The Mechanism of Rusting

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Introduction

Scaling and Rusting.—The rusting of iron (the formation of hydrated oxide in presence of oxygen and water) must be distinguished from scaling (the formation of anhydrous oxide). In scaling, the oxidation-rate falls off as the thickness of the oxide-scale increases. At high temperatures the thickening rate may be inversely proportional to the thickness. At room temperature the rate falls off more abruptly; recent measurements[1] record 16 Å after a day and 35 Å after a year. The latter thickness is insufficient to produce the interference colours seen on iron after brief heating in air within the range 250–350°c. Films formed on iron by unpolluted dust-free air at room temperatures generally produce no change in appearance; they can diminish reactivity towards certain reagents.

In contrast, the rate of rusting sometimes remains almost constant over considerable periods. The reason for the difference is that in scaling the oxide is formed upon the metallic surface, whilst in rusting it may happen that oxygen is reduced at one place, iron passes into solution at a second place, whilst the iron oxide appears, in hydrated form, at a third place where it cannot interfere with continued attack.

Conditions for Rusting.—A horizontal iron plate fully immersed in any natural water (fresh or saline) with air above the water surface suffers rusting, usually slowly. More rapid rusting occurs if the plate (placed vertically or sloping) is only partly immersed, oxygen being readily replenished where the plate cuts the water-line; as explained later, there is often an unattacked zone at or just below the meniscus.

The rust formed on atmospheric exposure is usually more adherent than that produced by immersion. Exposure outdoors (when the surface is alternately wet and dry) soon sets up rusting, but in highly polluted atmospheres sheltered surfaces sometimes rust more rapidly than those kept clean by rain. Indoors, an unpainted iron surface often remains bright for some time, except where salt particles can settle on it, or where the air contains appreciable amounts of sulphur compounds derived from fuel.

Mechanism.—The corrosion of iron (or zinc) immersed in water or salt solution is undoubtedly electrochemical; the currents have been measured by two in-

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[1] D. Gilroy and J. E. O. Mayne, *Corrosion Science*, 1965, **5**, 55.

dependent methods[2,3] and correlated with the corrosion-rate in the sense of Faraday's law; the good agreement between observed and calculated rates provides quantitative evidence for the electrochemical mechanism. For outdoor atmospheric rusting the evidence is less direct, although Russian measurements[4] on plates covered with a shallow layer of water show that electrochemical action is proceeding. For indoor conditions, also, it is difficult to explain the facts except by assuming an electrochemical mechanism.

Immersed Conditions

Rusting in Potassium or Sodium Salt Solution.—The contrast between scaling and rusting is seen (Figure 1) on comparing (A) the oxidation of steel plates exposed to dry oxygen at 175° and 225°[5] with (B) the corrosion of such plates partly immersed in salt solutions.[2]

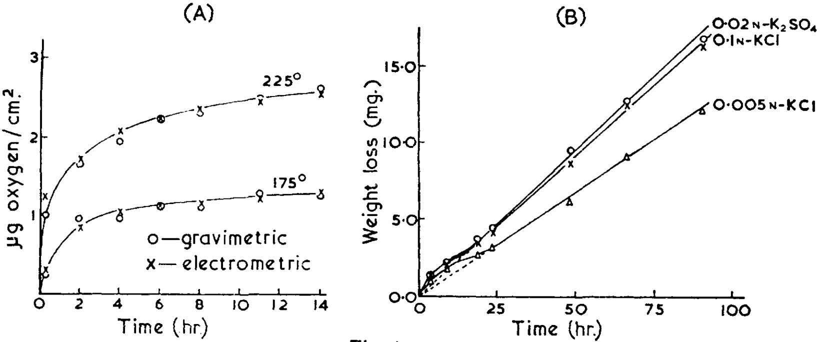

Fig. 1.

In (A) the oxidation-rate falls off with time; in (B), after initial irregularities, the corrosion velocity attains a constant value. This depends only slightly on the solution used. A twenty-fold reduction in the concentration of potassium chloride produces only a small reduction in the corrosion-rate, nor is there much change when sulphate is substituted for chloride. Other measurements have shown that the corrosion-rate on pure electrolytic iron is of the same order of magnitude as the rate obtained on steel.

The fact that the corrosion-rate is so little influenced by either metallic or liquid phase is due to the fact that it is largely controlled by happenings at the meniscus, the only region where oxygen can readily be replenished from the air. Here oxygen is reduced by a *cathodic* reaction, which occurs in steps, but can be summarised:

$$O_2 + 2H_2O + 4e = 4OH^-$$

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[2] U. R. Evans and T. P. Hoar, *Proc. Roy. Soc.*, 1932, *A*, **137**, 343.
[3] J. N. Agar, quoted by U. R. Evans, *J. Iron Steel Inst.*, 1940, **141**, 219P, esp. p. 221P.
[4] L. L. Rosenfel'd, First internat. Congress met. Corrosion, 1961 Report (Butterworths) 1962, p. 243; N. D. Tomashov, Collected papers on 'Corrosion of Metals and Alloys', 1963 (Moscow): English Translation by A. D. Mercer, ed. C. J. L. Booker.
[5] D. E. Davies, U. R. Evans, and J. N. Agar, *Proc. Roy. Soc.*, 1954, *A*, **225**, 443.

