

A Short Course of Rust

Pupil Research Brief

Teachers' Notes

Syllabus Coverage Subject Knowledge and Understanding

- some compounds are made of ions. The ions are formed when atoms of one element gain electrons from, or lose electrons to, the atoms of another element
- the atoms which lose electrons become positively charged ions and the atoms which gain electrons become negatively charged ions
- some metals are more reactive than others



Route through the Brief

- by observing how various metals react, a reactivity series can be produced. This is a list with the most reactive metal at the top
- a more reactive metal can replace a less reactive metal from its compounds
- when they are dissolved in water, ionic compounds conduct electricity because the ions are free to move
- the current is due to negatively charged ions moving to the positive terminal (electrode) and positively charged ions moving to the negative electrode
- at the negative electrode positively charged ions gain electrons (reduction), and at the positive electrode negatively charged ions lose electrons (oxidation)

Introduction

Corrosion is a multidisciplinary engineering science. Professional corrosion engineers require a knowledge of metallurgy (i.e. alloying metals), polymer science (i.e organic paints and coatings), ceramics (i.e. concrete), biology (i.e. microbial corrosion), physical chemistry (i.e. electrochemistry), microscopy and analytical techniques (i.e. for analysis of failures). Corrosion is thus both something we all come across daily and yet many aspects are too complex and specialised to teach in school. However, the study of corrosion can be stimulating, fun and practical, and at a fairly basic level it can be a good context for introducing some key scientific concepts. Furthermore, corrosion is a major problem and a costly one! This is all the more reason why we need to understand the process and perhaps more importantly, how we can control or indeed, prevent it. Pupils, therefore, should be aware of this and appreciate its impact on the economy and their own lives. The Brief is based on work carried out at the Corrosion and Protection Centre, UMIST.

This PRB focuses on pipeline corrosion and protection which is a field where there is a great diversity of current research taking place. This includes, for

example: research into the barrier properties and adhesive properties of organic tar epoxy and polythene tape coatings used to protect gas and oil pipelines; the use of voltage mapping techniques over the surface of buried pipelines under cathodic protection, to determine defects in pipe coatings; comparisons of the performance of zinc and aluminium sacrificial anodes used in buried land and offshore pipelines and structures; and the causes and effects of stray current corrosion arising from the stray currents produced, for example, by the Manchester Metrolink which interfere with the cathodic protection systems of nearby buried gas and water pipelines.

The PRB is designed to teach basic electrochemistry by experiment in the practical context of corrosion control. The background to the PRB lies in a common situation often encountered i.e training of overseas company personnel in aspects of corrosion relevant to their industry (in this case, the oil and gas industry). Companies frequently hire external experts for 'short course' training programmes. Hence the pupils are asked to imagine that they are members of the Short Courses Team at the Corrosion and Protection Centre, North Western University, who are asked to evaluate a training programme for Middle Eastern Oil Company engineers in Dubai on the corrosion and protection of buried pipelines. The Short Courses Organiser has asked the team to work through the activities themselves, checking experiments and questions and providing specimen results and worked answers. They are also required to consider the pre-course background reading material and suggest questions to accompany the reading. Also, additional practical exercises are included which are more advanced and would be suitable as optional extension work for higher-achieving pupils.

Clearly some of the experiments are demanding and more suitable for higher-achieving pupils. However, experiments such as 1, 3 and 4 along with key sections of the Pre-course background reading offer a less demanding route through the Brief.

Experimental and investigative skills

- planning experimental procedures
- obtaining evidence
- analysing evidence and drawing conclusions
- evaluating evidence

Prior knowledge

Pupils should be familiar with simple atomic theory, the formation of ions and a basic knowledge of ionic equations. They should also have a very basic knowledge of pH and pH indicators. A knowledge of the terms voltage, current, resistor, resistance, and conductivity and Ohm's law is required.

Running the Brief

Pupil grouping

Pupils could work in a number of groupings during this Brief. Suggestions are:

Initial briefing	-	whole class; teacher-led introduction
Introductory memo	-	groups of 2-4
Analysis of pre- course background reading material	-	tackled by all pupils in groups of 2-4
Practical activities	-	groups could tackle Experiments 1, 4 and 5, with 2 and 3 done by higher-achieving pupils, although, if time is available groups could do the first five experiments. Otherwise groups could tackle different experiments and report back to whole class
Analysing data, providing specimen results and answers	-	individuals, pairs or teams
Communication	-	individuals, if written reports assessed, otherwise pairs or groups
<i>Optional extension</i> <i>Experiments 6 and 7</i>	-	small groups of 2-4

Timing

The PRB should take about 5 hours of teaching time if all activities are undertaken. The pre-course reading could be given as a homework exercise. Less time would be needed if different groups tackled different experiments and reported back in a plenary or poster session. Optional extension experiments may add 2 to 3 hours or more, particularly if used as a project.

