

REVISED

NUFFIELD CHEMISTRY OPTIONS

File
Option 6
CHANGE AND
DECAY

Published for the Nuffield Foundation by Longman Group Limited



A 620.11223 DIL

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Acknowledgements

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The drawing in figure 18 is based on Jedrzejewska, H. (1970) *New York Conference on conservation of stone and wooden objects*. International Institute for Conservation. Volume 1, page 19.

Design and art direction by Ivan and Robin Dodd

Printed in Great Britain by Longman Resources Unit, York

Longman Group Limited

ASSOCIATED COMPANIES, BRANCHES, AND REPRESENTATIVES
THROUGHOUT THE WORLD

First published 1968

Revised edition first published 1976

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CORD 1

INTRODUCTION

This Option sets out to give you an idea of some of the problems caused by stone decay and metallic corrosion. By imitating some of the reactions involved, it also tries to explain the chemistry of these processes and some of the methods that are used to prevent them. As you study the Option you should try to relate your own experimental observations to what is happening to the stone and metal buildings and objects you see all around you every day.

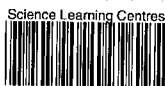
How to use this book

This book is intended to form a self-contained course, giving enough instructions for experiments, background information, and explanations to allow you to work through it almost on your own. A few of the experiments are suitable for you to carry out, or to extend, at home. If you find any of the ideas difficult, though, do not hesitate to ask your teacher for help.

You will see that there are several questions in the text. You should answer these as you come to them, in writing. Your first answer may not always be right but you will learn more if you stop and think and put your ideas down on paper — even if you change them later.

The names used for the acids and salts in this booklet are the common, current names. If you go on to more advanced chemistry courses you may meet the systematic names which are increasingly being adopted by chemists. Some examples of the two types of name are given below.

Common name	Systematic name
sulphurous acid	sulphuric(IV) acid
sulphite	sulphate(IV)
sulphuric acid	sulphuric(VI) acid
sulphate	sulphate(VI)
nitrous acid	nitric(III) acid
nitrite	nitrate(III)
nitric acid	nitric(V) acid
nitrate	nitrate(V)

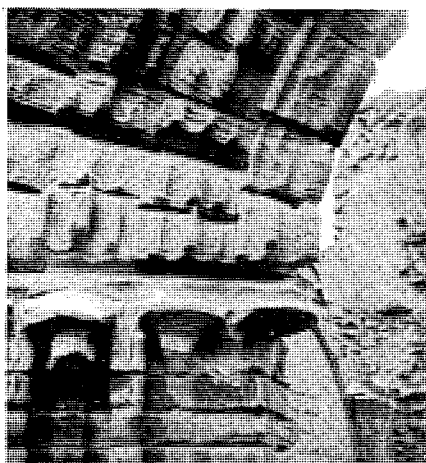


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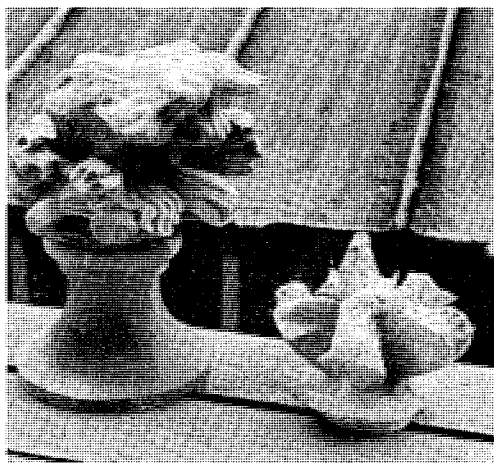
Section 1

THE DECAY OF STONEMWORK

Historic buildings such as churches are our link with the past and help to give us a sense of permanence. Yet, if we look closely, we see structures which, in some cases, are decaying at an alarming rate. When stonework decays, a building may lose much of its beautiful carved masonry. But besides this, its whole structure may be weakened.



a



b



c

figure 1

Some examples of stone decay in beautiful structures.

a. Crystallization damage caused by wind-borne sea salt, in Furness Abbey.

b. The decayed Portland stone sculpture, beside the one replacing it at St Paul's Cathedral, shows how much damage can take place in less than three hundred years.

c. A decayed sculpture from the Sheldonian Theatre, Oxford. It is undergoing a preservative trial and has been immersed in molten wax.

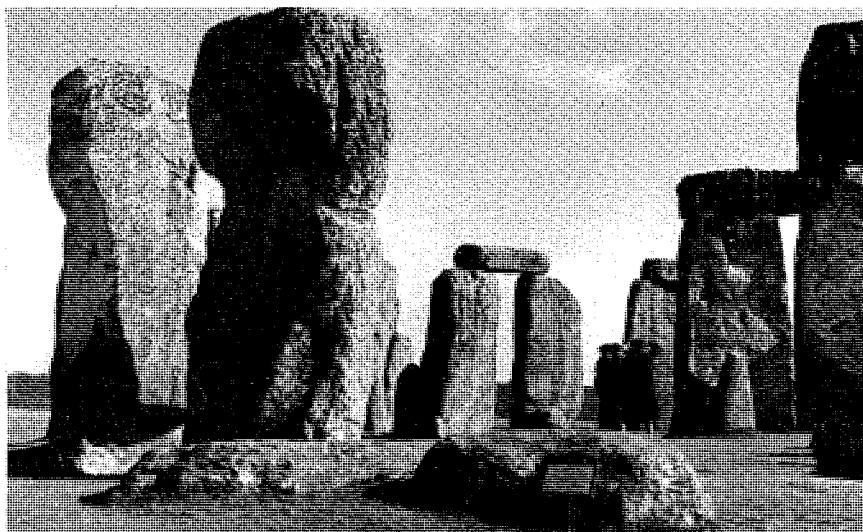
What evidence is there of stone decay in your area? What do you think causes stone to decay?

The decay of stone can result from chemical or physical processes. Chemical reactions involve interactions between chemicals in the atmosphere and the surface of the stone. To understand these reactions we must investigate the chemical nature of the reactants. Physical processes generally occur inside the stone and the extent of decay depends on the physical structure of the stone.

Before beginning sub-section 1.1 you need to set up a long-term experiment. This is Experiment 1.4a, part A, which will illustrate one of the physical processes of decay which occur in stone. The instructions will be found on page 16.

figure 2

Can you suggest why some structures, such as Stonehenge, have stood for thousands of years with only the slightest signs of decay?



1.1 The air and air pollution

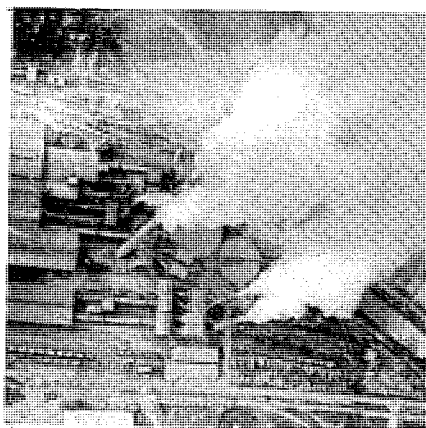
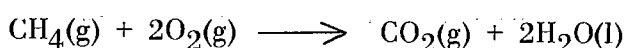


figure 3
Air pollution spreading from a cement works at West Thurrock.

'Pure, dry' air, which consists of nitrogen, oxygen, inert gases, and minor concentrations of gases such as carbon dioxide, offers very little threat to stonework. However, natural air of this composition exists in very few areas of the world. Can you suggest where it does exist? Normal air contains water vapour and this is enough to give air slight corrosive properties.

In heavily industrialized countries the atmosphere can become polluted by the introduction of gases and other materials which natural processes cannot remove. It might be said that man began to pollute the air when he first used fire for warmth and cooking.

When fuels burn, they use oxygen and replace it with less desirable substances. Fuels such as coal, oil, and gas contain carbon and hydrogen and so they produce carbon dioxide and water during combustion. Every tonne of coal can produce over 3 tonnes of carbon dioxide!



(Read Chapter 5 of *Chemists in the world* for more details of the nature and uses of coal, gas, and oil.)

However, there is a natural balance between oxygen and carbon dioxide. Plants use carbon dioxide and produce oxygen. Despite this, you can imagine that in heavily industrialized areas the carbon dioxide concentration may rise well above the average at certain times of the day.

Coal and oil contain sulphur compounds. The combustion of these fuels leads to the production of levels of sulphur dioxide (SO_2) which cannot be dealt with by natural processes. Sulphur dioxide is regarded as the major gaseous pollutant of the atmosphere and has detrimental effects on health, on plants, and on buildings.

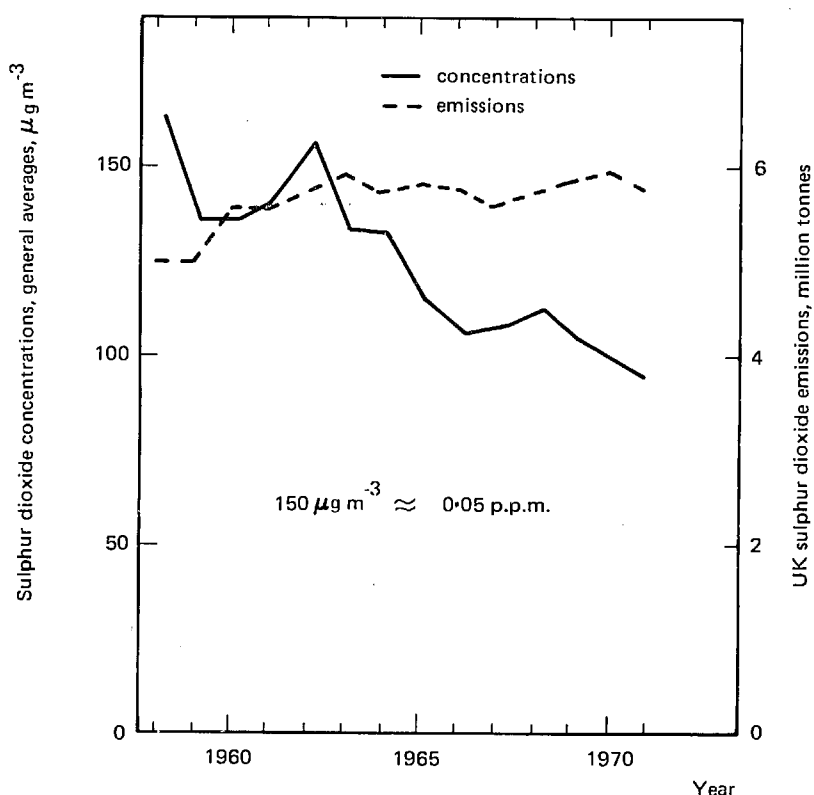
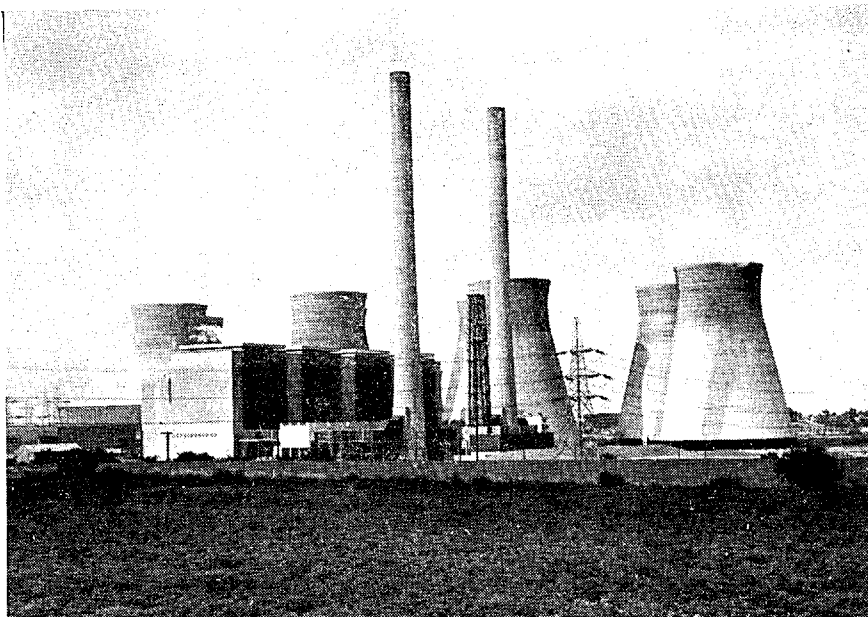


figure 4
A graph indicating trends between 1958 and 1971 in the amount of sulphur dioxide emitted and its urban concentration, in the United Kingdom. What are the main conclusions which can be drawn from the graph? Suggest how this partial success has been achieved. How could it be improved?

figure 5

The use of high stacks has helped to reduce the sulphur dioxide concentration at ground level. How? The picture shows one building where this course has been adopted. It is the Central Electricity Generating Board's 2000-megawatt, coal-fired, 'C' power station at Ferrybridge.