This requires four electrons, which are supplied by iron entering the liquid as cations at points lower down the specimen by an *anodic* reaction, which also occurs in steps, but can be summarised:

$$2Fe = 2Fe^{++} + 4e$$

Since the main ions in a potassium chloride solution are K^+ and Cl^-, the cathodic and anodic products can be regarded as potassium hydroxide and ferrous chloride; where they meet they will interact to give a precipitate of a yellow-brown rust consisting of hydrated ferric oxide Fe_2O_3,H_2O or FeO,OH, it being assumed that plenty of oxygen is present; if a narrow vessel is used, restricting the oxygen-supply, a ferroso-ferric compound may be formed. All these facts have been established by direct observation. The alkali and ferrous salt can be detected by simple chemical tests; the precipitation and settlement of the rust are obvious to the eye. The electric current, representing the upward movement of electrons through the iron from anodic to cathodic zone, can be measured directly on a meter if the specimen is cut along the line dividing the expected anodic area from the expected cathodic area [Figure 2(A)]; this is, however, a less accurate method of measuring the total current flowing than others available.[2,3]

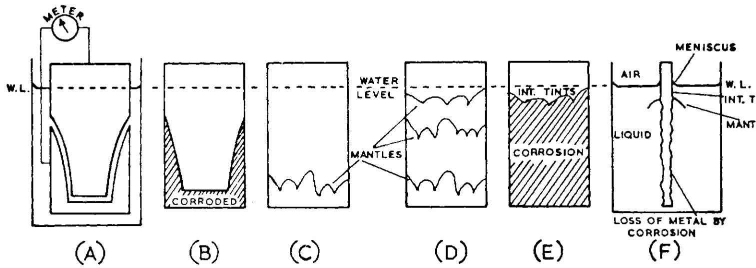

Fig. 2.

The 'corrosion pattern' varies with the physical character of the metal surface. On carefully rolled steel the anodic attack may occur only along the cut edges [Figure 2(B)], where the internal stresses left by the shearing probably prevent the maintenance of a protective film. With less carefully prepared steel, corrosion starts at defects on the face and spreads downwards and sideways over arch-shaped areas. These are first seen at points low down [Figure 2(C)] and later at points higher up [Figure 2(D)]. Arch-shaped 'mantles' of membranous rust grow out roughly at right-angles to the surface, representing the surfaces separating regions wherein OH^- and Fe^{++} respectively predominate. In the end [Figure 2(E) and (F)], nearly the whole surface is corroding, except the zone just below the water-line, where any iron ions escaping from the metal would find themselves in alkaline liquid, so that precipitation must occur in contact with the metal; this area suffers no appreciable corrosion, but usually develops a film thick enough to display interference colours when the specimen is taken out, washed, and dried.

The main body of the rust is precipitated well away from the metal. Its composition and appearance depends on the cross-section of the containing vessel which controls the oxygen supply. It is not impossible that Fe^{++}, OH^-, and O_2 can interact to give hydrated ferric oxide as the first solid phase, but it is generally assumed that ferrous hydroxide or a basic salt is first precipitated and then becomes oxidised. Such oxidation has been studied.[6] Given plenty of oxygen, the product can be α- or γ-FeO,OH, according as the pH value is high or low. With deficiency of oxygen, green ferroso-ferric compounds may appear; these have been studied at Berne,[7] and appear to be not simple hydroxides, but to contain Cl^- or SO_4^{--} groups. With some geometric arrangements, black magnetite is formed. Since, however, a solid formed out of contact with the metallic surface cannot protect, the composition and structure of the rust is not of primary importance. The rate of attack will remain almost constant, unless the liquid is one capable of forming a sparingly soluble substance as cathodic or anodic product. Such cases will now be considered.

Rusting in Magnesium Salt Solution.—The non-protective character of rust formed in a potassium or sodium salt solution is due to its precipitation at a distance from the metal; if formed in contact with the metal surface, rust provides a modicum of protection, as is shown by comparing behaviour of steel in magnesium and potassium sulphates. Steel partially immersed in magnesium sulphate has been found[8] to corrode at slightly more than half the rate caused by distilled water (of the quality used in preparing the solution); the rate was remarkably constant over the concentration-range 0·01–0·45M. In contrast, potassium sulphate corroded the steel much more quickly than the distilled water.