Activities

Pupils should be issued with the Study Guide, which provides them with a summary of what they should produce as they work through the Brief. It can also be used as a checklist so that they can monitor their own progress.

The PRB is not a role play. Rather, pupils are presented with a realistic scenario in the form of a memo from the Short Courses Organiser (SCO) at a university Corrosion and Protection Centre. This is accompanied by draft teaching materials for a 4-day short course for Middle Eastern Oil Company engineers in Dubai. It includes pre-course background reading materials and a set of seven experiments. Pupils work as the Short Courses Team who will be teaching the course in Dubai. The SCO has outlined in her memo what she would like her team to do, i.e. carry out the experiments themselves to check they work well, that instructions are clear and key teaching/learning points are identified. They are also asked to provide specimen results and worked answers and any suggestions for improvements. They should keep their notes to use at a whole class de-briefing session or at an informal session with the SCO (the teacher).

It is worth spending a little time at the start to set the scene (see Introduction at the beginning of the teachers' notes). Then acting as the Short Courses Organiser give out the Memo and the Draft Materials for the course. It is suggested all pupils tackle Experiments 1, 4 and 5. Experiments 2 and 3 are more demanding and should be used at the teacher's discretion. Experiments 6 and 7 are more suitable for higher-achieving pupils, particularly for optional extension/project work or for teacher demonstration. These experiments demonstrate how pipelines are protected by cathodic protection (sacrificial anodes and impressed current protection) and how corrosion engineers actually monitor the corrosion/condition of buried pipes. Pupils should be given the appropriate sheets depending on which experiments they are to tackle.

The Pre-Course Background Reading Material is used to give the pupils some background theory on electrochemical cells and the corrosion process. It also explains how corrosion occurs on a single piece of steel with two reactions happening at the same time. Although not required by the syllabus, it does explain how an electrochemical cell can be set up within a single piece of steel without the need for two separate and distinct electrodes. (This phenomenon is illustrated in Experiment 2). However, with a bit of cutting and pasting this section could be removed so that pupils are not given the explanation for Experiment 2 in advance. A little information is also given on the costs of corrosion, (scaled up by a factor of 10 to estimated 1997 levels) produced by the last major survey reported by the Hoar Committee in 1971. We have also provided some background on corrosion protection methods and some interesting information on bacterial corrosion of underground pipelines in the absence of air (anaerobic corrosion), which causes at least 50% of the leakages from

buried pipes - not in the syllabus but fascinating nevertheless! Pupils could work in their groups of 2-4, interrogating the reading material, summarising the key learning points and suggesting some suitable questions for the "course participants". Some of the readings are extracts from the actual research papers. Pupils can next work through the **Practical Activities**, carrying out the experiments and activities outlined in the memo. The time available and the prior knowledge and abilities of the pupils will determine the selection of activities. Pupils should make notes on their work and be prepared to give a debriefing to the teacher (as SCO) and possibly the whole class.

Investigation details

Experiment 1. Given that pupils are already likely to know that both oxygen and water are necessary for steel to rust, they are asked to design an investigation to demonstrate this. If they are familiar with the investigation you may decide to use this simply as reinforcement. You may also want the pupils to actually carry out the investigation.

Experiment 2. Although very simple to carry out, the explanation of the results will be difficult for some pupils. This could be an optional activity or a teacher demonstration.

In all cases corrosion is due to differential aeration cells.

The pH rises at the edge of the droplet due to the cathodic process of oxygen reduction and the formation of OH⁻ (phenolphthalein turns pink). This occurs at the edge because air access is easy there:

The anodic process of metal dissolution (i.e corrosion) occurs only at the centre of the droplet where air access is more difficult. The indicator turns blue at the droplet centre:

Between the two regions a brown ring of iron hydroxide (FeO(OH) - rust) can sometimes be seen. This is due to reaction of Fe^{2+} diffusing from the droplet centre with OH⁻ diffusing from the droplet edges (and further reaction with oxygen) to give:

$$Fe^{2+} + 2OH^{-} \longrightarrow Fe(OH)_{2}$$

2Fe(OH)² + ¹/₂O₂ \longrightarrow 2FeO(OH) + H₂O

Experiment 3. This is an interesting activity not usually found in school textbooks. It certainly illustrates how painting slows down corrosion but also how corrosion occurs in areas where paint coating is damaged.