The combustion of petrol in motor vehicles produces nitrogen oxides (nitrogen oxide, NO, and nitrogen dioxide, NO₂). These present a pollution problem in congested cities. However, the total emission of nitrogen oxides is about 20% that of sulphur dioxide.



figure 6

Car exhausts are the main source of nitrogen oxide pollution in cities.

Hydrogen chloride (HCl) pollution can arise from the combustion of solid fuels. Small concentrations of the gas may be present in the air near solid fuel power stations and chemical works. If you study Option 5, *Plastics*, you will investigate the production of hydrogen chloride gas during the incineration of waste materials containing PVC.

Clearly, the extent of air pollution varies according to area. Around chemical works, power stations, or city centres, the local pollution problems may be completely different from the general situation.

The major gaseous pollutants are:

sulphur dioxide, SO₂(g)
nitrogen dioxide, NO₂(g)
nitrogen oxide, NO(g)
hydrogen chloride, HCl(g)
carbon dioxide, CO₂(g)

Find out their physical characteristics. How are they detected and recognized?

Use a data book to find the solubility of the gases in water, compared with that of oxygen and nitrogen. What is the effect of temperature on the solubility of gases? How might the relative solubilities of gases be demonstrated?

The polluting gases SO₂, NO₂, and HCl are extremely soluble in water; carbon dioxide is fairly soluble. Water vapour in the air can thus freely absorb these gases. Rain is most probably saturated with carbon dioxide and, in heavily polluted areas, may contain quite high concentrations of other gases.

Experiment 1.1a

Investigating the properties of solutions of CO_2 , SO_2 , NO_2 , and HCl

Record your observations in a table like this:

Test	Boiled distilled water	0.05M CO_2 solution	0.05M SO_2 solution	0.1M NO_2 solution	0.1M HCl solution	0.5M HCl solution
effect on indicator paper						
effect on magnesium						
effect on CaCO_3						

table 1

You will need:

6 test-tubes, 125 x 16 mm

Test-tube rack

Conical flask, 100 cm^3

Carbon dioxide generator

Tapers

Dropping pipette

Narrow range pH paper
(pH 1–4.5, 4.5–7.5)

Marble chips

Magnesium turnings

Calcium carbonate powder

Freshly boiled, distilled water

Limewater

Saturated CO_2 solution (0.05M)

0.05M SO_2 solution

0.1M NO_2 solution

0.1M HCl solution

0.5M HCl solution

Effect on indicator paper. Take drops of each solution and spot onto the narrow range indicator paper. Compare the colours with the standard colour chart and estimate the pH of each solution and the boiled, distilled water.

Reaction with magnesium. Into six test-tubes, put a small measure of magnesium turnings and add about 3–4 cm depth of boiled distilled water to one, and a different solution to each of the others. Note what happens to each tube and attempt to identify any gases evolved. Is there an 'order of reactivity' among the solutions?

Reaction with calcium carbonate (marble). Put a fairly large marble chip into each of six test-tubes and then add 3–4 cm depth of a different solution to each. Note any observations and any 'order of reactivity' and identify any gases which are evolved.

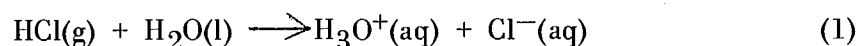
Calcium carbonate is insoluble in water, and it is very unlikely that you observed any reaction between CO_2 solution and marble. Do the following experiment to investigate further a possible reaction between CO_2 and calcium carbonate.

Half fill a 100- cm^3 flask with distilled water and add a *very small* pinch of powdered calcium carbonate. The liquid should look slightly cloudy when shaken. Bubble CO_2 into the liquid for several minutes. What happens? (If you study Option 1, *Water*, you will meet this reaction when investigating hardness in water.)

The effect of dissolving the polluting gases of the air in water, then, is to produce solutions which show the characteristic properties of acids.

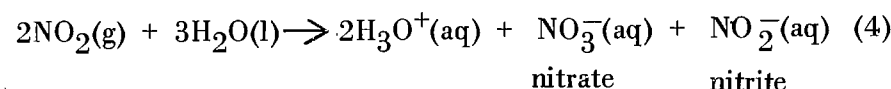
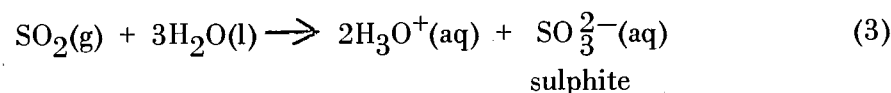
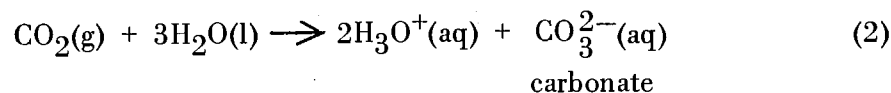
1.2 Acids and their 'reactivity'

Hydrogen chloride shows no acidic properties unless water is present. Then a reaction takes place in which hydrogen chloride donates a proton (hydrogen ion, H^+) to a water molecule to produce an oxonium ion, H_3O^+ .



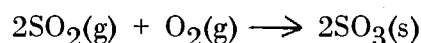
The presence of oxonium ions, $\text{H}_3\text{O}^+(\text{aq})$, which is sometimes written $\text{H}^+(\text{aq})$, is responsible for the acidic properties of substances.

In the case of the non-metal gaseous oxides, similar reactions must take place with water to produce oxonium ions.

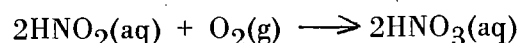
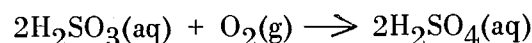


The way in which this occurs is not fully understood in all cases but it is thought that intermediate species are produced. Table 2 summarizes these reactions.

Sulphur trioxide is included in table 2 since a small amount of sulphur dioxide is oxidized by oxygen in the air.



Solutions of sulphurous acid and nitrous acid are also slowly oxidized to sulphuric and nitric acids respectively.



Sulphurous, nitrous, and carbonic acids have never been isolated as pure compounds.

Accepting that the intermediate acids mentioned in table 2 are produced, in what way is the production of the oxonium ion from the acid similar in each case? Does the same mechanism apply to HCl solutions?

Using equations 1 to 4, calculate the concentration of oxonium ions, H_3O^+ , which you would expect to obtain in each of the gas solutions used in Experiment 1.1.

Except for the 0.5M HCl solution, what do you notice about the predicted H_3O^+ concentration in each case? What effect should this have on the acid reactivity of each solution?

The pH of a solution is a measure of the concentration of H_3O^+ ions present in a solution and is defined as:

$$\text{pH} = \log \frac{1}{\text{H}_3\text{O}^+ \text{ concentration}}$$

<i>Name and formula</i>	<i>Initial reaction with water</i>	<i>Acid produced</i>	<i>Subsequent reaction</i>
sulphur dioxide SO_2	very soluble, some reacts $\text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_3$	sulphurous acid H_2SO_3	$\text{H}_2\text{SO}_3 + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_3\text{O}^+(\text{aq}) + \text{SO}_3^{2-}(\text{aq})$ sulphite
sulphur trioxide SO_3	reacts violently $\text{SO}_3(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_4$	sulphuric acid H_2SO_4	$\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_3\text{O}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$ sulphate
carbon dioxide CO_2	fairly soluble, some reacts $\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{CO}_3$	carbonic acid H_2CO_3	$\text{H}_2\text{CO}_3 + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_3\text{O}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$ carbonate
nitrogen dioxide NO_2	reacts $2\text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{HNO}_2 + \text{HNO}_3$	nitrous acid HNO_2 nitric acid HNO_3	$\text{HNO}_2 + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{NO}_2^-(\text{aq})$ nitrite $\text{HNO}_3 + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$ nitrate

table 2

Reactions of some non-metal oxides with water.

table 3

<i>Gas</i>	<i>Equation</i>	<i>Gas concentration (mol dm⁻³)</i>	<i>Concentration of H₃O⁺ ions predicted by the equation (mol dm⁻³)</i>	<i>Actual H₃O⁺ ion concentration from pH measurements (mol dm⁻³)</i>
hydrogen chloride	(1)	0.1		
carbon dioxide	(2)	0.05		
sulphur dioxide	(3)	0.05		
nitrogen dioxide	(4)	0.1		
hydrogen chloride	(1)	0.5		

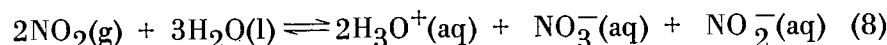
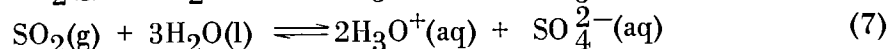
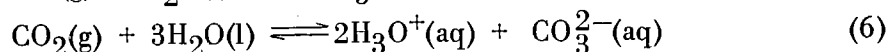
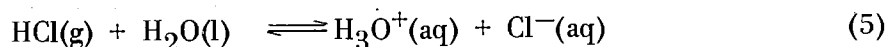
Thus, if the H_3O^+ concentration is 0.01 mol dm^{-3}

$$\text{pH} = \log \frac{1}{0.01} = \log 100 = 2.0$$

What effect does increasing the H_3O^+ concentration have on the pH?

Now try to calculate the actual H_3O^+ concentration for the solutions in Experiment 1.1, from the experimentally determined pH values. If you have difficulties with the calculation, your teacher will give you a table to show the inter-relationship between pH and H_3O^+ concentration.

From your calculations, you will see that in some solutions the actual H_3O^+ concentration is close to that expected, whilst in others it is very much lower. To explain this it is assumed that the reactions are reversible and are in a state of dynamic equilibrium. Equations 1 to 4 become



We see that reaction 5 proceeds almost to completion. By increasing the concentration of HCl(g) in solution, more H_3O^+ ions should be produced. Did your comparison of 0.1 and 0.5M HCl solutions confirm this?

In reaction 6 very few oxonium ions are produced and the equilibrium must lie well to the left.

Even small amounts of pollutants such as SO_2 , NO_2 , and HCl can have the effect of making rain water quite acidic, whereas water saturated with CO_2 will be only mildly acidic. Also, as the concentrations of pollutants increase, so does the acidity of the rain water.

Consider the difference between rain water in town and country. The pH of unpolluted rain due to carbon dioxide is 5.6. By contrast, the pH of urban rain is commonly 4.5 and often as low as 4.

What is the pH of rain in your area?

1.3 The chemical interaction between rain and stone

Most of the building stone used in this country can be roughly divided into two types – limestone and sandstone. Both are sedimentary rocks. Their distribution in the British Isles is shown in figure 7.

Limestone is a popular building material. St Paul's Cathedral and other famous London buildings are made of Portland stone – a limestone quarried at Portland in Dorset (see figures 1b and 8). Portland stone is analysed in table 5.

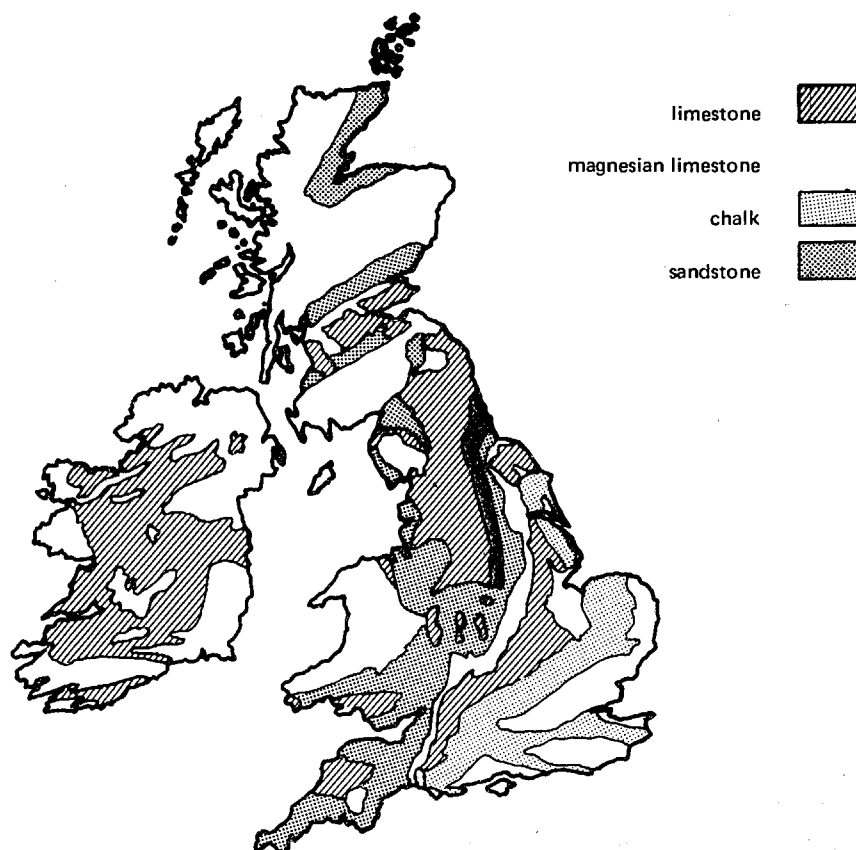


figure 7
A simplified geological map of the British Isles.