Observations of the attack made the reason quite clear. In a potassium sulphate solution, ferrous sulphate is formed below the mantles and potassium hydroxide above them. The potassium hydroxide, being soluble, is soon dispersed into the liquid, and, except on the interference-tint zone just below the meniscus, there is no protection. With magnesium sulphate, there is a similar formation of arch-shaped areas, first low down [Figure 2(C)] and then higher up [Figure 2(D)]. But here the magnesium hydroxide formed by cathodic action just above the lowest arch-shaped mantles does not disperse, being sparingly soluble. It is deposited on the metal, and, when the attack becomes directed on higher points, the ferrous ions formed by anodic action underneath the adherent magnesium hydroxide convert it into an iron compound. First a green ferroso-ferric layer appears and then a brown rust; these clinging deposits contain magnesium, and the green is far brighter and the brown distinctly lighter than corresponding deposits containing no magnesium; probably, in the green substance, some Mg^{2+} ions replace Fe^{2+}. In the end, the whole area is covered with clinging rust except for a narrow horizontal strip of white magnesium hydroxide 1 to 2 mm. broad at the meniscus. The important feature of the situation is that

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[6] J. E. O. Mayne, *J. Chem. Soc.*, 1953, 129.

[7] W. Feitknecht and G. Keller, *Z. anorg. Chem.*, 1950, **262,** 61.

[8] U. R. Evans, *J. Soc. Chem. Ind.*, 1928, **47,** 55T, esp. p. 58T.

the solid matter is deposited upon the metallic surface instead of being precipitated at a distance, so that there is appreciable interference with attack.

Rusting in Sea-water.—Magnesium and calcium are invariably found in sea-water. At one time N/10 sodium chloride was often used to represent sea-water in laboratory corrosion tests, but generally it corrodes more rapidly. At first the difference may not be great, but it becomes important after times sufficient for clinging rust to be formed; in experiments lasting 128 days, sea-water, collected from the English Channel, caused only one third of the corrosion of N/10 sodium chloride.[9]

In certain circumstances, however, sea-water may be more corrosive than sodium chloride solution. Harbour waters containing organic sulphur compounds, such as cystine, can be very dangerous, whilst the mud of estuaries may contain sulphate-reducing bacteria, which render the oxygen of SO_4^{2-} available for the cathodic process. Atmospheric rusting near the coast is probably favoured by magnesium chloride in the salt, which prevents drying.

Rusting in Hard Fresh Waters.—Many waters used for supply purposes contain calcium bicarbonate as main constituent. A pure solution of calcium bicarbonate is unstable and would deposit solid calcium carbonate if an excess of carbonic acid were not present; the amount of carbonic acid needed for stability depends on the $Ca(HCO_3)_2$ concentration, and the relationship between stabilising carbonic acid and hardness has been established by German work;[10,11] the results accord well with calculations based on the law of mass action, if allowance is made for activity coefficients.

If water carries more carbonic acid than is needed for stability, the excess is known as 'Aggressive Carbonic Acid'. Such water will dissolve solid calcium carbonate, the pH rising as a result. The old 'marble test', useful for providing a rough forecast of the corrosive character of a water, consisted in determining the pH value before and after contact with marble dust, the difference between two values being known as the Langelier Index; its significance as a measure of corrosive power has perhaps been overestimated, since other constituents of a water affect behaviour, but any water in which marble produces an appreciable pH rise is open to suspicion, and should be subjected to more reliable tests based on iron or steel specimens.

If a water is free from aggressive carbonic acid (*i.e.*, if it would fail to dissolve calcium carbonate), it will quickly deposit on iron or steel a layer of chalky rust (or rusty chalk) possessing some protective character. If, for instance, such a water is run through a pipe, any incipient corrosion will raise the pH by the cathodic reaction, and a layer of chalk, later converted in part into ferrous carbonate and thereafter to clinging rust, will be deposited, gradually spreading

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[9] C. A. J. Taylor, quoted by U. R. Evans 'Corrosion and Oxidation of Metals', Arnold, London, 1960, p. 165.

[10] G. Bodländer, *Z. phys. Chem.*, 1900, **35**, 23.

[11] J. Tillmans and O. Heubleim, *Gesundheits-Ingenieur*, 1912, **35**, 669.

over the surface, as in the experiments with magnesium sulphate; this will be equally true, whether the cathodic points are particles of mill-scale remaining on the surface, or cementite particles within the steel, or again areas where the oxygen is preferentially renewed. The protection is not complete, but, in absence of complicating factors, the corrosion will be much less severe than that produced by water containing aggressive carbonic acid, which can build no continuous 'chalky film'.

A non-aggressive water may become aggressive if softened by base-exchange, since the replacement of $Ca(HCO_3)_2$ by $NaHCO_3$, even if only partial, lessens the requirements for stabilising carbonic acid, so that some of the H_2CO_3 present becomes 'aggressive'. The danger could be removed by passing the water over limestone or (better) calcined dolomite, but this would re-introduce some hardness. Much of the excess of carbonic acid can be removed by simply passing the water down a series of cascades, or even allowing it to overflow from the top of a vertical pipe. Such treatment has been found useful at water-works for avoiding corrosion complaints, not only from softened water, but also from water which contains carbonic acid derived from the vegetation of the collecting area, especially at certain seasons of the year.

