

CXCVIII.—*The Influence of a Soluble Fluoride on the Corrosion of Iron.*

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AMONG the properties of the soluble chlorides are those of accelerating the corrosion of iron immersed in water or aqueous solutions of salts, and, if the solution contains an inhibitor of corrosion, of causing localised attack due to the penetration by the chloride ions of the protective film formed on the metal by the inhibitor.

Marked differences are often observed, however, between the properties of chlorides and those of the corresponding fluorides, and it seemed desirable to determine whether the chlorides and fluorides were dissimilar with regard to their corrosive effects on iron. Experiments were therefore carried out on the corrosion of iron foil in solutions of potassium fluoride alone or with the addition of one of the inhibiting agents, sodium carbonate or potassium chromate, and essential differences were observed between the results of these and of control experiments conducted with corresponding solutions of potassium chloride.

EXPERIMENTAL.

Potassium fluoride was employed for the preparation of the solutions, as it can easily be obtained in a state of purity and is readily soluble in water. The iron foil (0.11 mm. thick) gave the following analysis: C, 0.035; Si, 0.005; Mn, 0.02; S, 0.011; P, 0.005%; Ni and Cr, absent. It was cut into strips, 100 mm. by 25 mm., which were cleaned by rubbing with carborundum powder (No. 120) on a wet cloth, washed with water, dried on a soft cloth, and, for the quantitative experiments, kept in a desiccator for an hour before being weighed. Each strip was placed at an angle of 30° to the vertical in a tumbler containing 150 c.c. of the solution to be tested, the total area immersed in the liquid being 35 sq. cm. The condition of the metal surfaces was examined from time to time, and in some cases the loss in weight of the metal was determined (compare Evans, *J. Inst. Metals*, 1923, **30**, 257; *J. Soc. Chem. Ind.*, 1925, **44**, 163T; 1927, **46**, 347T; *J.*, 1929, 111). All experiments were carried out in duplicate.

Corrosion in Solutions of Potassium Fluoride or Potassium Chloride.—In solutions of potassium fluoride or chloride of concentration 0.7*N* or below, corrosion occurred in exactly similar fashion, an immune area of small but variable depth being left immediately below the water line, whilst the remainder of the specimen underwent general corrosion and became coated on its upper surface with a loose blanket of rust.

The same phenomenon was observed in stronger solutions of potassium chloride up to saturation point, but when the concentration of the potassium fluoride solutions was increased to 0.85*N* and above, corrosion abruptly ceased, a few specimens showing a slight localised dulling of the surface but the majority remaining bright. Two series of quantitative experiments gave the following results (after corrosion the metal was cleaned with a bristle brush before being washed and dried):

Series 1.

Conc. of KF or KCl, <i>N</i>	0.0 (water)	0.1	0.5	1.0
Loss in weight (mg.) after 70 hours	{ in KF	20.9	18.1	0.3
	{ in KCl	12.1	19.8	16.6

Series 2. KF only.

Conc., <i>N</i>	1.0	0.95	0.90	0.85	0.80	0.70	0.50
Loss in weight after 70 hours (mg.).....	0.2	0.2	0.0	0.4	17.6, 1.2	17.6	18.5

Each of these values is the mean of two concordant results with the exception of those at 0.8*N*, where general corrosion took place in one specimen and the attack was confined to a small area in the other. This concentration represents the border-line between inhibition and acceleration of the corrosion process.

The potassium fluoride used gave a clear solution in water and the inhibition occurred equally well when the solution was prepared and the iron exposed in vessels coated internally with paraffin wax. The abrupt transition from acceleration to inhibition, therefore, was not due to the deposition on the metal of a film of silicon compound derived either from the original salt or from the glass of the vessel; neither was it caused by the solutions being or becoming alkaline, for indicator tests showed that a p_H value of 7—8 was maintained throughout the experiments.

The conclusion, therefore, seems inevitable that the attack on the metal is prevented by a protective film formed on its surface as an immediate corrosion product, probably consisting of a fluoride or double fluoride of iron. This view furnishes an explanation of the abrupt change in the properties of the fluoride solution at 0.8*N*-concentration, which thus corresponds with a stage at which the film becomes completely self-repairing; and it is confirmed by the behaviour of the metal in *N*-fluoride solutions containing potassium chloride (*N*/200, *N*/50, and *N*/10). In these solutions the metal was attacked, not over the whole surface, but only at the water line,* which is usually one of the weakest places in a protective film (compare Evans, *loc. cit.*).