		%
Calcium carbonate	CaCO_3	95
Magnesium carbonate	MgCO_3	1.2
Silica	SiO_2	1.2
Aluminium oxide	Al_2O_3	0.5
Iron oxide	Fe_2O_3	
Water		1.9

table 5
Analysis of Portland stone.

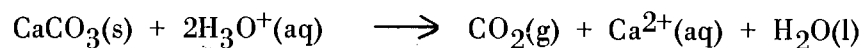
Magnesian limestone, found in a narrow belt running from Nottingham to Durham, contains a high proportion of magnesium carbonate. York Minster is built from this stone.

Warwick Castle and Worcester and Lichfield Cathedrals are of sandstone. This consists of small grains of silica, SiO_2 , cemented together. If the 'cement' is calcium carbonate, the stone is called a calcareous sandstone.

What factors might have dictated the type of stone used for a particular structure? Why do you think Canterbury Cathedral and St Albans Abbey were built from stone imported from Caen in France?

What is the underlying rock type in your area? Are there any stone quarries nearby? What type of stone was used for your local buildings?

Carbonates make up almost 100 per cent of limestones and hold together the structure of some sandstones. However, we have seen already that acidic solutions react with and eventually dissolve carbonates.



Reaction between acidic rain water and calcium carbonate can cause very rapid decay of calcareous sandstones, since disintegration of the carbonate 'cement' results in the loss of large numbers of silica grains, causing the stone to crumble.

In the case of limestones the stone slowly dissolves and, on exposed surfaces, the salts produced in the reaction are washed away. On sheltered surfaces, reaction products accumulate and form a hard dirty scale.

What difference would you expect between the effects of polluted rain and of unpolluted rain on a carbonate-based stone?

In the following experiment you will determine the relative rate of reaction of calcium carbonate with solutions of different pH in the range 3.0 to 5.2. You will use *buffer* solutions. These can be prepared with accurately known pH values and they maintain their pH even if diluted or if small amounts of acid or alkali are added.

figure 8

A Portland stone statue of St James the Great, on top of the West Front of St Paul's. This shows the damage done by the combined effects of acidic rain water and repeated crystallization of calcium sulphate.



Experiment 1.3

An investigation into the effect of pH on the rate of reaction of an acid with calcium carbonate

You will need:

Conical flask with side arm, 100 cm³

Rubber bung

Capillary delivery tube (see figure 9)

Crystallizing dish

Measuring cylinder, 5 cm³ and 100 cm³

Stopclock

Calcium carbonate

Buffer solutions (pH range 3.0–5.2)

Water saturated with CO₂

Measure out 1.0 g of calcium carbonate and put the powder into the side arm flask fitted with a delivery tube.

Fill a 5-cm³ measuring cylinder with water saturated with CO₂ and invert it in a crystallizing dish of similar water. Clamp the cylinder so that the mouth is just below the surface of water in the dish. Check that the delivery tube can be easily positioned under the mouth of the cylinder.

Put 40 cm³ of a selected buffer solution in a measuring cylinder. Pour the solution into the flask, quickly fix the bung, and gently swirl the flask for no more than two to three seconds. Place the delivery tube under the inverted measuring cylinder and simultaneously start the stopclock. Swirl the flask steadily and continuously and record the time, t , that it takes to collect 5 cm³ of gas.

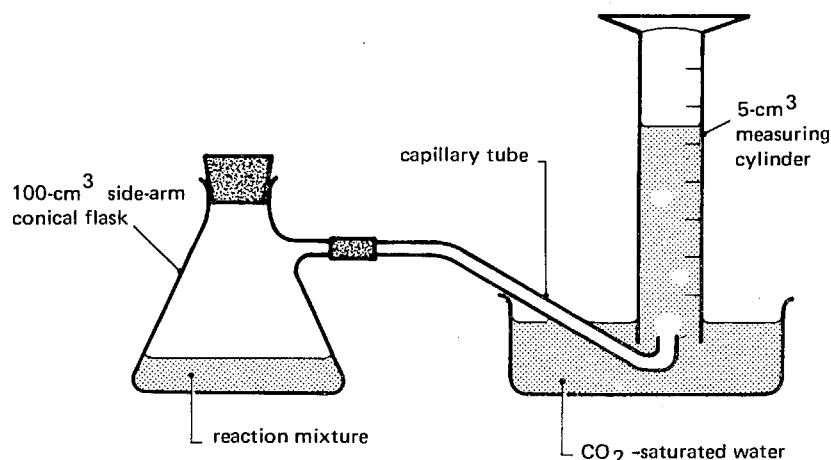


figure 9

The apparatus for Experiment 1.3.

Repeat the experiment several times, using different buffer solutions. Aim to cover the pH range 3.0 to 5.2. In between each experiment, wash the flask thoroughly and refill the small measuring cylinder.

Record your results in a table.

pH	Time, t , to produce 5 cm ³ gas (s)

Obtain the class average for the times at different pH values and plot a graph of pH (y-axis) against time, t (seconds) to produce 5 cm³ gas (x-axis).

From the graph, estimate the time it would take to obtain 5 cm³ of gas at pH 5.6. Call this $t_{\text{pH}=5.6}$. Remember, pH 5.6 is approximately the pH of unpolluted rain.

Since the rate of reaction $\propto \frac{1}{t}$, the relative rate of reaction at pH 4 (heavily polluted rain) to that at pH 5.6, i.e.

$\frac{\text{rate}_{\text{pH}=4}}{\text{rate}_{\text{pH}=5.6}}$, is given by:

$$\frac{\text{rate}_{\text{pH}=4}}{\text{rate}_{\text{pH}=5.6}} = \frac{t_{\text{pH}=5.6}}{t_{\text{pH}=4}}$$

Calculate this ratio.

What would be the effect on calcium carbonate of the rain water in your area relative to unpolluted rain?

What would be the effect on the experiment of using a single 1-g piece of calcium carbonate instead of powder?

What would be the effect of temperature on the reaction?

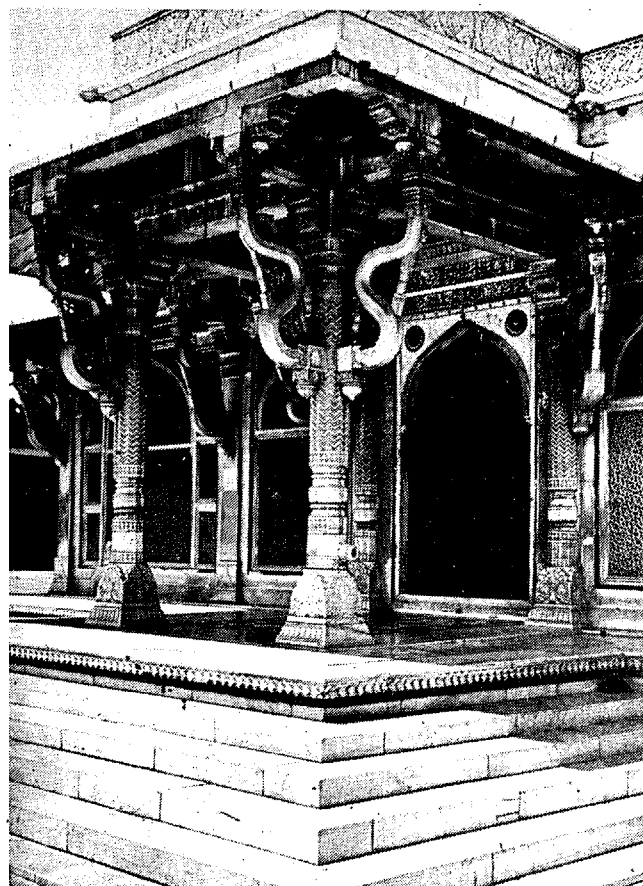
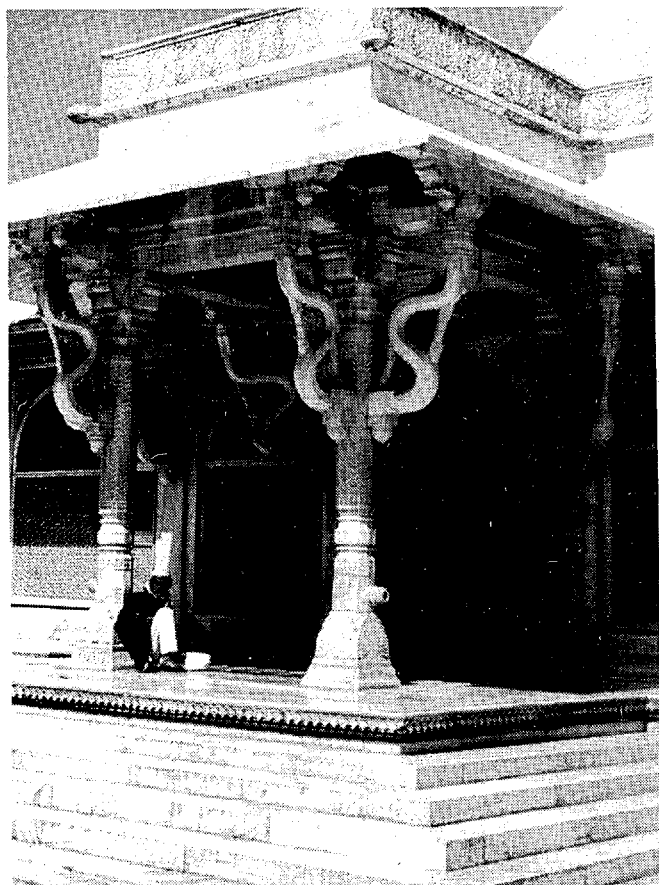
Do you think your results can give any useful information about the effect of a polluted environment on a limestone building or statue?

figure 10

In unpolluted areas, the decay of stone may be very slow. Compare these two pictures of the four-hundred-year-old tomb of Sheikh Selim Chisti at Fatehpur Sikri, in India. The one on the left was taken in 1972 and the one on the right is a high quality photograph taken about 1870. You can see that there has been practically no decay over the last century. Despite the annual monsoon, the intricately carved marble looks as good as new.

Would you expect the decay of limestone by polluted rain to be fastest or slowest in winter? Remember, gases are more soluble at low temperatures.

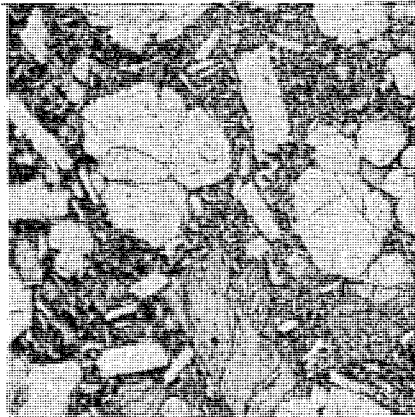
Whatever type of stone is involved, the process of decay by chemical reaction is made faster if there are gaseous and solid pollutants in the air. Solid particles, such as soot, form a nucleus onto which water and gases such as sulphur dioxide are adsorbed. When such particles, on which the acid concentration may become quite high, are deposited onto stone, they act as local 'hot spots', initiating points of corrosion.



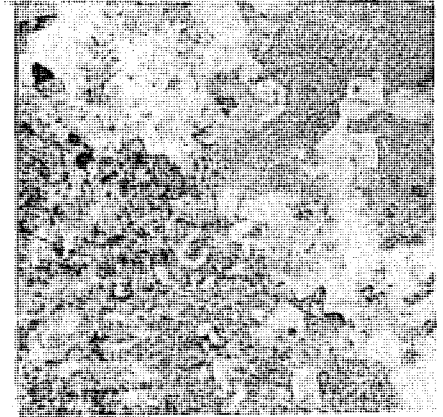
1.4 The decay of stone by physical processes

figure 11

The physical structures of volcanic rock, granite, limestone, and sandstone.



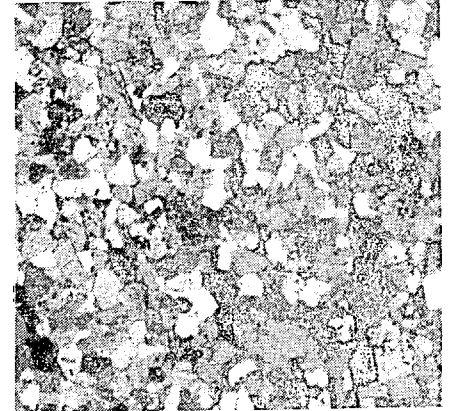
Volcanic rock is igneous. The crystals are usually very small because the lava has cooled down quickly. In this rock section the large crystals, interspersed among the smaller ones, evidently grew at depth before the lava gushed out.



Granite is another igneous rock. In this rock section the crystals in the top right hand corner are large and those in the bottom left hand one are much smaller. Which would you suppose grew first — the larger or the smaller crystals?