Rusting of Totally-immersed Iron under Stagnant Conditions.—Long-period studies on horizontal discs fully immersed at a known distance below the surface have been carried out at Teddington,[12] the reaction being followed by measuring the disappearance of oxygen from the air-space above the liquid, generally a solution of potassium chloride. Under stagnant, vibration-free conditions, the rate of attack is usually slow, being controlled by the rate at which oxygen reaches the disc. It is greatest when the upper surface of the disc is very close to the water surface. On a disc of fixed diameter the corrosion-rate rises with increasing breadth of the containing vessel, which provides a larger area of water surface; if it is assumed that only a small fraction of water molecules striking a water surface pass into the body of the liquid, this would be expected. Corrosion is accelerated if the oxygen pressure in the gas space above the liquid is increased, but at a certain level (about 25 atm.), protective-film formation begins to retard attack; even at lower pressures (2–5 atm.) corrosion is diminished if the specimen is exposed dry to oxygen *before* the liquid is introduced.[13]

Under conditions where oxygen-supply is limited, ferroso-ferric products appear as well as ferric rust, generally black magnetite rather than the green compounds mentioned above. In the Teddington experiments in N/10 potassium chloride, the corrosion-rate was constant for twenty days and then declined, owing to an 'alteration in the physical character of the anodic film'. For the first 500–600 days the corrosion product consisted of a thin layer of magnetite overlain by a loose mass of hydrated ferric oxide, which could be shaken off without

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[12] G. D. Bengough, A. R. Lee, and F. Wormwell, *Proc. Roy. Soc.*, 1931, *A*, **134**, 308; 1933, *A*, **140**, 399; Third Report of Corrosion Committee, 1935, p. 123 (Iron and Steel Inst.).

[13] G. D. Bengough and F. Wormwell, quoted by U. R. Evans 'Metallic Corrosion, Passivity, and Protection', Arnold, London, 1946, p. 297.

affecting the corrosion rate. Later, a change to a more coherent form was accompanied by a steady decrease in the corrosion-rate.

A French study[14] of iron in distilled water or soft water also revealed fairly adherent magnetite covered with brown ferric rust. Apparently the magnetite formed the cathode of a corrosion couple and the iron the anode, for the corrosion of iron was found to be stimulated by contact with magnetite, whereas contact with rust had little effect.

Rust Prevention by Inhibitors.—Whilst magnesium or calcium salts merely slow rusting, certain inhibitors, like sodium hydroxide, sodium phosphate, or potassium chromate, can prevent it altogether. Instead of loose rust, an invisible film is produced; the film formed on iron placed in a solution of sodium hydroxide or phosphate has been identified by electron diffraction[15,16] as γ-ferric oxide;* that formed in chromate generally contains chromium.[17]

In sodium hydroxide, the film-formation can be ascribed to OH^- ions driven up to anodic points by the current, or attracted by adsorption forces; the anodic reaction consists in the removal of the H from the oriented hydroxyl, leaving oxide on the surface [Figure 3(A)]; the process can be repeated [Figure 3(B)] until the oxide becomes sufficiently thick for protection (or perhaps until the store of loosely bonded iron atoms becomes exhausted). If the liquid contains Cl^- in excess of OH^- [Figure 3(C)], there will be places where Cl^- is adsorbed instead of OH^-, and the anodic reaction will there be the movement of a metal ion into the

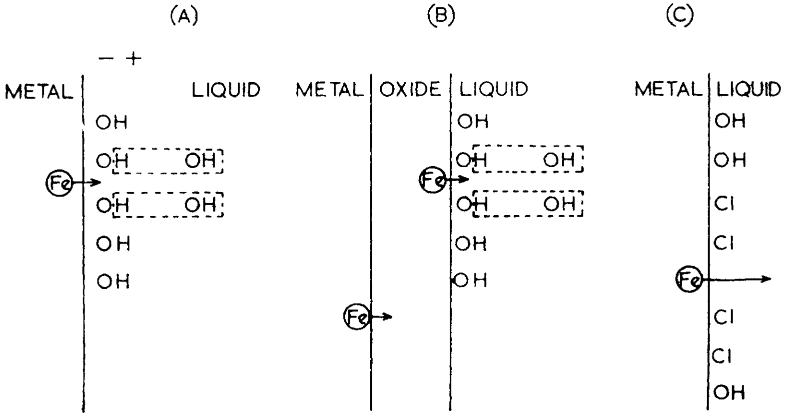

Fig. 3.

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* The so-called γ-ferric oxide often contains hydrogen and is sometimes regarded as magnetite with the ferrous ions replaced by pairs of protons (M. C. Bloom and L. Goldenberg, *Corrosion Science*, 1965, **5**, 623); this view is not held universally.

[14] E. Herzog, *Bull. Soc. chim. France*, 1936, **3**, 1530; 1938, **5**, 187; *Corrosion et Anti-corrosion*, 1964, **12**, No. 5.

