

The Atmospheric Corrosion of Iron and Steel -- a Historic Review and Future Perspectives

Martin Stratmann
MPI für Eisenforschung, Düsseldorf

The atmospheric corrosion of iron and steel has always been of prime interest for electrochemists and corrosion engineers as it is the most wide spread corrosion process found in nature and as it leads to the destruction of the material, which has shaped the industrial age and therefore is responsible for immense financial losses.

The history of atmospheric corrosion research may be divided into the following stages:

1. Studies by Vernon and Buckowiecki (30th to 50th) [1,2]

During this period of time it was realised, that thin water layers being present on the steel surface are responsible for the atmospheric corrosion. It was proven, that the critical humidity necessary to trigger the corrosion reaction is linked to the presence of hygroscopic salt particles. This was the first evidence that the atmospheric corrosion cannot be described as a simple oxidation reaction but has to be discussed in the framework of electrochemical reaction kinetics.

2. Studies by Schikorr (60th) [3]

Schikorr was among the first to discuss a unique electrochemical mechanism of the atmospheric corrosion. During this period of time acid rain and the thereby triggered atmospheric corrosion of steel was of prime interest. Schikorr developed an electrochemical model (sulphate nest), which explained the catalytic acceleration of the corrosion rate in the presence of SO₂ by the formation of sulphuric acid and the deposition of iron oxides in zones of decreased pH.

3. Studies by Evans (70th) [4]

U.R. Evans was among the first to develop an electrochemical reaction model, which took explicitly into account the continuous wetting and drying of the surface during atmospheric corrosion. He considered for the first time besides oxygen reduction the reduction of iron(III) oxides as a potential second cathodic reaction and realised, that this reaction could only be of importance for in stationary corrosion conditions like wetting of a dry surface. Therefore the atmospheric corrosion of steel would be distinctly different from the usual corrosion mechanism of iron under immersed conditions.

4. Studies by Misawa (70th) [5]

Misawa took over some of the ideas of the reaction model by U.R. Evans and did extensive work on the chemistry of iron oxides in aqueous electrolytes. He complemented his investigations by IR-spectroscopy and showed, that a high number of thermodynamically metastable phases exist – in particular so called green rust phases – which are quite important in an understanding of the formation of stable oxides.

5. Studies by Pourbaix (70th) [6]

Pourbaix was also interested in the cyclic corrosion behaviour of steel surfaces during atmospheric corrosion and in addition tried to explain the specific corrosion mechanism of weathering steel. He performed several 100 wet/dry cycles and found passivation like phenomena for the weathering steel which he explained by a particular rust reduction kinetics.

6. Studies by Stratmann (80th–90th) [7]

Stratmann concentrated also first on studies referring to rust reduction and reoxidation using rust covered Au-electrodes and found very specific reactions taking place in the potential scale of interest. He then could prove the importance of rust reduction for the atmospheric corrosion by measuring in parallel the rate of metal dissolution and the rate of oxygen reduction technique during wet/dry cycles. By comparing both rates it could be proven that rust reduction plays a dominant role during the dry → wet transition of the atmospheric corrosion. During the wet → dry transition the highest corrosion rates are observed and these corrosion rates are linked to the electronic properties of the iron oxides, which result from the rust reduction reaction.

7. Studies by Graedel and Leygraf(90th) [8]

Most recently, studies by Graedel and Leygraf have again concentrated on the adsorption of gaseous species into the corroding surface and subsequent chemical reactions occurring in the thin electrolyte layer. These studies mainly aim to an understanding of the atmospheric corrosion of electronic materials.

7. Future

Still not well understood is the atmospheric corrosion of alloys and the slow “passivation” of the alloy surface. Studies will have to concentrate on the rust morphology as a function of the alloy composition and on the electronic properties of the oxide scale which is highly doped by the alloying elements. On this basis new self protecting steel surfaces could be developed, which do not need further inorganic or organic coatings.

References:

1. W.H.J. Vernon, Trans. Farad. Soc.; **31** (1935) 1668
2. A. Buckowiecki, Schweiz. Archiv Angew. Wiss. Techn.; **23** (1957) 97
3. G. Schikorr; Werkstoffe und Korrosion **14** (1963) 69
4. U.R. Evans, C.A.J. Taylor; Corros. Sci. **12** (1972) 227
5. T. Misawa, K. Hashimoto, S. Shimodaira; Corros. Sci. **14** (1974) 131
6. M. Pourbaix; Corros. Sci. **14** (1974) 25
7. M. Stratmann; Ber. Bunsenges. Physik. Chem.
8. C. Leygraf, T. Graedel; Atmospheric Corrosion, ISBN 0-471-37219-6, 2000