Limestone is a sedimentary rock. It consists chiefly of calcium carbonate extracted from the sea by small creatures to make their shells. This section shows a variety called colitic limestone in which the rock contains large numbers of small spheres, like the roe of a fish — hence the name 'oolite' meaning roestone.



Sandstone is also a sedimentary rock. It consists of even-sized grains of silica cemented together, usually by calcium carbonate. The grains may vary in size from less than 0.1 mm to about 1 mm.

What are the physical differences between igneous and sedimentary rocks?

How were igneous and sedimentary rocks formed?

Stone, like brick and concrete, has a granular structure with holes or pores of varying sizes, ranging from very fine, almost invisible pores to coarse ones which are easily visible. Such materials can absorb water, filling the pores. The porosity of a material is given by:

$$\text{porosity} = \frac{\text{volume of air in material}}{\text{volume of sample of stone}} \times 100\%$$

The porosity of stone can range from 0% to more than 40%.

How could you determine the porosity of stone? What assumptions would you be making?

What effect would you expect the particle size to have on the porosity of a stone? Would you expect granite to be more or less porous than limestone?

The porosity of stones varies considerably, as does the distribution of pore sizes. These factors dictate the susceptibility of the stone to physical decay and hence its suitability as a building material.

Damage by weather

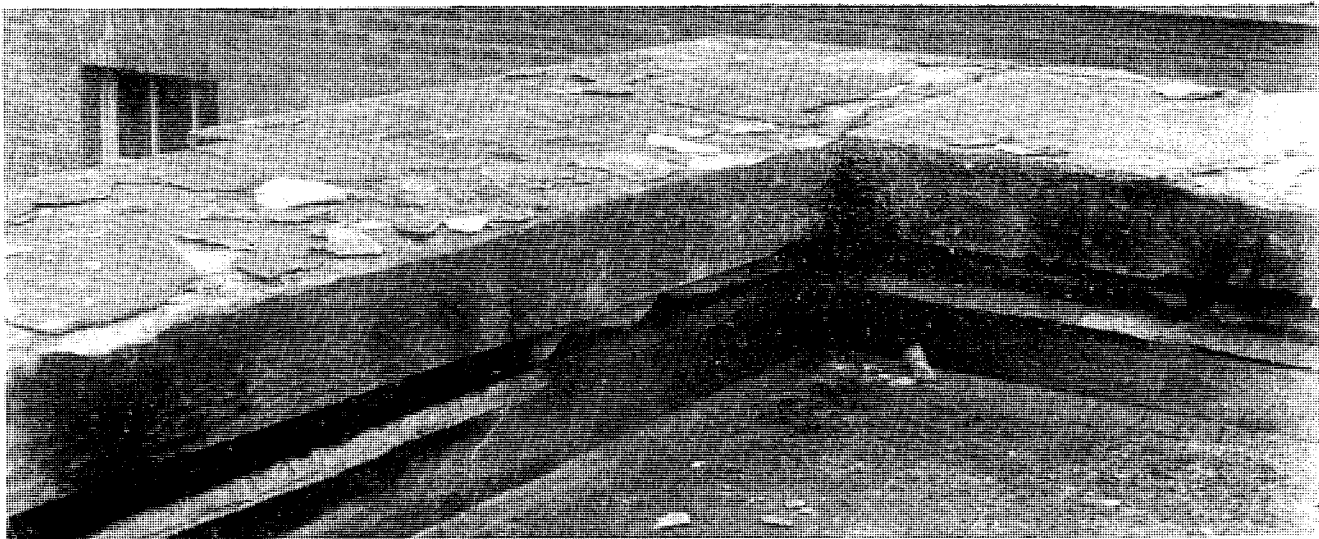
Stone can be seriously damaged by frost.

Have you ever noticed the effect a hard frost can have on concrete or paving stones? What do you see?

figure 12

Two examples of frost damage in stone.

Figure 12 shows examples of stone damaged by frost.



Frost damage only occurs in stone which is very wet and often frozen, and the susceptibility to damage depends on the pore size distribution. The mechanism of the decay is not fully understood, although there are two current theories.

One theory is based on the fact that an ice crystal in a large pore is more stable than one in a smaller pore, and that a crystal under pressure is less stable than one under no pressure. The growth of ice crystals in stone therefore starts in the large pores. As the crystals grow and fill the large pores, pressure is exerted against the pore walls. This pressure on the crystal may reduce its stability to the point at which it becomes no more stable than a crystal in a smaller pore, and the crystal then starts to grow out into the surrounding fine pores. On the other hand, the pressure exerted by the large crystal may exceed the tensile strength of the stone before this point is reached, and the stone then breaks up.

The second theory uses the fact that when water is frozen it expands. It is suggested that if stone is saturated with water, or if water is trapped in a stone – for example, by ice crystals in large pores trapping water in the finer pores – then the forces created by the expanding ice may exceed the tensile strength of the stone.

Can you think of other examples where the expansion of ice causes damage?

What evidence is there from figure 12 that both theories may be correct?

The crystallization of salts

A result of the chemical attack of rain on stone, described in Section 1.3, is the production of salts.

What is a 'salt'?

How would you prepare a dry crystalline sample of magnesium sulphate from magnesium carbonate? (Magnesium carbonate is insoluble in water; magnesium sulphate is fairly soluble.)

Sulphur dioxide dissolves in rain water, producing a solution of sulphurous acid which is oxidized to sulphuric acid. Hence, polluted rain leads to the formation of calcium sulphate from limestone and both magnesium and calcium sulphate from magnesian limestone.

Calcium sulphate is not very soluble in water and is readily crystallized in the pores at the surface of the stone. Magnesium sulphate is more soluble but crystals are formed in the pores as water evaporates. Over a long period of time, as fresh water penetrates into the pores, the salts dissolve and are recrystallized many times. On exposed surfaces, salts formed on (as opposed to 'in') the surface are washed away.

Experiment 1.4a Crystallization damage on stone

You will need:

Glass trough or sandwich box

Volumetric flask, 1000 cm³

Monks Park (or similar) stone, roughly
20 cm x 5 cm x 5 cm

M sodium sulphate solution

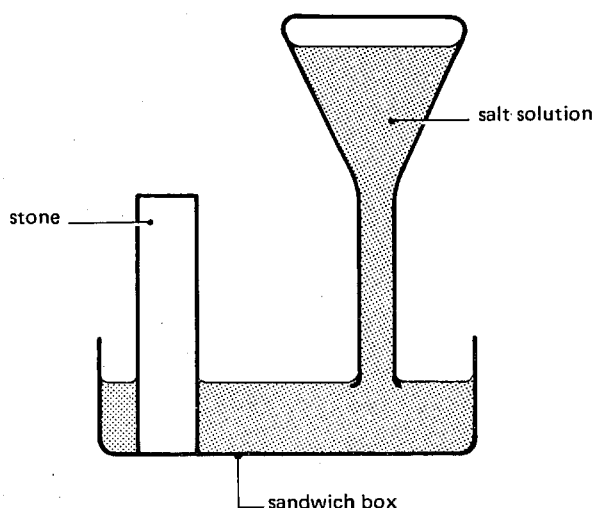
M sodium chloride solution

M sodium citrate solution

Distilled water

figure 13

The apparatus for Experiment 1.4.



Into the open container, pour about 30 mm depth of one of the salt solutions or of distilled water. Each of four groups should use a different solution. Put the container where it will remain for the next few weeks.

Fill a volumetric flask with the same solution and invert it with the open mouth under the level of the solution in the container. Carefully raise the flask until the mouth is about 25 mm from the bottom of the container and clamp it at that height, near the side of the container. Make sure that the stand is stable. The inverted flask of solution is a reservoir and ensures a constant level of solution.

Place a piece of stone, on its small face, in the solution and leave it for 2 to 3 weeks. (Figure 13.)

Part B After 2 to 3 weeks examine the stone. Describe what has happened and draw diagrams to illustrate your observations.

Wash away any salts which have crystallized on the stone and examine the fresh surface. Is there any evidence of damage to the surface? Tap the stone gently with a hammer. Does it chip or break easily?

Compare the effect of different salts, using the stone which was stood in water as your reference or control.

This 'accelerated' experiment should show you in a few weeks an effect which takes years in the real world of masonry decay. How was the process accelerated? How does this experiment differ from the real situation?

Examples of crystallization damage to masonry are widespread. See figures 14 and 15.



figure 14

This figure on Wells Cathedral shows the decay brought about in limestone by the repeated crystallization of calcium sulphate which causes powdering or blistering of the surface of the stone.



figure 15

Howden Church. In this picture you can see deep cavernous decay in a magnesian limestone, caused by the repeated crystallization of magnesium sulphate.

1.5 The protection and preservation of stone

Experiment 1.5 Protection of stonework

You will need:

6 test-tubes, 125 x 25 mm

Beaker, 400 cm³

Cotton

Bunsen burner

Tripod

Gauze

Oven

Chips of limestone or marble

Paraffin wax

2% silicone fluid in butanone

0.5M sulphuric acid

0.5M hydrochloric acid

Calcium sulphate formed as a result of SO₂ pollution causes much damage. What other salts are likely to be formed on limestone in heavily polluted areas? Why do buildings in coastal areas appear to decay quickly? Other common sources of salts include the soil and cleaning materials. Some cleaning preparations do more harm than good. There is a report of a well-intentioned but misguided attempt to preserve a church by applying sodium chloride to the stonework!

On sheltered stonework, salts formed on the surface are not washed off and form a hard, dirty crust which can trap water, allowing crystallization to continue in the pores.

The mechanism of crystallization damage is not fully understood but it is thought to be similar to that of frost damage, according to the first theory discussed on page 15. One established fact is that a limestone with a fairly high porosity and a high proportion of fine pores tends to be susceptible to crystallization damage. An example is Monks Park stone, a limestone quarried near Bath.

Can you suggest why some salts have a more disastrous effect than others?

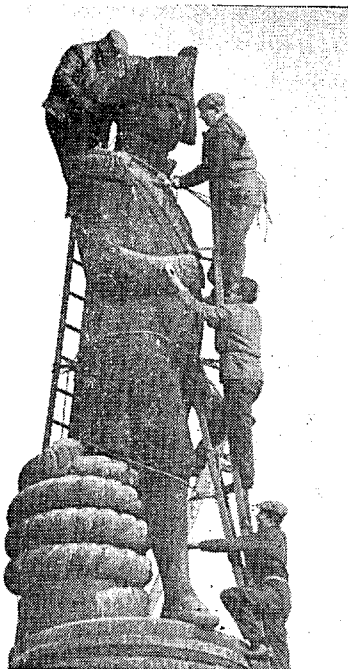
Can you also suggest why the effect produced by magnesium sulphate in magnesian limestone is different from the effect of calcium sulphate in limestone?

By knowing something about the mechanisms which cause decay, we can suggest methods by which stone might be protected. What suggestions can you make?

Since water plays an essential part in all the decay mechanisms we have considered, surface treatment with a water-repellent such as wax or silicone might appear to be an effective form of protection. Indeed, on sheltered stone surfaces the hard crust of barely soluble salts might be expected to offer natural protection from further chemical attack.

1. Tie cotton onto two equal-sized chips of stone and lower one chip into dilute sulphuric acid for about 30 seconds. The surface will become coated with calcium sulphate. Remove the chip and allow the excess acid to drain. Put the treated and untreated chips into dilute hydrochloric acid in two test-tubes. Compare the initial rates of reaction.
2. Melt paraffin wax in a test-tube immersed in boiling water. Lower a chip of stone into the molten wax for a few minutes and then withdraw it and allow it to cool. Put the treated stone into dilute hydrochloric acid and compare the rate of reaction with that of an untreated chip.
3. Allow a chip of stone to stand in 2% solution of silicone fluid in butanone for about 5 minutes. Then remove it and place it in an oven at 150 °C for 15 minutes. After cooling it, investigate the reaction with dilute hydrochloric acid as before.

Could any of these methods provide an effective and practicable means of preserving a stone structure? What problems do you foresee?

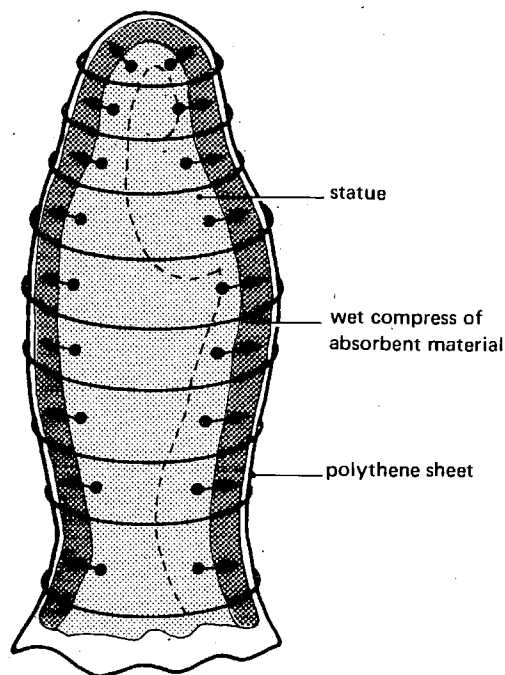


figures 16 and 17

The statue of Lord Nelson in Trafalgar Square in 1963 before it was cleaned, and in 1968 after cleaning.

figure 18

This diagram shows another, more sophisticated way of removing salts. A wet compress of an absorbent material is tightly bound to the structure and draws salts from the surface. The technique has limited applications.