[15] J. E. O. Mayne, J. W. Menter, and M. J. Pryor, *J. Chem. Soc.*, 1950, 3229.

[16] J. E. O. Mayne and J. W. Menter, *J. Chem. Soc.*, 1954, **99**, 103.

[17] R. M. Brasher and E. R. Stove, *Chem. and Ind.*, 1952, 171.

liquid, not the detachment of H from OH; the two reactions involve the same electron transfer, but only if Cl^- is present will there be corrosion and rusting. If to a chloride solution, OH^- is added in quantity just insufficient to prevent corrosion at the most susceptible spots (*e.g.*, where the iron atoms are most loosely packed), it will attack iron locally but intensely; the immune area provides a large cathode for oxygen-reduction, and, since the attack is concentrated on small anodic spots, the corrosion per unit area will there be rapid, and the rate of penetration serious. A small anodic area surrounded by a large cathodic area generally represents a dangerous combination.

The criteria deciding between (1) film-formation and (2) passage of ferrous ions into the liquid, with rust formation where they interact with alkali from the cathode, have been discussed elsewhere.[18] Under nearly reversible conditions the preferred reaction will be that which leads to the greatest drop of free energy. But where a high anodic current density is imposed by happenings at the cathodic area, there may be an insufficient supply of ions possessing the necessary activation energy to pass through the positive zone, and the iron may become 'passive' even when the free-energy criterion would predict continuing attack. A reducible substance capable of stimulating the cathodic reaction may thus favour passivity; under certain circumstances oxidising agents inhibit corrosion, although the situation is complicated. Pertechnetates, although less strong oxidising agents than chromates as judged by the redox potention, are better inhibitors, as shown by work at Oak Ridge;[19] they possess, however, only academic interest, since the supply, coming from certain atomic energy plants, is limited.

Atmospheric Conditions

The Rǒle of Sulphur Dioxide.—Iron exposed to humid air in absence of dust and sulphur dioxide suffers little or no rusting. The rapid formation of rust in industrial and urban districts has long been attributed to acidity, but earlier investigators regarded carbon dioxide as responsible. Work at South Kensington and Teddington[20] showed that sulphur dioxide was the main cause of atmospheric corrosion at inland places, and that carbon dioxide could even retard attack. The opening stage of rusting in moist air containing sulphur dioxide proceeds rapidly, and is probably analogous to the opening stage of the 'fogging' of nickel, which was found in South Kensington work[21] to require sulphur dioxide (or suspended sulphate particles) and a relative humidity exceeding a critical value (about 70%). Sulphur dioxide is adsorbed and then combines at catalytically active points with atmospheric oxygen and water giving sulphuric acid, which collects more water; this attacks the metal by well-established reactions, today regarded as electrochemical, producing iron (or nickel) sulphate. When once ferrous sulphate has appeared on an iron or steel surface, the specimen can be

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[18] U. R. Evans, First internat. Cong. met. Corrosion 1961. Report (Butterworths), p. 1.

[19] G. H. Cartledge, *J. Phys. Chem.*, 1955, **59**, 979; 1956, **60**, 28, 1057; 1957, **61**, 973; *Corrosion*, 1965, **21**, 217.

[20] W. H. J. Vernon, *Trans. Faraday Soc.*, 1924, **19**, 886; 1927, **23**, 159; 1935, **31**, 1678; *Chem. and Ind.*, 1943, p. 318; *J. Roy. Soc. Arts*, 1949, **97**, 589.

[21] W. H. J. Vernon, *J. Inst. Metals*, 1932, **48**, 121.

exposed to an atmosphere containing moisture but no sulphur dioxide, and rusting can nevertheless continue; in fact, an iron specimen carrying lines of ferrous sulphate crystals, develops rust along those lines when exposed to a moist atmosphere. One atom of sulphur can cause the transformation into rust of many atoms of iron, a point brought out by detailed researches at Stuttgart.[22] Any theory of the formation of rust by ferrous sulphate must embody a regeneration mechanism; it must also explain the fact that, whilst the outer part of the rust is loose (it can be wiped off on filter paper), the inner part is adherent and resists vigorous scrubbing.

One suggestion is that the ferrous sulphate is oxidised to the ferric state and that hydrolysis produces ferric rust and sulphuric acid, which then attacks a further quantity of iron. This 'oxidative hydrolysis' may indeed be responsible for the loose outer portions of the rust (the detection of a trace of ferric sulphate supports the idea), but it can hardly account for the tightly adherent layer. If the acid liberated by hydrolysis were continually attacking the metallic surface to which the rust was attached, adhesion would be impossible. It is more likely that there is electrochemical action, with the anodic attack on the iron in pits and reduction of oxygen on the face outside (Figure 4). It has been demonstrated[23] that such action can indeed produce highly adherent rust at a well-ærated cathodic zone. Since as many ferrous ions are produced by the anodic attack as are used up in cathodic rust-deposition, complete regeneration is provided, and the mechanism explains a curious fact that, although soluble salts are easily detectable in the opening stages of rusting, they seem largely to disappear later; presumably, the anions migrate into the pits, thus hiding themselves 'underground'.