Painting is the most common method of corrosion control. Generally, paints function not by keeping water or oxygen from the metal surface (most paints are, in fact, very permeable) but by interposing a path of high electrical resistance between the metal and the environment. Since corrosion cannot continue unless ions move, it slows down the corrosion rate.

The electrical resistance of a paint to the flow of current between the solution and the metal in contact with the solution can be determined by measuring the current flowing. Where there is a defect in the paint, the current will flow via this route. Hence, for the same total surface area, but different size defects, the current flowing at a fixed applied potential will be approximately proportional to the defect area. In practise, defects in paints are initially microscopic and subsequently grow; more sophisticated electrochemical techniques can follow these changes to assess paint performance.

The current increases in approximate proportion to the defect size. Problems may arise where the edges are not properly shielded by tape or where the connection is accidentally immersed. An additional source of uncertainty lies in the fact that it is difficult to define accurately the abraded defect area. Finally, the currents may be rather small in some cases so that inaccuracy of electrical measurement with small defect areas may be a problem. It may be useful to plot a composite set of results for all the class to show the trend more clearly.

Experiment 4. This is a standard experiment to illustrate the reactivity series of metals. If pupils are already familiar with this activity you may decide to use it simply as reinforcement.

This experiment demonstrates construction of the reactivity series for metals in two different solutions. It is likely that the measured voltages will not be stable with time. This is intrinsic to the experiment and voltages should always be measured after a period of immersion of at least 5 minutes. Excessive instabilities are usually caused by poor cleaning of the metal before immersion.

The absolute value of voltages will vary, so there is little point reproducing them here. The order of reactivity is generally:

copper < iron < zinc < magnesium

For more able pupils it might be useful to compare the values obtained with those predicted from standard reduction potentials:

Cu/Cu ²⁺	E° = + 0.34 V (hydrogen scale)
Fe/Fe ²⁺	E° = -0.45 V
Zn/Zn ²⁺	$E^{\circ} = -0.76 V$
Mg/Mg ²⁺	E° = - 2.34 V

The main reason why values predicted from the electrochemical series (theory) are different from those measured in practice (galvanic series) is, of course, that during corrosion the metal ion concentration is very far from the standard state of 1 Molar.

Experiment 5. This is an idea suggested by the Short Courses Organiser who wants the team to develop it. Pupils are therefore required to carry out an experiment to compare the effectiveness of zinc and magnesium as sacrificial anodes in the cathodic protection of steel. Solutions which simulate the electrical conductivity of soils are required (details given in Experiment 6) along with readily available materials and apparatus suggested in the experiment sheet.

Both zinc and magnesium are used commercially as sacrificial anodes. Magnesium will give a bigger voltage leading to higher current in soils of high electrical resistance. Zinc is used in soils of low resistance.

Experiment 6. This is a fairly advanced experiment, more suitable for extension/project work. One group could investigate electrolyte A and another electrolyte B. Alternatively, it could be done as a teacher demonstration.

The activity demonstrates how steel can be protected electrically underground; either by an active anode (e.g. zinc), or by another anode and an external voltage supply (e.g. steel anode and 1.5V battery). The method is generically known as "cathodic protection" (CP) because the protected structure is made the cathode during operation. CP can be applied using two approaches: *sacrificial protection*, commonly using zinc, aluminium or magnesium alloy anodes; or *impressed current protection* using special alloy anodes with very low corrosion rates (e.g. silicon iron, platinised titanium) and an external voltage supply.

The measurement uses a reference electrode to monitor the electrochemical potential of the protected steel and how this varies with distance from the anode and also with electrolyte conductivity. Details for making up a reference electrode, if necessary, are given as part of the experimental details.

The measured voltage (strictly potential) between the protected steel and the reference electrode should diminish in absolute value with increasing distance from the anode end. If the correct polarity is used then the steel will be negative with respect to the reference electrode, thus the electrochemical potential will increase (or become less negative) with increasing distance from the anode. This will be the other way round if the polarity of connections is reversed. The potential between the steel and the copper/copper sulphate reference electrode will typically be about -0.8V which will decrease to about -1.1V when connected to the anode (perhaps a bit more negative using the steel anode and 1.5V cell).

As the solution becomes less conductive, the measured potential change with distance will increase.

It is suggested that magnesium could be used as an anode instead of steel and a 1.5V battery. Pupils could compare and comment on their results from the zinc and magnesium anodes.

Answers to Questions

1. Cathodic protection can be used to protect any metal in any environment provided the correct anode materials or impressed voltage is used. CP is used widely to protect buried structures and in all marine environments.