The idea that the crust of calcium sulphate might prevent further chemical attack may be true, but it does not prevent decay. Water and salts trapped behind the skin allow crystallization damage to continue. The same is true of any preservative which simply provides a water-repellent coating.

Any successful treatment must also arrest crystallization damage, either by removing salts or by impregnating the stone with a preservative to a considerable depth, say 25 mm, or a combination of both.

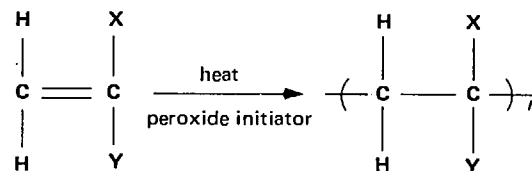
Cleaning stone with pure water either as a high pressure jet or a fine spray or with steam, together with gentle brushing, might be regarded as ways of preserving stone; most salts just under the surface are removed. What are the dangers of high pressure jets?

If impregnated chemical preservatives are to arrest crystallization damage, they must be rigid enough inside the stone either to encapsulate the salts, making them inaccessible to water, or to modify the structure and strength of the stone, making it more resistant. Yet, the preservative must have a very low viscosity when applied, to allow deep penetration.

Possible preservatives might be high molecular mass polymers. One method of application would be to dissolve the polymer in a solvent, apply the solution to the surface, and then evaporate the solvent. This method has disadvantages: the polymer molecules may migrate back to the surface as the solvent evaporates and in any case they may be too big to enter the fine pores. Consequently, attempts to preserve stone in this way have not been very successful.

Current research involves attempts to form polymers within the stone. Remember that the small molecules, called monomers, from which polymers are made are often very volatile liquids. When monomers are heated with an initiator solid polymers are produced.

For example,

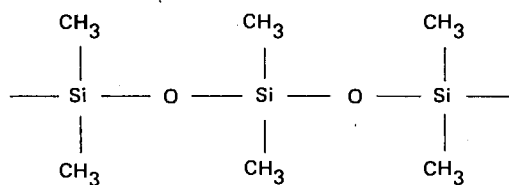


where $\text{X} = \text{CH}_3$ Perspex
 $\text{Y} = \text{COOCH}_3$

methyl methacrylate (methyl 2-methylpropenoate)

polymethyl methacrylate (poly(methyl 2-methylpropenoate))

Methyl methacrylate (methyl 2-methylpropenoate) and an initiator have been applied to stone structures and heated in an attempt to make a polymer in the stone. A similar technique has been used to introduce silicones. Some success is reported. What practical problems do you foresee?



a silicone (why are silicones water-repellent?)

Perhaps the surest way of reducing future stone damage is to reduce air pollution! How can we help?

Summary

In this section you have seen that some pollutants of the air, when dissolved in rain water, produce fairly acidic solutions. Chemical reaction between acidic rain water and limestones and calcareous sandstones, which contain carbonates, can result in the slow dissolution of limestones and the crumbling of sandstones.

Damage caused by salt crystallization and damage caused by frost result from physical processes occurring in the stone, and are the main causes of stone decay. The extent of damage depends on the pore size distribution.

Any attempt to protect stone must prevent attack by water and arrest the crystallization of salts in the stone.

Section 2

THE CORROSION OF METALS

What happens when metals are exposed to air or water? You probably know that most of them undergo *corrosion*. In this section you will be investigating some of the reactions involved in corrosion and some ways of preventing it.

Rusting is the term used to describe the corrosion of iron and steel. This section is mainly about steel, since it is such a commonly available and useful structural metal. In particular, it is about 'mild steel'. This is an alloy of iron containing up to 0.3% carbon and traces of other elements; chemically it is very similar to iron although it is much stronger and more frequently used. This is the alloy you will be using when the instructions refer simply to 'steel sheet'.

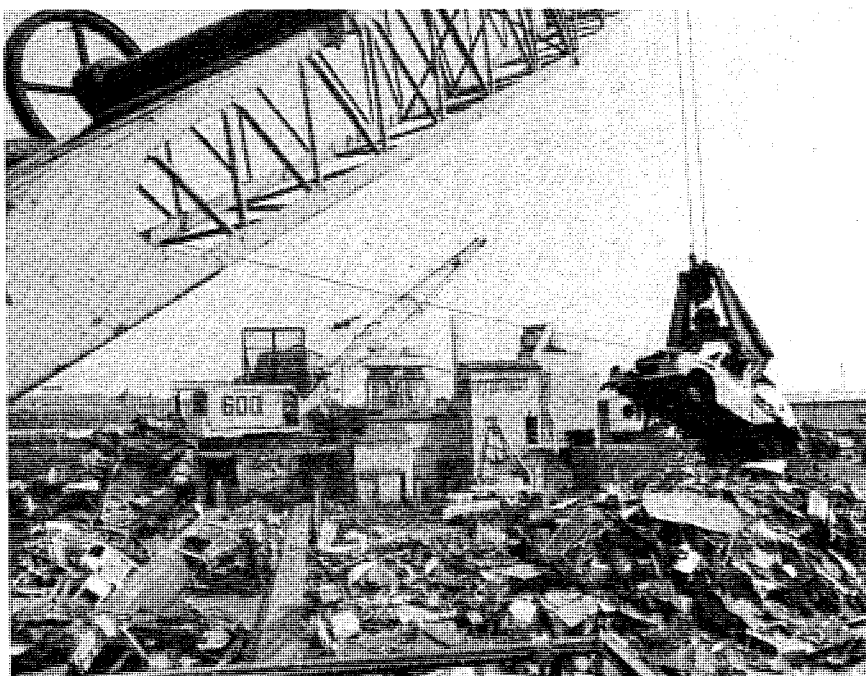


figure 19

Metal corrosion around us: cars in a breaker's yard.

2.1

Metallic corrosion all around us

Have a look at your bicycle — or someone else's. Unless it is very new, it is likely that the metal parts are beginning to corrode. Where is the corrosion worst? Which metals do you think these parts are made of? Is the corrosion uniform or in patches? Where does it start — in the middle of a piece of metal, at the edges, at the joints?

What steps has the manufacturer taken to minimize the corrosion and how effective have they been? What do you do (what should you do, if you want your bike to last) to reduce corrosion?

Metals, as we know them, are in a chemically unnatural state. Most of them occur naturally in the ground combined with oxygen or other elements and a number of chemical reactions have to be carried out on these compounds (ores) to extract pure metals from them. Corrosion is the reversion of metals to their more stable, natural forms. It is interesting to note that those metals which are most easily extracted

from their ores, or which occur uncombined in nature, are the ones which are most resistant to corrosion. These are also the earliest metals to have been discovered and used and many articles made of gold many thousands of years ago are still in good condition today.

Try to make a list of some of the common metals and the approximate dates when they were first discovered or used, putting the most recent ones at the top. Compare your list with the reactivity series, which you met in Stage I, and the galvanic series shown on page 31.

Metal articles may be protected from corrosion by a suitable surface coating. This may be metallic, applied by electroplating as with nickel, or by dipping in the molten metal as with zinc. Non-metallic coatings such as paint or enamel are also used (figure 20). Sometimes the product of corrosion itself forms a protective coating. The rust formed on steel flakes off and leaves the surface exposed to further attack, but aluminium and nickel form layers of oxide which stick tightly to their surfaces and are impervious to moisture and oxygen. 'Stainless steels' are produced by alloying iron with chromium,

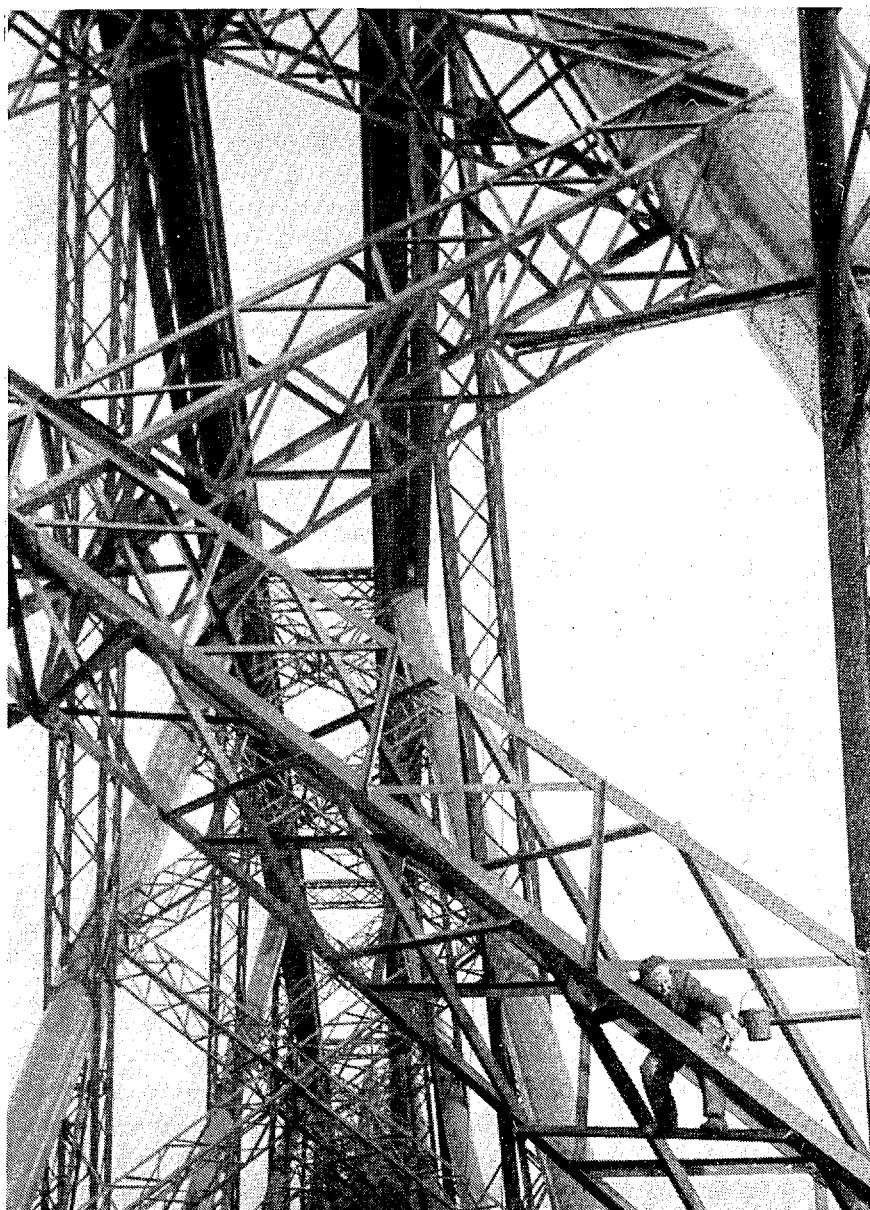


figure 20
Painting the metal girders of the Forth
Railway Bridge.

although other elements such as nickel and molybdenum are also commonly added to enhance still further their resistance to corrosion. The resistance results from a surface layer of chromium oxide. Products made from these alloys are expensive, not only because of the cost of the added elements, but also because these materials may be difficult to machine and generally fabricate.

In all the experiments which follow, the surfaces of the metals must be carefully prepared to remove any corrosion already present. When the instructions tell you to 'clean' a sample you should first rub it with emery paper until all the surface dirt has been removed and the surfaces are shiny. Then remove grease with cottonwool or a tissue soaked in acetone (propanone). After this, handle the sample only by its edges or with tweezers.

2.2

Dry and wet corrosion

Experiment 2.2a

Corrosion of metals by reaction with oxygen

You will need:

Bunsen burner

Tongs

Tweezers (if available)

Tissues or cottonwool

Emery paper

Samples of copper, steel, and aluminium sheet

Acetone (propanone)

(DANGER – highly inflammable)

Perhaps the most obvious way in which metals might corrode is by reaction with oxygen in the air. The following experiment investigates this process and increases the extent of the reaction by heating the metal.

Heat a cleaned sample of copper for a few minutes in a hot flame. Allow it to cool and examine its surface. What colour is the surface-coating and what is it called? How does it differ from the corrosion product formed on a copper roof or statue in the open air?

Repeat the experiment with a cleaned sample of steel. Does the surface-coating look like the familiar rust?

Heat a cleaned sample of aluminium gently in a small flame with the air-hole of the burner half-open, being careful not to melt the sample. Does the surface of the aluminium change very much?