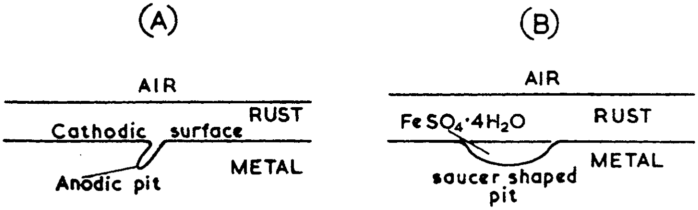

Fig. 4.

Although in the early stages the pits may be crevices [Fig. 4(A)], they seem to extend laterally, and after a time become saucer-shaped [Fig. 4(B)]. At that stage the ferrous sulphate becomes accessible. On steel exposed outdoors for some years, it has been identified independently at Northwich[24] and Battersea[25] as $FeSO_4,4H_2O$. The appearance of the tetrahydrate is significant and confirms the fact that the ferrous sulphate is an anodic product; towards

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[22] G. Schikorr, *Werkstoffe u Korrosion*, 1963, **14**, 69; 1964, **15**, 457.
[23] U. R. Evans, *Nature*, 1965, **206**, 980.
[24] R. S. Thornhill, personal communication, 1952.
[25] A. G. Tanner, *Chem. and Ind.*, 1964, p. 1027.

pure water the heptahydrate is the stable phase, but anodic action is known[26,27] to develop acidity, and the presence of sulphuric acid would favour the formation of a lower hydrate.[28] It would be expected that, sooner or later, the lateral extension of the anodic area would undermine the rust layer, and this indeed occurs. The periodical shredding of atmospheric rust in large flakes has been noted by several investigators.

In the early stages, the cathodic reaction may be the reduction of O_2 to OH^-. When once rust has accumulated, however, the cathodic reaction can be an entry of ferrous ions into the ferric rust to form a ferroso-ferric compound, which is then reoxidised to the ferric state by atmospheric oxygen.[*] This two-stage (catalytic) mechanism may well proceed more smoothly than the direct reduction of oxygen; the matter is under investigation. Whatever the details, the electrochemical mechanism of atmospheric attack is today generally recognised.

In the advanced stages of outdoor rusting, formation of fresh rust is seen preferentially at points where nests of ferrous sulphate exist in the existing rust; this supports the catalytic mechanism. The effect of ferrous sulphate nests is shown by work at Stuttgart[29] and also, in connection with paint-breakdown, at Cambridge.[30] The presence of ferrous sulphate or chloride in rust is the main reason why painting over rust gives poor protection. Owing to their strong adhesion, rust traces are difficult to remove; if shut in below a paint-coat, they cause local formation of fresh voluminous rust, which pushes away the coat and causes it to break.

Corrosion Probability.—Common observation shows that when steel is exposed to the atmosphere, rusting starts locally and parts may still be bright after long periods. It is necessary, therefore, to consider the probability of the inception of corrosion. One method of measuring probability[31] consists of placing drops of distilled water on a horizontal surface and counting the proportion which developed rust. When the atmosphere is an oxygen–nitrogen mixture, the probability declines as the oxygen content is raised, although the 'conditional velocity' of the corrosion, produced by those drops which corrode at all, increases. Below the drops which produce no obvious change, the iron probably

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[*] Omitting combined water, we can write the cathodic reaction $Fe^{2+} + 4Fe_2O_3 + 2e = 3Fe_3O_4$; this destroys the same amount of Fe^{2+} as is liberated by the anodic reaction, $Fe = Fe^{2+} + 2e$. Since the oxidation of $3Fe_3O_4$ by air will yield 4·5 Fe_2O_3 instead of the original 4·0 Fe_2O_3, it is evident that the iron destroyed in the pits is appearing as rust on the face. Two-stage experiments, now being carried out by C. A. J. Taylor, (with iron exposed first to moist air containing SO_2 and then to moist air without SO_2) show that the rusting continues as quickly as it does when SO_2 is present in the second stage; if, between the two stages, the iron is immersed in water, there is practically no rusting in the second stage. This shows that it is the soluble iron sulphate and not the rust which causes the rusting to continue in the absence of SO_2. Other experiments at Cambridge have provided evidence of the *electrochemical mechanism of atmospheric corrosion.*

[26] T. P. Hoar, *Trans. Faraday Soc.*, 1937, **33**, 1152.

[27] C. Edeleanu and U. R. Evans, *Trans. Faraday Soc.*, 1951, **47**, 1121.

[28] T. P. Hoar, personal communication, 1965.

[29] H. Schwarz, *Werkstoffe und Korrosion*, 1965, **16**, 93, 208.

[30] J. E. O. Mayne, *J. Appl. Chem.*, 1959, **9**, 673.