2. The method will absolutely not work without an electrolyte!

3. If the electrolyte conductivity is poor many anodes are needed, anodes need replacing and, if impressed current is used, there is a continuous consumption of electrical power.

4. The zinc anode will dissolve with time. Its weight could be measured to check this but make sure to remove all adherent corrosion product first.

5. Painting or coating the steel. Some might say galvanising, which is of course, a zinc coating.

6. There is indeed a current flowing, it could be calculated by measuring the voltage across the 10hm resistor and using Ohm's law. The rate of corrosion of

the zinc anode can be calculated from the current using Faraday's law.

7. Voltage (and therefore current) decreases as the distance from the anode increases. The effectiveness of the anode to protect the steel bar from corrosion decreases therefore with distance along the steel bar.

8. Anodes should be placed at regular intervals along the steel pipeline. The voltage should be monitored at intervals along the pipeline and where necessary anodes replaced.

Experiment 7. Like Experiment 6 this is also more suitable for extension/project work. It could be done as a teacher demonstration. The reference electrode is required. In industry, monitoring of buried pipelines is regularly carried out at ground level. Semi-automatic equipment has been developed to log the values of potential. However, the method is still dependent on people "walking the line" taking regular measurements, sometimes as frequently as every metre.

This experiment could be omitted as it is essentially an extension of Experiment 3. However, useful additional information is transferred, and also a decent longer-term test can be set up. The surface potential should be the most negative above the anode, an intermediate value above the defect and least negative above the intact paint.

Trial and error might be required in order to find the size of defect and depth of burial at which the method works.

Over the longer term, the zinc anode should lose significant mass. Thus, reweighing after the completion of the experiment should give the mass loss and hence corrosion rate. If this is done, it is important to remove all corrosion product, otherwise a false reading results.

Organic coatings, i.e. paints, are unable to withstand the alkali generated adjacent to bare metal defects (it acts as paint stripper!). Thus, after the long-term test, the paint may be blistered and poorly adherent close to the edge of the defect. If the sand near the defect is removed carefully, its pH can be checked, it will be alkaline.

Technical details

Necessary experimental details, apparatus and equipment are given in the experimental sheets themselves. The following pointers are worth bearing in mind.

For *Experiment 2*, cleanliness is very important. The metal strips must be degreased and free of any oxide (thoroughly abraded). Also, the droplet must not be too spread out - it should be quite convex. Size of droplet is not important - although if it is too small the changes will be hard to see. If these conditions hold the experiment works well.

For *Experiment 3*, thin pre-painted steel can be obtained from many places, e.g. DIY stores and Motor Shops.

For *Experiment 6*, although the reference electrodes are quite easy and cheap to make they are probably best prepared well in advance of the activity. Plastic tubes are better as they do not break. Any softwood can be used as a porous plug - better still if it can be machined or sanded to a point. It should be soaked for about 1 week in the sodium chloride solution. Alternatively, commercial silver/silver chloride electrodes can be used, although they can be quite expensive. Any flat, fairly shallow container is fine, e.g. photographic paper developing trays.

It is advised that *Experiment 7* be tested out first as the results are particularly dependent on the quality and conductivity of the builders sand and in some cases there might be insufficient surface variation in potential to measure.

One frequent reason for failure is that the sand is too dry. It should be kept significantly damp and not allowed to dry out. The damp conductivity of the sand may also be altered by washing in tap water (to reduce it) or 0.1M sodium chloride solution (to increase it). Backfill mixture is salt, fine sand, powdered graphite and water in the approximate proportions 2:2:2:1. This represents 'reality' where a more conductive and salty region is *deliberately* placed near the anode. It also seems to help the lab experiment.The experiment seems to work best if a large tank or tray is used, such as a fish tank.

Safety issues

PLEASE NOTE: It is also important that you prepare your own risk assessments for the practical work in this Brief in the usual way.

Calcium Chloride Irritant.

If swallowed wash mouth and give water to drink. Seek medical attention as soon as possible. If in eyes flood eye with flowing tap water for at least 10 minutes. Seek medical attention as soon as possible. If on skin flood area with water. Remove contaminated clothing.

Wear eye protection.

Sulphuric Acid (1M) Irritant.

If swallowed wash mouth and give water to drink. Do NOT make the person vomit. Seek medical attention as soon as possible. If in eyes flood eye with flowing tap water for at least 10 minutes. Seek medical attention. If on skin flood area with water. Remove contaminated clothing. If skin blistered or large area affected, seek medical attention.

Wear eye protection.

Potassium Ferricyanide Minimal hazard. If swallowed wash mouth and give water to drink. Seek medical attention. If in eye flood eye with flowing tap water for at least 10 minutes. Seek medical attention. If on skin flood area with water. Remove contaminated clothing.