The reaction between dry oxygen and a metal is usually called *tarnishing*, rather than corrosion, and results in the formation of a very thin oxide film on the metal surface. The products in Experiment 2.2a do not look like the familiar ones produced naturally, outside the laboratory. The next experiment investigates the corrosion of metals in water (which will certainly contain some dissolved oxygen) and accelerates the process by dissolving salt in the water to produce a corrosive medium like sea water.

Experiment 2.2b

Corrosion of metals in salt solution

Clean and prepare the following samples and put them in labelled test-tubes containing enough salt solution to cover them completely:

A a steel nail

B a sample of zinc sheet

C a sample of copper sheet

D a steel nail, with a thin strip of zinc wrapped tightly round it, just below the head, covering about a quarter of the shank

E a steel nail, with a thin strip of copper wrapped tightly round it,

You will need:

Test-tubes large enough to contain the samples (or Petri dishes or plastic cups)

Test-tube rack

Labels

Tweezers (if available)

Tissues or cottonwool

Emery paper

Desiccator

Strong scissors or snips

Acetone (propanone)

DANGER – inflammable)

Steel nails

Samples of copper, steel, zinc, and stainless- steel sheet

Tin-coated steel sheet (tinplate)

Zinc-coated (galvanized) steel sheet

Salt solution (5% sodium chloride)

Distilled water

just below the head, covering about a quarter of the shank

F a sample of steel sheet

G a sample of zinc-coated steel sheet which has been scratched along the centre of one face for about half its length; the scratch must be deep enough to expose the underlying steel surface

H a sample of tin-coated steel sheet, scratched as in G

I a sample of stainless steel

J a thin strip of stainless steel, folded double and pinched together so that the inside faces are in contact for part of their length and a V-shaped crevice is formed.

Two further sets of samples should be prepared and left available for all to see. One set should be placed in labelled tubes of distilled water and the other kept dry in a desiccator, as a control.

Inspect the samples after a few minutes and again, after a day or a few days. In doing so, be careful not to disturb them until you have recorded your initial observations although, afterwards, you may wish to remove them to see whether the corrosion products are easily wiped off or strongly stuck to the surfaces.

Compare and record, perhaps by drawing diagrams:

1. the colour of each corrosion product and where it is forming.
2. the amount of corrosion – ‘none’, ‘slight’, ‘moderate’, or ‘severe’.

Is there any difference in the rates of corrosion in distilled water and in salt water?

Is there any difference in the rates of corrosion of steel

- a. on its own,
- b. in contact with a less reactive metal (copper or tin),
- c. in contact with a more reactive metal (zinc)?

If neither of the two pieces of stainless steel in salt solution has started to corrode, return them to the solution. Inspect them again a few days, or a few weeks, later.

It appears from these experiments that the corrosion of a metal, in contact with an electrolyte solution, may be made faster or slower by contact with another metal. The effect of the electrolyte solution is clearly important, since it causes the familiar form of rust on steel which is not obtained in dry conditions.

This important ‘bimetallic’ effect is used in galvanized steel where, at a small gap in the zinc coating, the steel is protected from corrosion at the expense of the surrounding zinc.

2.3

Metallic corrosion and the flow of electrons

You have seen from sub-section 2.2 that metals corrode in the presence of water. You have also seen that the process may be speeded up if the metal is in contact with a less reactive metal and if the water, with which they are both in contact, contains a dissolved electrolyte. This arrangement forms an electrochemical cell. We must now examine such a cell to explain the reactions causing corrosion.

Experiment 2.3a

A simple electrochemical cell

You will need:

a small, clean strip of copper and one of zinc

You may remember, earlier in your chemistry course, setting up a cell and using it to light a bulb. However, similar types of cell may occur naturally or accidentally. One such cell arises when two different metals are in electrical contact so that electrons can flow from one to the other if both are in contact with an electrolyte solution — that is one which contains ions which are free to move and carry a current. Even pure water, containing oxonium and hydroxyl ions, has a high enough concentration of these ions to act in this way.

Tap water, rain water, and sea water contain higher concentrations of other ions and so can conduct current more easily. List some of the dissolved ions which you think are likely to occur in tap, rain, and sea water.

This simple experiment shows how a cell may be set up in unusual circumstances.

Hold the two strips of metal between your finger and thumb so that they are not in contact and touch both ends on to the tip of your tongue. Now hold them so that the ends are in contact and again touch the free ends on your tongue. Describe what you feel or taste.

You have set up a simple electrochemical cell. The two pieces of metal are the electrodes. What is the electrolyte solution? You should be able to feel the current being conducted across or through your tongue by ions.

We usually try to detect or measure a current by placing a bulb or ammeter between the two electrodes outside the solution. Since the currents involved in the following experiments are fairly small, you will be using a milliammeter.

Experiment 2.3b

Electrochemical cells and the flow of electrons

You will need:

Beakers, 100 cm³

Milliammeter (centre-reading, if possible)

Plug-leads and crocodile clips

Tweezers (if available)

Tissues or cottonwool

Emery paper

Acetone (propanone)
(DANGER — inflammable)

Samples of zinc, steel, and copper sheet (about 7 cm x 3 cm)

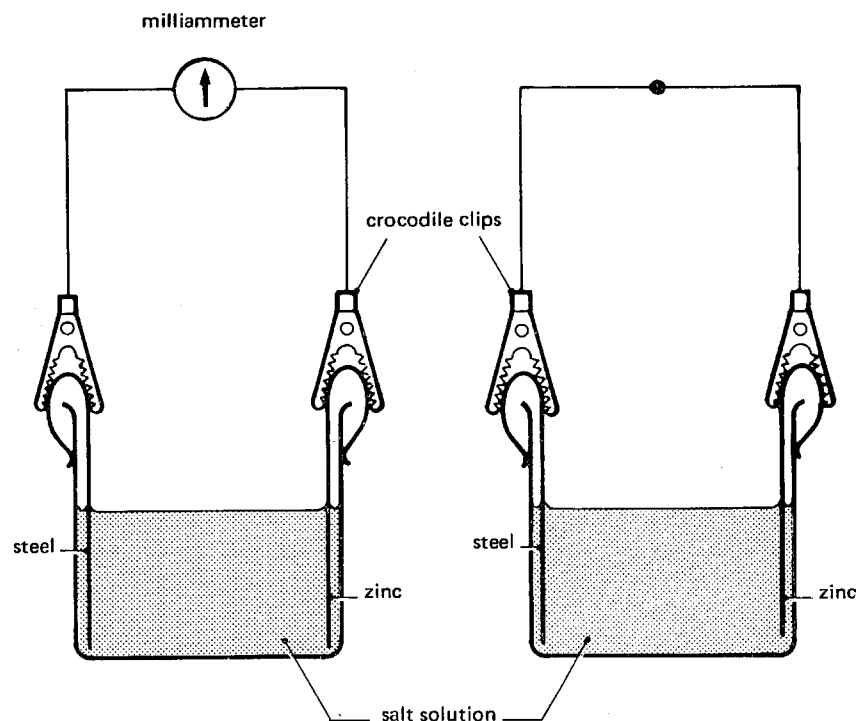
Salt solution (5% sodium chloride)

Two metals in contact with each other and with an electrolyte solution form a cell through which electrons flow. Now investigate the direction in which they flow, using three of the metals whose corrosion has been observed.

Clean a strip of zinc and one of steel. Construct a cell, as shown in figure 21, in a beaker, half-full of salt solution. Fold the strips over the top of the beaker and hold them in place with crocodile clips. These also form the electrical contacts. Connect the cell to a milliammeter and observe the current flowing at first and then after ten minutes. If you are not using a centre-reading ammeter you will have to be very careful about which way round you connect the cell. Ask your teacher first.

If the cell is disconnected from the meter during the ten minutes, make sure that current is still allowed to flow, by completing the circuit. This is shown in figure 22.

figures 21 and 22
The apparatus for Experiment 2.3b.



Decide which way the electrons are flowing through the ammeter and, hence, which electrode is 'supplying' electrons. Ask your teacher for help if you are not sure about this. Record your observations in a table.

Cell	Salt solution				Distilled water			
	direction of electron flow from	to	electrode supplying electrons	current	direction of electron flow from	to	electrode supplying electrons	current

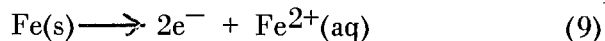
Repeat the experiment, using distilled water in place of salt solution, and clean strips of metal.

Now repeat both experiments, using first steel and copper, and then zinc and copper, in place of the original electrodes.

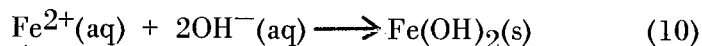
List the three metals in order of their readiness to supply electrons, putting at the top the one which will supply electrons to both the other two. Compare this list with the reactivity series of metals which you learned about in Stage I and with the galvanic series on page 31.

In order to understand what is happening when steel corrodes, in contact with another metal, consider the reactions occurring in the steel/copper cell.

The electrons flowing through the wire from steel to copper are being supplied by the iron atoms, which then become positive ions and go into solution



Negative ions already in solution, OH^{-} (from the water) and Cl^{-} (from the sodium chloride), move towards the steel where they meet the Fe^{2+} ions. Iron(II) hydroxide, being insoluble, is then precipitated on or near the steel



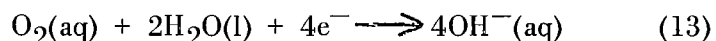
(Iron(II) chloride is soluble, so the Cl^{-} ions simply remain in solution.)

The iron(II) hydroxide then reacts with oxygen dissolved in the water to form a mixture of compounds in which iron appears as Fe^{3+} . The compounds include the hydrated oxide $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, and are collectively known as rust.

The reactions at the copper electrode may be more complicated and we need not be too concerned with their details, except to recognize that they must be reactions which use up electrons (otherwise a build-up of electrons would occur at the copper and stop any current flowing) and that the copper is not reacting. Positive ions in the solution, H^{+} (from the water) and Na^{+} (from the sodium chloride), move towards the copper, where the H^{+} ions may be discharged



But another reaction taking place is between the electrons and water and oxygen dissolved in the water



In electrochemical cells, just as in electrolysis cells, the electrons flow through the wire (and the meter) *from the anode to the cathode*. So, in the above cell, the steel, forming the *anode*, is *losing electrons* and *corroding*. The *cathode* is *not corroding*.

Steel will not always form the anode in an electrochemical cell. When the other electrode is zinc, the steel forms the cathode and the zinc the anode. In this case, therefore, the zinc loses electrons and corrodes whilst the steel is 'protected'. Look again at the galvanic series for metals in sea water given on page 31. A metal high in the series will act as an anode when in contact with another metal lower in the series, if both are in contact with sea water. Thus the metal higher in the series is liable to corrode in this combination. In fact, reasonable predictions can be made about any 'wet' bimetallic system from this series, since the order of metals is rarely changed in other electrolytes. However, there are exceptions and the only positive test of any prediction is experimental observation. You may notice the considerable similarity between this and the familiar reactivity series of metals.

As the cell runs, there will generally be an accumulation of hydrogen at the cathode (reactions 11 and 12) and corrosion products around the anode. These form barriers to the incoming ions and reduce the flow of electrons. This effect is known as *polarization*. Did it occur in your cells? What will be its effect on the rate of corrosion?

If the following pairs of metals are in contact with each other and with an electrolyte solution, which would you expect to corrode and which to be protected in each case?

1. Steel and magnesium (when you have decided, look at figure 31)
2. Aluminium and copper
3. Silver and brass.

Experiment 2.3c A cell with 'identical electrodes' — and the corrosion of a single metal

You will need:

Beakers, 100 cm³

Milliammeter (centre-reading, if possible)

Plug-leads and crocodile clips

Filter paper

Clean glass tube or drinking-straw

Tweezers (if available)

Tissues or cottonwool

Emery paper

Acetone (propanone)
(DANGER — highly inflammable)

Samples of steel sheet (c. 7 cm x 5 cm)

Salt solution (5% sodium chloride)

The last experiment offered an explanation of the process of corrosion when two different metals are in contact. The next one illustrates one case where the two electrodes are of the same metal.

For this experiment, it is important that we should be able to treat the salt solutions around the two electrodes in different ways, so the cell is separated into two 'half-cells', each in a separate beaker. If, however, a current is to flow, the circuit must be complete. Therefore, a passage is provided for the ions to flow between the two solutions through a 'salt bridge', which consists of a strip of filter paper soaked in salt solution.

Clean two pieces of steel and support each in a separate beaker. Fold the tops over and hold them with crocodile clips, as before. Half-fill each beaker with salt solution and connect the two half-cells with a piece of filter paper soaked in salt solution. This should dip into the solution in each beaker, as shown in figure 23. Connect the electrodes to a milliammeter; if a small current flows you may ignore it (or you may prefer to speculate what causes it). Using a clean glass rod or a drinking-straw, blow air into the solution in one of the beakers so that the bubbles pass over the surface of the steel.