[31] R. B. Mears and U. R. Evans, *Trans. Faraday Soc.*, 1935, **31**, 527.

develops a protective film.

It has been found[32] that the presence of sulphur in the steel, and also its presence in air (generally as SO_2), increases both corrosion probability and also conditional velocity. This largely explains the bad behaviour of unpainted steel in modern times, and also the surprisingly good behaviour of ancient iron in unpolluted atmospheres.

The influence of the sulphur dioxide content of the air on the rate of atmospheric rusting was clearly brought out in the British corrosion tests[33] by a comparison of behaviour at exposure stations representing different degrees of pollution, and equally in the German[34] and Indian[35] tests by a comparison of behaviour at different seasons.

Oriental Iron.—Iron produced in Eastern countries in early times, presumably with charcoal as fuel, must have contained very little sulphur; some of the old iron beams, pillars, or chains are in places still remote from industrialisation, where the air is almost free from sulphur dioxide. The Delhi pillar, probably erected in the fourth century and moved to the present site in the twelfth century, provides an example. Three analyses quoted in an Indian publication[36] record only a 'trace' of sulphur in the portion above ground and 0·008% in the underground part. The upper portion of the pillar has remained rust-free, and most of it is described as bronzy or bluish by different writers; evidently, of the two alternative reactions, oxide-formation has prevailed, and during sixteen centuries exposure at temperatures periodically elevated by the sun, the film has reached visible thickness. The Reviewer is inclined to ascribe the immunity to low probability rather than low velocity; in the lowest part (possibly owing to salts from the soil) corrosion has occurred. However, numerous other views have been expressed. One author[37] attributes the good behaviour simply to the absence of atmospheric pollution; others to the absence of manganese[36] or the presence of phosphorus.[36]

Mediæval British Wrought Iron.—The good performance of wrought iron in our mediæval buildings is responsible for the belief that, if only the traditional process of making wrought iron could be revived, rusting would be avoided. It is, however, probable that the absence of sulphur compounds from the air in early days was responsible for the comparative absence of corrosion trouble. Exposure tests[38] carried out about 1931–1938 showed that wrought iron suffered

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[32] R. B. Mears, *Carnegie Schol. Memoirs* (*Iron and Steel Inst.*), 1935, **24,** 69.

[33] J. C. Hudson, Sixth Report of Corrosion Committee, 1959, p. 9 (Iron and Steel Inst.).

[34] G. Schikorr, *Werkstoffe und Korrosion*, 1964, **15,** 457.

[35] B. Sanyal and P. D. V. Bhadwar, *J. Soc. Ind. Res.* (*Kanpur*), 1951, **18A,** 69; B. Sanyal, G. K. Singhania, and V. K. Nigam, *Lardev J. Sci. Tech.*, *India*, 1965, **3,** 104.

[36] National Metallurgical Laboratory Technical Journal (Jamshedpur), Feb. 1963 (Delhi Iron Pillar number). The paper by W. E. Bardgett and J. F. Stanners on p. 24 appeared also in *J. Iron Steel Inst.*, 1963, **201,** 3.

[37] J. C. Hudson, *Nature*, 1953, **172,** 499.

[38] J. C. Hudson, 'Corrosion of Iron and Steel' (Chapman and Hall) 1940, p. 82; J. C. Hudson and J. F. Stanners, *J. Iron Steel Inst.*, 1953, **180,** 27.

corrosion only slightly more slowly than ordinary mild steel and at a rate rather similar to steel containing 0·2% of copper. It is right to note that the wrought iron used for these tests probably contained more sulphur than the iron made in mediæval times when charcoal was used as fuel both in the puddling furnace and the forge. But Swedish iron made with charcoal corroded more rapidly than the British iron. The subject is complicated by the fact that British wrought iron, after puddling and piling, contains much slag, and consists of a series of parallel layers, some very susceptible to attack and others resistant;[39] as a result, the corrosion velocity parallel to the layers is much faster than in the normal direction. It would, however, not be possible, when beating out iron ornaments at the forge, to arrange that the resistant layers are always parallel to the surface. There is little doubt that it is the increased sulphur content of the air, and not that of the metal, which explains the enhanced rusting of modern times.

Low-alloy Steels.—It has been mentioned that the addition of 0·2% of copper to mild steel reduces the corrosion-rate roughly to the level of wrought iron. Small amounts of nickel, chromium, aluminium, and molybdenum (often in combination with copper) provide even better results, as shown by extensive tests in the U.S.A.[40] and the U.K.[38] These 'low-alloy' steels are not non-rusting and must be distinguished from the stainless steels containing 13% of chromium (or, in the austenitic type, 18% chromium and 8% nickel). They do, however, corrode more slowly than unalloyed steel, and are relatively cheap; one commercial product with 0·5% copper, 1·0% chromium, 0·16% phosphorus, and 0·8% silicon corrodes at about one-third of the rate of ordinary mild steel.[38] That chromium gives protection will cause no surprise, but the action of copper is less easy to explain. An American authority,[40] who observes that the rust on the more resistant steels is darker, more adherent, and of finer texture than that on the less resistant, believes that the presence of copper or nickel locks up the sulphate in insoluble form as a complex basic salt.