Corrosion in the Presence of Inhibitors.—In concentrations of 0.7*N* and under, *i.e.*, less than the minimum required to produce a self-repairing protective film, the corrosive effects of solutions of potassium fluoride and potassium chloride were indistinguishable. It seemed, therefore, of interest to determine whether this resemblance extended to the property possessed by the chloride ion of penetrating the films formed on the metal surface by inhibitors of

* One specimen in *N*-potassium fluoride and *N*/10-potassium chloride developed general corrosion, and one in *N*-potassium fluoride and *N*/200-potassium chloride remained unattacked.

corrosion. Sodium carbonate and potassium chromate were selected as the inhibitors, and their effects on the corrosive properties of solutions of potassium fluoride and of potassium chloride were compared.

An $N/2$ - or $N/10$ -solution of potassium fluoride which was also $N/10$ (i.e., $M/20$) with respect to sodium carbonate had no visible action on the iron foil. The fluoride ion evidently penetrates the protective film produced by the sodium carbonate less easily than the chloride ion, for localised attack with formation of rust spots took place in $N/10$ -sodium carbonate when as little as $N/50$ -potassium chloride was present (compare Friend and Marshall, J., 1914, **105**, 2776).

Localised attack occurred in $N/1$ -, $N/20$ -, and $N/50$ -solutions of potassium chloride containing potassium chromate up to $M/20$ -concentration and in $N/100$ -potassium chloride containing $M/40$ -chromate. With potassium fluoride in place of the chloride, no corrosion occurred in N -solutions whatever the concentration of chromate (between $M/10$ and $M/500$). With $N/10$ -fluoride, the formation of rust spots did not take place until the chromate concentration was reduced to $M/100$, or with $N/50$ -fluoride, to $M/200$, a result which is in agreement with the lesser penetrating power of the fluoride ion deduced from the sodium carbonate experiments.

In this series, however, another form of local corrosion took place, especially with $N/10$ -potassium fluoride containing $M/100$ — $M/200$ -potassium chromate and occasionally when as much as $M/20$ -chromate was present. During the course of about 24 hours from the commencement of the experiment, a variable number of tiny black spots appeared on the surface of the specimen, which otherwise was sometimes unattacked and sometimes showed separate rust spots. The black spots grew in size for some days and then remained unchanged on further standing. Their final size varied from 0.2 mm. to 3 mm. in diameter, the smaller ones being roughly spherical and the larger tapering to a point at the end away from the specimen. Underneath each spot a pit was found, shallow in the case of the small spots and perforating the metal in the case of the large ones. When perforation occurred, an almost flat, black spot appeared on the distant side of the foil. The blackness was confined to a thin layer on the outside, and the interior consisted of a white crystalline material. Qualitative examination of the material of the spots after prolonged washing on the metal showed the presence of ferrous and ferric iron, potassium, fluoride, and a trace of chromate.

The formation of these black spots may be explained as a result of the interaction of the chromate in the solution with the iron

fluoride obtained as a primary corrosion product. In fluoride solutions containing very little chromate, the fluoride ions, like chloride ions, are capable of penetrating weak spots in the protective film, attacking the iron and forming a fluoride. Instead of reacting with the alkali formed at the cathodic areas, the iron salt reacts with some of the chromate in solution, forming a film of iron chromate near to, but not in contact with, the metal, and impervious to more chromate ions although allowing fluoride and potassium ions to enter. Beneath this coating, further attack of the metal proceeds and a mass of white iron potassium fluorides is built up, the chromate cover expanding as the bulk of its contents increases and any discontinuity being at once repaired by interaction of the iron compounds with the chromate outside. When the metal is perforated, the chromate obtains access to the iron salts from the other side, and the flat black spot appears on the back of the metal.

Summary.

1. Experiments have been carried out on the corrosion of a particular iron foil in various aqueous solutions containing a soluble fluoride.

2. Solutions of potassium fluoride of concentration less than 0.8*N* corroded the iron in a manner similar to potassium chloride solutions of equivalent concentration.

3. Unlike the corresponding chloride solutions, potassium fluoride solutions of concentration 0.85*N* and above did not corrode iron foil, and exercised an inhibiting influence upon the corrosive action of chloride ions. The effect is ascribed to the formation of a protective film of a fluoride or double fluoride of iron on the surface of the metal.

4. The attack of a dilute fluoride solution was inhibited by sodium carbonate or potassium chromate in concentrations much lower than were needed for a chloride. This is attributed to the fluoride ion being less able to penetrate the protective film formed on the metal by the inhibitor.

5. A special type of corrosion phenomenon was exhibited in solutions containing potassium fluoride and chromate within certain limits of concentration. The nature and cause of this phenomenon are discussed.