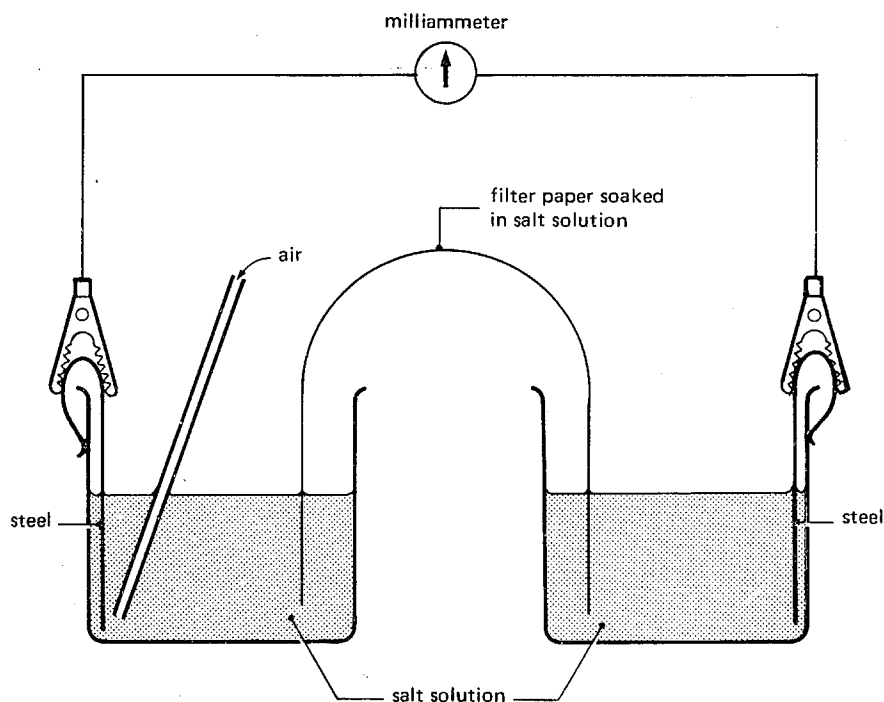


figure 23
The apparatus for Experiment 2.3c.

Record the size of the current and the direction of electron flow and decide which electrode is supplying electrons (the anode).

Which of the gases in the air do you think is responsible for the difference in the two cells which causes the current to flow? Your teacher may show you an experiment to test your opinion.

Notice that the steel which is freely supplied with oxygen is the one which is protected. The steel in the solution containing a lower concentration of oxygen corrodes. At a small crevice on a steel surface which is in contact with an electrolyte solution the oxygen supply is very restricted by comparison with the 'open' areas; thus, the oxygen-starved region corrodes. It is this 'differential aeration' effect which is important in the corrosion of stainless steel. What has happened to sample J from Experiment 2.2b, in which a crevice was deliberately formed?

2.4 The application of cells to corrosive situations

Can you now explain how steel is protected by zinc-coating and how corrosion can be accelerated by tin-coating? Look at figures 24 and 25, showing cracks in such coatings, remembering that they are likely to be surrounded by atmospheric moisture, rain water, or other solutions.

figures 24 and 25
Cracks in zinc-coating and in tin-coating, around steel.

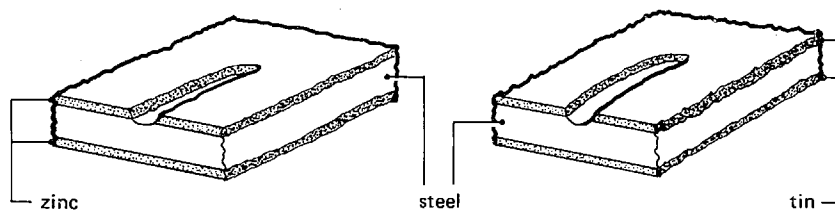
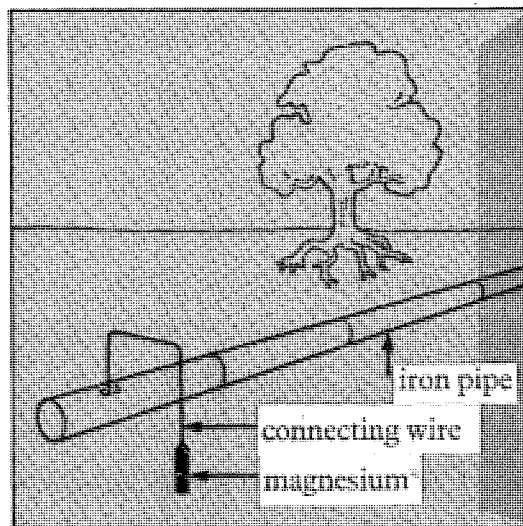
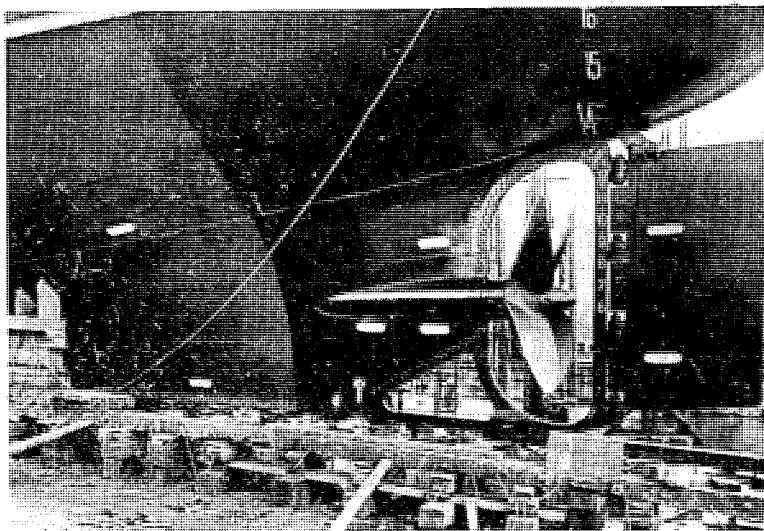


Figure 26 shows zinc blocks ('sacrificial anodes') fitted to the stern and rudder of an ocean-going tug, to provide 'cathodic protection'. Can you explain how they help? The diagram in figure 27 shows how magnesium can be used in a similar way to protect an iron pipe.

figure 26
How do the zinc blocks protect the hull?

figure 27
The cathodic protection of an underground iron pipe with a magnesium anode.

Cathodic protection can also be given by passing through a metal a direct electric current that counterbalances the current in the corrosion cell. This is done, for example, in many newly erected piers and jetties. (Compare Experiment 2.5, part E.)



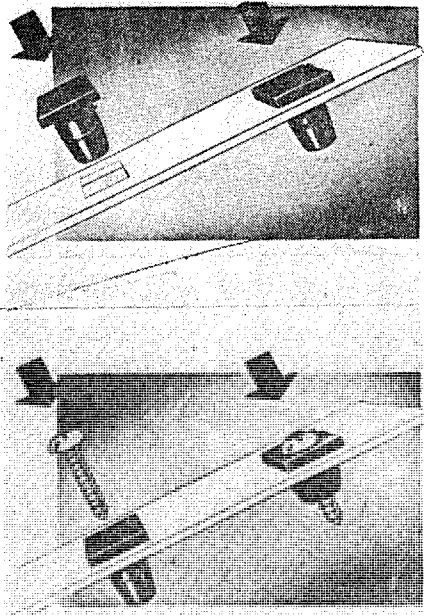


figure 28

The use of plastic sheathing to insulate fasteners, if they are of a different metal from the component metal they are joining together.

Because of the tendency of dissimilar metals to form bimetallic corrosion couples, it is advisable, wherever possible, to ensure that any fasteners are constructed from the same metal as the components that are being joined together. If this is not possible, it is important to ensure that the dissimilar metal fasteners (screws, nuts, bolts, washers, or rivets), whether they are anodic or cathodic to the component metal, are thoroughly insulated electrically from the components, to avoid corrosive attack at the joints. Depending upon the nature and design of the joints, the use of plastic sheathing, non-metallic washers, plastic wrapping tape, paint, or a suitable mastic or resin can be considered for insulating the dissimilar metals from each other. (Figure 28.)

Anodic and cathodic regions can form on a single piece of metal if the supply of oxygen varies across the surface. For example, the metal plate in figure 29 has been starved of oxygen in the crevices under the washers and, after the screws and washers have been removed, the resulting corrosion can be clearly seen.

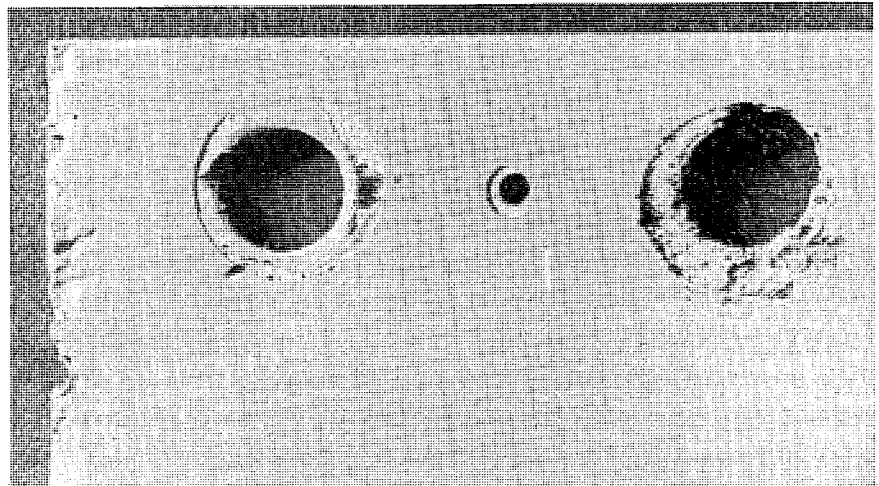


figure 29

Crevice corrosion where a metal plate has been covered by screws and washers. Corrosion has resulted from oxygen shortage below the washers. The diagram shows how the corrosion cell is formed.

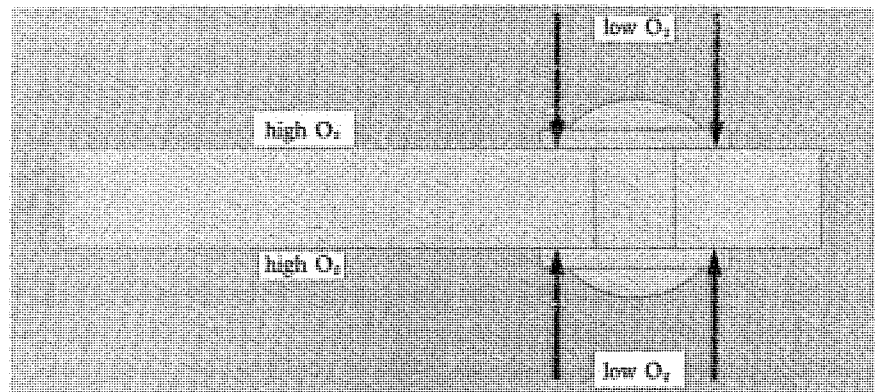


Figure 30 shows a stainless steel woodscrew which was used for fastening an echo-sounder plate to a timber-hulled fishing vessel. The threads, starved of oxygen, have mostly corroded away, although the head, which had an adequate supply of oxygen from the sea water to which it was exposed, appears perfectly sound.

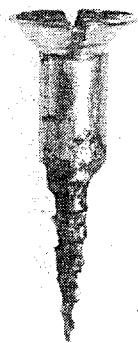


figure 30

A corroded stainless steel woodscrew.

But other factors such as the presence of corrosive substances in the wooden hull or the poor quality machine finish of the thread surfaces may also be at least partly responsible for the more rapid and extensive corrosion of the screw threads.

2.5 Rapid indicator tests and another cause of corrosion in a single metal

Ferroxyl indicator

Experiment 2.5 Ferroxyl indicator tests

You will need:

Petri dishes or plastic cups

Plug-leads and crocodile clips

Tweezers (if available)

Tissues or cottonwool

Emery paper

1.5 volt battery or 1–2 volt d.c. supply

Acetone (propanone)

(DANGER – inflammable)

Steel nails

Strips of zinc and copper

Ferroxyl indicator (DANGER –
potassium hexacyanoferrate(III)
is poisonous)

The corrosion of steel in salt solution can be demonstrated very quickly by using *ferroxyll indicator*. This is a solution of sodium chloride containing two indicators. One is potassium hexacyanoferrate(III), which reacts with the iron(II) ions passing into solution from steel at the start of rusting (reaction 9), to give a blue colour. The other is phenolphthalein, which reacts with the hydroxyl ions formed at a cathode (reaction 13), giving a red colour.

In the experiment which follows, remember that a blue colour indicates the start of rusting around steel (which is acting as an anode). A red colour shows that the metal (forming the cathode) is being protected.