Wear eye protection.

Phenolphthalein solution Minimal hazard.If swallowed wash mouth and give water to drink.Seek medical attention as soon as possible.If in eyes flood eye with flowing tap water for at least 10 minutes. Seek medical attention.If on skin flood area with water and wash with soap and water. Remove contaminated clothing.

Wear eye protection.

Magnesium (strip) Highly Flammable. If swallowed wash mouth and give water to drink. Seek medical attention especially if diarrhoea results.

Copper Sulphate Solution Poisonous.

If swallowed wash mouth and give water to drink. Seek medical attention.

If in eyes flood eye with flowing tap water for at least 10 minutes. Seek medical attention.

Assessment issues for *Experimental and Investigative Science* (National Curriculum for England and Wales)

PPlanningOObtaining evidenceAAnalysing evidenceEEvaluating evidence

There are a number of possible investigations in this Brief. Each of the practical activities (Experiments 1 to 7) is fairly prescriptive. However, a number of investigative opportunities are suggested, often in the supplementary questions at the end of the instructions for carrying out the experiment (see Experiments 1, 5 and 7). Obviously where methods are set out for pupils to follow, **Skill Areas P** and **O**

will not be assessable. However, teachers will find opportunities to assess **Skill Areas A** and **E**. Pupils should have opportunities to achieve high marks, particularly where a high level of subject knowledge has to be used to interpret the results. The introductory memo asks pupils to try out the various experiments to see if they work and to identify any problems which might arise, and also to make changes to any of the activities (experiments and supplementary questions) where necessary, as a result of their 'trialling'. This should provide ample opportunity to assess **Skill Area E**.

Possible investigations following on from Experiments 1, 5 and 7 should provide pupils with opportunites to achieve high marks in all skill areas.

Assessment issues for *Experimental and Investigative Science* (Northern Ireland Curriculum)

P Planning O Obtaining evidenceI Interpreting and Evaluating

See notes for England and Wales. Refrence to Skill Areas A and E will apply to the single Skill Area I in Northern Ireland syllabuses.

Scottish syllabus coverage

Standard Grade Chemistry - Corrosion

Further pupil research opportunities

Experiments 6 and 7 offer scope for further research. In Experiment 7 in particular, a long-term investigation is suggested. Pupils can be encouraged to research the literature for themselves. There are a number of general textbooks on corrosion science and engineering and although usually aimed at advanced work parts of them can be accessible; e.g:

Corrosion for Science and Engineering - 2nd Ed, KR Tretheway, J. Chamberlain. pub. Longman, 1995.

Corrosion Science: an Experimental Approach, E Heitz, R Henkhams, A .Rahmel, pub. Ellis - Horwood (Simon and Schuster) 1992.

The major author of this PRB, Dr Stuart Lyon, is a senior lecturer at the Corrosion and Protection Centre, University of Manchester Institute of Science and Technology. Much information about the

Centre's work of relevance to this PRB is available on the Internet at:

http://www.cp.umist.ac.uk/CPC/

Additional Demonstrations/Investigations

All demonstrations use the same indicator solution used in Experiment 2. This should be gelled by dissolving about 5g agar per 100ml in hot solution. All experiments should be prepared at least 1 hour before observations - they can usually be kept for up to 48 hours.

1. Clean steel nail in petri dish. Place nail head on side of dish (so that it is angled inside dish) and add indicator solution. When set, pink colouration appears near where the head is exposed to the air, blue colouration appears at base of dish.

2. Half-galvanised nail in petri dish. Dissolve the zinc coating from about one-half of the length of the nail in dilute acid. Wash and dry. Place nail flat on base of petri dish and add indicator solution. When set, pink colouration appears on the bare steel section. There is no blue colouration (the iron is protected by zinc dissolving which may give a white colouration).

3. Attach insulated wires to two steel nails. Place one nail at the base of a measuring cylinder or other tall vessel, suspend the other nail near the top. Fill the vessel with solution. When set, connect the two nails via an milliammeter which will eventually record a current of a few mA.. The bottom nail will become the anode and corrode (blue colouration) while the top one will become the cathode (pink colouration). Note that the cathode does not corrode! Note also the polarity of current flow (or size of the emf) between the two nails.

4. A variant of (3) has the two nails at the same height in the tall vessel whereupon there should be no current recorded (or very little).

An article by Stuart Lyon in the first edition of the PRI pupil journal *PRISM*, entitled *Corrosion of Steel Reinforcement in Concrete* would make interesting background reading. Questions could be set on the content of the article and would make a useful extension activity.