The Role of Salt.—It is common knowledge that atmospheric rusting occurs quickly near the sea. At places where both temperature and humidity are high, corrosion is particularly rapid; probably the presence of hygroscopic magnesium chloride along with the sodium chloride here helps corrosion, retarding evaporation of droplets that strike a steel surface.[41] Careful study in West Africa[42] has shown how the amount of air-borne chloride, and with it the corrosion-rate, decline as the distance from the sea increases; later trials conducted in the U.K. have brought out a similar relationship.

Even far inland, dry salt particles may be present in dust; if these are hygroscopic, they may set up corrosion where they settle on steel. The fact that dust

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[39] J. P. Chilton and U. R. Evans, *J. Iron Steel Inst.*, 1955, **181**, 113; 1957, **185**, 497; 1957, **186**, 98.

[40] H. R. Copson, *Proc. Amer. Soc. Testing Materials*, 1945, **45**, 554; 1948, **48**, 191; 1952, **52**, 1005.

[41] U. R. Evans and S. C. Britton, *J. Soc. Chem. Ind.*, 1930, **49**, 173T.

[42] H. R. Ambler and A. A. J. Bain, *J. Appl. Chem.*, 1955, **5**, 437; 1960, **10**, 213.

can cause rusting has long been known, and classical work at South Kensington[43] has shown that different types of particle behave very differently; silica was found to be harmless, but particles of ammonium sulphate initiated rust spots. When a steel surface was exposed to dust-free air for eleven weeks, it was found to become relatively immune from rusting even if, later, dusty air was admitted. It should not, of course, be assumed that it requires eleven weeks to produce a film over the surface; optical measurements at Trondheim[44] show that an invisible oxide-film 20 Å thick can appear within 10 minutes; probably the need for the long exposure is due to the fact that at first the film keeps cracking, and only after internal stresses have been used up in repeated cracking followed by repair can the invisible film contribute effectively to protection.

Particles of hygroscopic salts are the most dangerous, at least indoors, and an analytical study of dust in factories might assist corrosion control. Early work at South Kensington and Teddington[20,43] has shown the importance of the relative humidity (R.H.) of the air. Interesting results have also been obtained at Zürich.[45] Saturated sodium bromide solution stands in equilibrium with air of 59% R.H. at 20°C; thus a solid particle of sodium bromide will become damp if the air humidity exceeds 59%. It was found that steel inoculated with sodium bromide remained unrusted in air of 50% R.H., and developed rust at 60% R.H. But the passage from immunity to rusting was not always sharp. Saturated sodium chloride solution is in equilibrium with air of 78% R.H. Steel carrying sodium chloride becomes strongly rusted at 80% R.H. and remains bright at 60%; at 70%, the salt particles become brown, and there is some attack. Among hygroscopic salts liable to set up rusting even in unusually dry air may be mentioned the chlorides of zinc, lithium, magnesium, and calcium; their saturated solutions stand in equilibrium with air of 10%, 15%, 32%, and 32·3% R.H. respectively.

The rusting set up at a point where a salt-particle rests on iron or steel may spread, if humidity conditions are favourable. Uniform spreading gives expanding circles, but frequently if, through some irregularity, advance commences more quickly at certain points on the periphery than others, thread-like growths develop. This 'filiform' corrosion cannot be discussed here. The reader is referred to an excellent paper from Teddington,[46] in which an electrochemical mechanism is favoured.

Final Remarks

General Conclusions.—The place of formation of rust is all-important. Under immersed conditions a hard water which can throw down a sparingly soluble compound by the cathodic reaction, so that the rust is formed in contact with the metal, will cause less rapid corrosion than a water causing loose rust. Under atmospheric conditions, the closely adherent character of the rust is a less welcome feature making removal difficult; the rust usually contains soluble

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[43] W. H. J. Vernon, *Trans. Faraday Soc.*, 1924, **19**, 886; 1927, **23**, 159.

[44] A. B. Winterbottom, *Trans. Electrochem. Soc.*, 1939, **76**, 326.

[45] A. Bukowiecki, *Schweizer Archiv. angew. Wiss.*, 1957, **33**, 97.

[46] R. St. J. Preston and B. Sanyal, *J. Appl. Chem.* 1956, **6**, 26.

ferrous salts, paint coats applied over rust-traces may be pushed away at the situations of salt-nests, suffering breakdown. Special paints designed to convert ferrous sulphate to harmless compounds are described elsewhere.[47]

Thanks are due to F. Wornwell, R. S. Hudson, J. F. Stanners, and J. E. O. Mayne for useful discussions, and to C. A. J. Taylor who drew the diagrams.

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[47] U. R. Evans and C. A. J. Taylor, *Trans. Inst. Metal Finishing*, 1962, **39**, 188; 1965, **43**, 169.