atomic relaxation energy values, both relatively, $\Delta R_{\text{D}}^{\text{ea}}(1s)$ with respect to $\Delta R_{\text{D}}^{\text{ea}}(2p)$ and for the ratio of the two values, which indicates the likely formal valency of sulphur in the compound. In certain cases the type of nearest neighbour may also be deduced. Correlation with inter-ionic anion-cation distance and molar polarizability give further help in identification.

In the light of these results work was undertaken to investigate the corrosion of CuNi(90,10) which may be stimulated by deaeration of sea-water. This work is reported in Chapter 3.

The stimulated corrosion appeared to be accompanied by pick-up of sulphur, and in well corroded samples a sulphide has been identified by X-ray diffraction. The initial deaeration of sea-water was known to give rise to an acceleration of the cathodic reaction, and it was thought that this might be due to the pick-up of sulphur from
solution.

To investigate this two approaches were used:

1) The deposition and electrochemical monitoring of sulphur monolayers on CuNi (90,10).

2) The electrochemical monitoring and surface analysis of a sample of CuNi (90,10) exposed to a stream of \( \text{H}_2\text{S} \). Alternative sources of sulphur were not successful.

The results from the first approach using sulphur deposited from the gas phase onto clean CuNi (90,10) showed a slight inhibition of the oxygen reduction cathodic reaction at \(-300\text{mV vs SCE}\); cycling about the corrosion potential showed no definite stimulation of corrosion.

Using \( \text{H}_2\text{S} \) however, corrosion was quickly observed after a short induction period as a stimulation of the cathodic reaction followed by stimulation of the anodic reaction, since a loosely adherent, black copper sulphide was formed after longer exposure. The blackening of the sample was preceded by an increase in the cathodic reaction. Since neither the deposition of a monolayer nor the formation of a bulk sulphide, \( \text{Cu}_2\text{S} \), are electrochemical reactions, the rise in the cathodic reaction was interpreted as the catalytic stimulation of the oxygen reduction cathodic reaction. As the partial pressures of \( \text{HS}^- \) and \( \text{H}_2\text{S} \) rose in the solution the sulphide was formed and the anodic reaction accelerated as the corrosion potential fell to a
more negative value.

Surface analysis results from the sample taken out of solution during the rise in cathodic current density, but before the blackening of the sample, indicated that sulphur was present, probably as a sulphide. However, the lowering of the Auger parameter from that for a monolayer, by bound water/hydration is not ruled out.

Semi-quantitative surface analysis results for the metal/sulphur ratio are in good agreement with prepared standards of sulphur monlayers on the alloy.

Thus this work, with the enormous help afforded by the use of radio-tracer techniques, has confirmed that corrosion of CuNi(90,10) by stimulation of the cathodic reaction, occurs in the presence of a sulphur monolayer, adsorbed from solution. However, stimulation is not found for the monolayer deposited from the gas phase on the clean alloy surface.
We have shown that sulphur is a very important element in corrosion in many different materials and environments, especially in the monolayer state. The growing importance of interface control and characterisation in modern materials technology presents a need for surface analytical methods for the characterisation of the chemical state of sulphur.

We have further shown how high energy XPS fulfills this need. When used to its full capabilities valence state and nearest neighbour character in sulphides, sulphates and gaseous sulphides can be distinguished by evaluation of extra-atomic relaxation energies. In particular cases, principally sulphides, good agreement was shown between extra-atomic relaxation energy and inter-ionic distance.

We have examined, in particular, the role of sulphur in the corrosion of CuNi (90,10), using a monolayer of sulphur deposited from the gas phase and adsorbed from H₂S-dosed chloride solution. The stimulation of the cathodic reaction, oxygen reduction, occurs in the presence of approximately a monolayer of sulphur adsorbed from H₂S in solution, but not in the presence of the gas phase deposited monolayer of sulphur onto clean samples.

We find that the chemical state of sulphur on the cathodically stimulated surface is similar to that of a sulphide, although it is acknowledged that further work is
required to distinguish the sulphur monolayer in the presence of bound water from a sulphide.
SUGGESTIONS FOR FUTURE WORK

1) In conjunction with thermal balance techniques the effect of adsorbed and crystallised water on the Auger parameter and the extra-atomic relaxation parameters should be investigated.

2) The prospects for further examination of extra-atomic relaxation energy are particularly good for sulphur, because it can adopt such a variety of valence states, and participate in many types of bonding in both inorganic and organic compounds. It is suggested that future work should include consideration of the valence band information and molecular orbital calculations where necessary.

3) Further investigation of the role of sulphur in the corrosion of CuNi(90,10) should consider the use of controlled \( \text{H}_2\text{S} \) addition, so that the amount required to stimulate the cathodic reaction may be identified. Similar experiments on pre-tarnished samples (at different anodic potentials) will permit examination of the role of the alloying elements, Ni and Fe, at different relative concentrations, in enhancing the catalytic effect.

4) The deposition of monolayers of sulphur onto the tarnish film is also suggested in order to explore further the role of sulphur in corrosion of CuNi.
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