The corrosion products of other metals do not give a blue colour with potassium hexacyanoferrate(III); for example, corroding zinc forms a white precipitate with this indicator.

Prepare:

A a steel nail around which a strip of zinc has been tightly wrapped near the head

B a steel nail around which a strip of copper has been tightly wrapped near the head

C a piece of zinc-coated steel, scratched as in Experiment 2.2b (G)

D a piece of tin-coated steel, scratched as in Experiment 2.2b (G)

E two steel nails, one connected to one terminal and one to the other terminal of a 1.5-volt dry cell (or 1–2-volt d.c. power supply); the nails should be placed alongside each other but not in contact

F a single steel nail.

Immerse each of these in a shallow dish of ferroxyl indicator. A single dish can hold several specimens so long as they are not in contact. Be careful not to disturb or move the dishes once the samples have been placed in them. (Some care is needed in setting up E, since the crocodile clips should not touch the solution; however, in this case, there is no need for the nails to be fully immersed.)

Draw diagrams of what you see after a few minutes and explain your observations in Experiments A to E.

Experiment F gives an interesting result. Whereabouts on the nail are the anode areas (blue colour with indicator) which are starting to corrode? Is any part of the nail being protected – at least at first? Does this fit in with your observation of the single steel nail corroding in salt solution in Experiment 2.2b (sample A)?

If part of the metal has been treated in such a way that its structure has been disturbed – for example by hammering or cutting – the atoms may be easier to remove from the surface (as positive ions). Thus, when the piece of metal is in contact with an electrolyte solution, these deformed regions can behave as anodes relative to the less disturbed areas in which the atoms are more tightly held. (Does this suggest a possible explanation for any small current which may flow between two apparently identical steel electrodes at the start of Experiment 2.3c, even before air is blown into one of the half-cells?)

Summary

A metal may tarnish in a dry atmosphere by the formation of a very thin oxide film on its surface. However, a more important process involves solutions or atmospheric moisture as well.

When two metals are in contact with each other and with an electrolyte solution, corrosion can occur as electrons flow from the anode to the cathode of the cell which is set up. The anode gives up electrons as its atoms turn into ions which then form part of the corrosion product. In many cases it can be reasonably predicted that the metal higher up the galvanic series will form the anode and will corrode; this bimetallic effect can be used to protect important structures.

It is not necessary for the two touching pieces of metal to be composed of different types of atoms. One piece of steel, starved of oxygen, is anodic towards another piece of the same metal whose surface is freely supplied with oxygen. Anode and cathode regions can also form on a single piece of metal if these areas have received different mechanical treatment.

The galvanic series in sea water

APPENDIX TO SECTION 2

The 'corroded end' (anodic)

- magnesium
- magnesium alloys
- zinc
- galvanized steel
- steel (mild steel)
- cast iron
- 18—8 stainless steel (active)
- lead
- tin
- nickel (active)
- brass (copper/zinc)
- bronze (copper/tin)
- copper
- nickel (passive)
- 18—8 stainless steel
- silver
- titanium
- gold

The 'protected end' (cathodic)

Note. 'Passive' stainless steel and nickel are covered with oxide films and resist corrosion. When this film is destroyed the metals become more anodic and are said to be 'active'.

figure 31

Magnesium (forming the anode) is cast around a hollow steel core (forming the cathode). At the interface where the two metals touch the magnesium has begun to corrode.

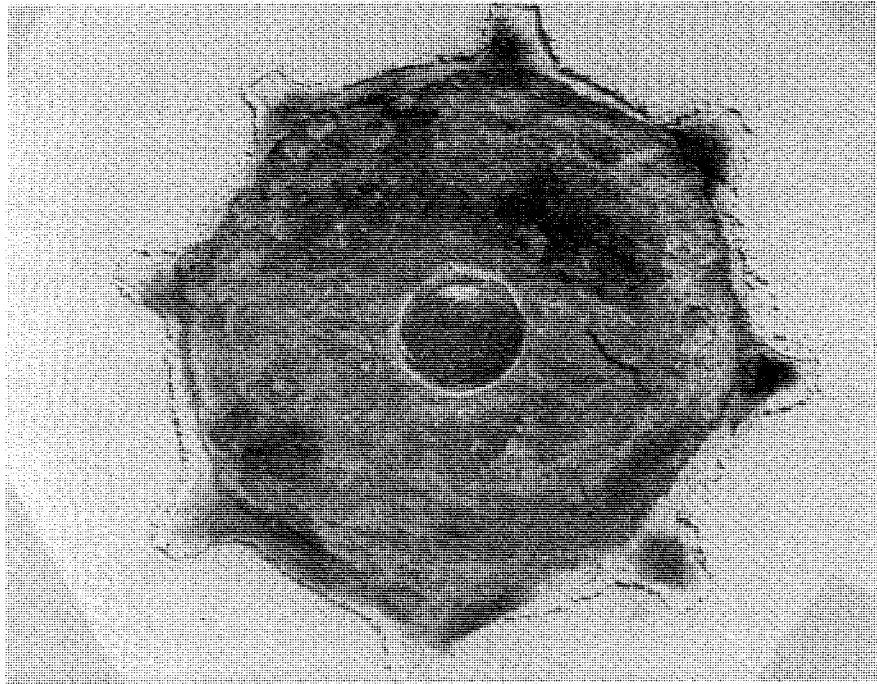
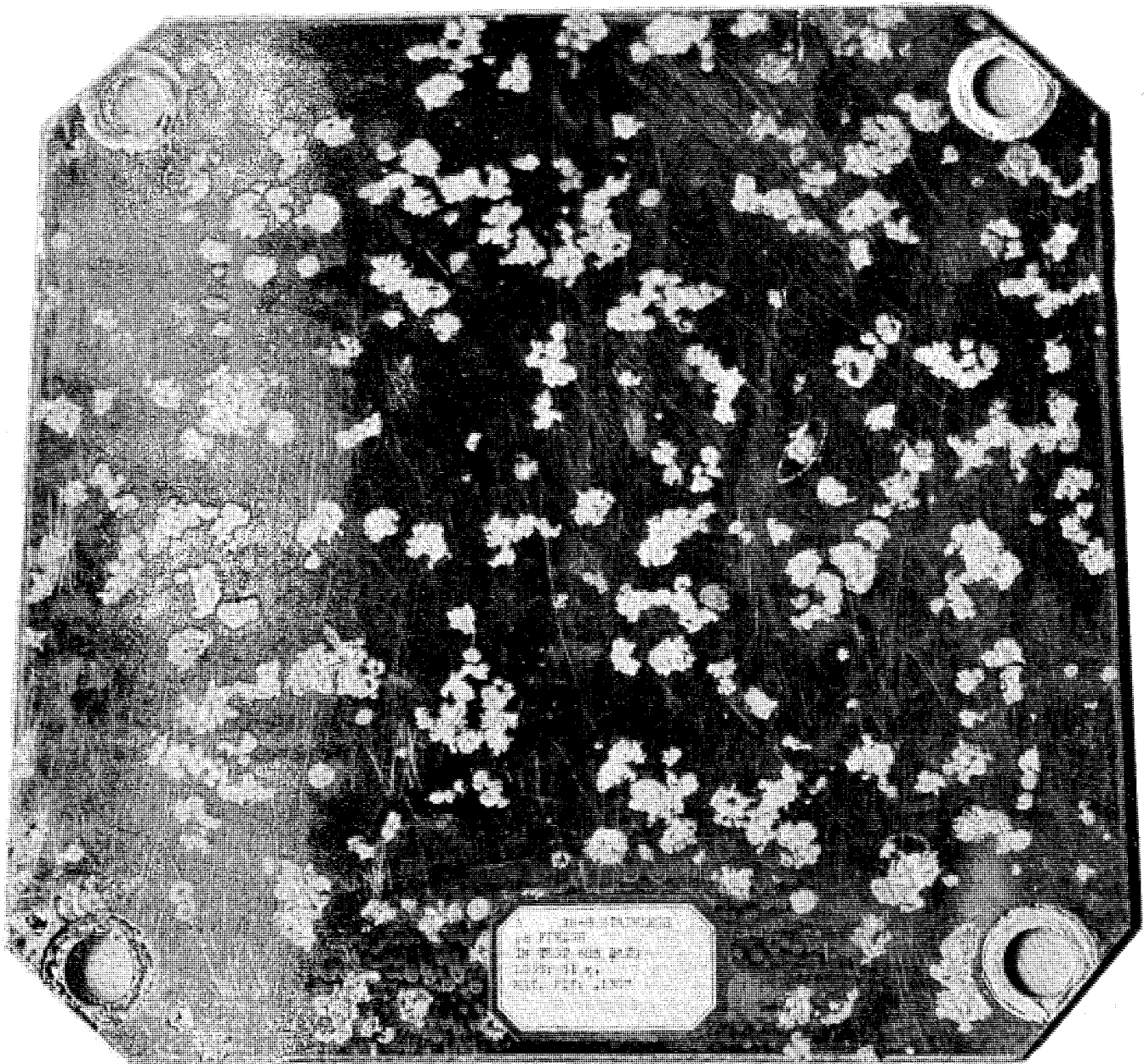


figure 32

Pitting in a metal surface, resulting from local corrosion under marine organisms that became attached to the plate while it was immersed in sea water.



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DECAY

REVIEW QUESTIONS

CORROSION

SECONDARY CHEMISTRY

1. A new stone, Nuffield Pride, is being quarried and you are asked to assess its suitability as a durable building material. Describe any experiments you would carry out to aid you in your assessment. Using chemical tests, how would you find out if the stone is a limestone or a sandstone?
2. It is planned to build a large chemical works and power generating station in your area. A public enquiry is being held to hear objections to the scheme. Outline the case that you, as secretary of a local society concerned with the conservation of historic buildings, would present.
3. Some of the statues in your city are quite badly decayed and the rate of decay seems to be increasing. You are approached by the city architect for your advice. In a written reply, suggest reasons for this and outline possible ways in which the situation could be improved. Point out any problems you foresee.
4. Air pollution is the cause of stone decay! Discuss this statement.
5. You are invited by the local anti-pollution league to give a lecture on the connection between air pollution and stone decay. Describe the experiments you would use to illustrate your lecture.
6. How would you protect the following against corrosion?
 - a. The bodywork of an aircraft
 - b. A motor car body
 - c. A solid gold watch
 - d. Iron railings
 - e. An underground pipe.
7. Water storage tanks are often made of zinc-coated steel. At a *small* break in this coating, the steel will be protected by the zinc. However there have been cases where a plumber has dropped a large steel spanner into such a tank accidentally and has not bothered to recover it. What do you imagine might happen to the zinc after the spanner has been lying on the bottom of the tank for some months?
8. The shrouds (wires supporting the mast) on a seagoing racing dinghy are often made of stainless steel. On one particular boat these were covered by the owner with a fairly close-fitting tube of plastic to provide extra protection against corrosion. After a slight collision with another yacht, a small hole was found in the plastic covering although the exposed metal surface stayed bright and shiny for a long time. Where would you advise the owner in such a case to look for possible corrosion of the shrouds and what action would you recommend him to take to avoid further trouble?
9. What steps would you take in the *design* of a bicycle to minimize the risk of corrosion?
10. Imagine a new metal, 'newfeldium' (Nf), has just been discovered. It is extracted from its ore, newfeldium oxide, by heating with coke. However, when a piece of newfeldium oxide is added to copper sulphate solution it becomes coated with copper and the blue colour of the solution fades. It seems to have promise as a constructional metal. Large quantities of the ore are available. It is melted fairly easily in a furnace but it is nevertheless mechanically strong.

Plan and describe a series of short-term and long-term experiments to investigate the corrosion resistance of newfeldium and methods of protecting it where necessary.

This is one of ten pupils' Options, designed for Stage III of the Revised Nuffield Chemistry course. It is intended that the pupil should undertake two of these Options. Pupils may wish to pursue further some themes they met in Stage II or to study one or two themes in the Alternative they did not do.

This pupils' book aims to present the chemistry of its subject attractively and to stress its relationship to everyday life. It is fully illustrated. Experimental details, including the apparatus required, are given for every investigation which the pupils conduct themselves. Details of teacher demonstrations are given in the corresponding chapter of *Teachers' guide III*, as are all other notes and background information required by the teacher.

The other Options in the series are:

- | | |
|-----------------------|--|
| 1 Water | 7 Periodicity, atomic structure, and bonding |
| 2 Colloids | 8 The chemical industry |
| 3 Drugs and medicines | 9 Analysis with a purpose |
| 4 Metals and alloys | 10 Historical Topics |
| 5 Plastics | |

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The Editor acknowledges with thanks the advice of Dr C.A. Price of the Building Research Station, Garston, Watford, and of Mr E. D. Queenan of the BISRA Corrosion Advice Bureau, in the preparation of the materials.

Teachers' Reference Sets of the materials and multiple copies of the pupils' OPTIONS for classroom use are available through a subscription scheme.

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ISBN 0 582 04645 9