RAS M-334

2. Effects of chemistry on corrosion–erosion of steels in water and wet steam

Ph. Berge, J. Ducreux, and **P. Saint-Paul,** EDF, Moret-sur-Loing

It has often been observed, particularly in steam production plants that numerous cases of degradation of steels occur when in contact with water or wet steam circulating at high velocity : in feed or discharge pumps, water reheaters, etc. (ref. 1). When the phenomenon occurs without any mechanical wear of the metal or the oxide from the impact of solid particles (abrasion) or droplets (erosion), it is called corrosion-erosion. The phenomenon usually occurs between 100 and 250°C, as has been confirmed by an empirical study of the thermal and hydraulic factors which govern it (ref.2). Corrosion rates can reach 1 to 2 mm/year, for a carbon steel pipe where water treated with ammonia circulates at about pH 9, at 200°C, and at a velocity of 5 to 10 m/s. Usually the remedy is either a change in the steel quality, for example, the choice of a chromium steel, or the lowering of the flow velocity of the liquid or the wet steam. But in certain cases the only possible action is by chemical treatment of the water. In fact the part played by the water chemistry on the development and even perhaps on the occurrence of the phenomenon has been noted, but without it being possible to make a quantitative estimation and without the mechanism of this action being clearly established.

In this study we propose to evaluate the part played by the factors solely connected to the chemistry of water, with respect to the kinetics of the corrosion-erosion phenomenon.

MECHANISM OF THE PHENOMENON

Whereas oxidation of steels in dry steam follows a parabolic development, at least when an homogeneous oxide formed adheres to the metal, in the case of oxidation occuring in circulating water, it is quite different. This difference is due to the fact that ferrous oxides which are formed either directly by the action of water on steel, or according to a more recent hypothesis by reduction by hydrogen of the magnetite formed (ref. 3-7), have a high solubility in water. One can then observe a linear rate of oxidation after a relatively short time (Fig. 1) (ref. 4). The slope of the linear curve depends on the nature of the steel, the temperature, the hydraulic conditions and the water chemistry. This linear function is due to the fact that the oxide layer formed attains a constant protection, i.e. a constant thickness in this case. The metal is thus oxidized in the form of soluble ferrous species. Dissolution by reduction of the magnetite layer, by the equation :

$$\frac{1}{3}\,Fe_3O_4 + (2-b)H^+ + \frac{1}{3}\,H_2 \longrightarrow Fe(OH)_b^{(2-b)^+} + (\frac{4}{3} - b)H_2O \qquad (1)$$

is accompanied by the formation of a new magnetite layer of the same thickness by direct oxidation of the metal. This oxidation is itself accompanied by the formation of soluble iron which diffuses towards the exterior of the layer in a quantity more or less equal to half the mass of oxidized iron. One can therefore assume that corrosion is equal to twice the rate of dissolution of the external surface of the magnetite layer.

The dissolving rate, following the reaction (1), for a given pH and hydrogen concentration, is proportional to $C_{eq}^n - C^n$ (ref. 8) where C_{eq} is the concentration of ferrous iron in equilibrium (the equation being reversible) and C the concentration of ferrous iron at the surface of the oxide layer, n depends on the order of the reaction (1). The following calculations have assumed, as a first hypothesis, n = 1, which leads to a relatively simple expression of the corrosion rate, by stating that the mass transfer (ferrous iron) towards solution is equal to $\lambda(C - C_o)$ where λ is the mass transfer coefficient and C_o the concentration of ferrous iron in the solution.

$$\frac{dm}{dt} = \lambda\,(C - C_o) \qquad (2)$$

$$\frac{dm}{dt} = 2K\,(C_{eq} - C) \qquad (3)$$

from which one gets

$$\frac{dm}{dt} = \frac{2K\lambda}{2K+\lambda}\,(C_{eq} - C_o) \qquad (4)$$

where K depends on the dissolving rate of the magnetite under given chemical and hydraulic conditions.

The tests in process should make it possible either to verify the proportionality between the corrosion and the difference $(C_{eq} - C_o)$, or to determine a factor n giving a more complex expression of corrosion.

Template Serg_028

DS-03

U.S. NUCLEAR REGULATORY COMMISSION
In the Matter of Entergy Nuclear Vermont Yankee LLC
Docket No. 50-271 Official Exhibit No. E 4-19-VY
OFFERED by [✓ Applicant/Licensee] Intervenor ____________
NRC Staff Other ____________
IDENTIFIED on 7/23/08 Witness/Panel NEC 4
Action Taken: [✓ ADMITTED] REJECTED WITHDRAWN
Reporter/Clerk MAC

DISCUSSION

- These hypotheses only take into account the mass transfer of soluble iron in the aqueous phase in the vicinity of the surface. It can either be a diffusion in pressurized water, or in the case of wet steam, a renewal of the liquid layer, necessarily present if this mechanism is involved.

- It is not applicable to any mechanism involving a mechanical degradation of the oxide.

- In the case when the solution is saturated in ferrous iron, for example under isothermic and static conditions (autoclave), the long term corrosion rate is practically nil (Fig. 1).

- When the solution contains complexing agents, for example chlorides, the value of C cannot be considered as a resultant of the equilibrium of the reaction (1), and the corrosion is much higher.

- In the presence of oxygen, ferrous iron oxidizes into ferric iron which has a very low solubility and a different protective oxide forms which can markedly slow down the corrosion rate (ref. 9-11).

- If the metal is protected by an oxide formed under not very turbulent conditions, starting up of rapid linear kinetics can take a certain time, called the incubation period of the phenomenon.

EVALUATION OF THE PART PLAYED BY pH ON CORROSION

The value of C_{eq} depends on the pH of the solution, the hydrogen concentration, and the temperature :

$$C_{eq} = K1\ (H^+)^2 (H_2)^{1/3} + K2\ H^+\ (H_2)^{1/3} + K3\ (H_2)^{1/3} + \frac{K4}{H^+}\ (H_2)^{1/3}$$

The value of the constants has been determined by F.H. Sweeton and C.F. Baes (ref. 3).

As an example, we have calculated the values of C_{eq} in boiler water treated with ammonia or morpholine, at 250°C. This case corresponds to conditions of a once-through steam generator of an electric power plant, which developed severe corrosion-erosion at the end of the evaporation zone, the steam quality being about 90 % with an ammoniated water at pH 8.9 - 9.

Table 1 shows the corrosion rate in different pH according to (4), for $C_o = 0$. The pH is raised either with NH_3, at different concentration, or with morpholine, the dissociation coefficient of which at 250°C being higher, and the partition coefficient between water and steam more favourable than for NH_3.

The measurement of hydrogen produced in the generator has made it possible to ascertain that correlation with the calculation was reasonably good over the whole range of pH tested around the working pH level having shown corrosion (Fig. 2).

EXPERIMENTAL STUDY

The Ciroco test loop (Fig. 3) makes it possible to evaluate various physical and chemical factors governing corrosion-erosion in pressurized water. Most of the tests made to date have investigated the behaviour of mild steel (either preoxidized or not) exposed to a flow of demineralized, deaerated and alkalized water.

Before entering the test section, water is alkalized with ammonia or morpholine at a pH within the range of 8.5 to 9.7. It is also conditioned with 20 ppb of hydrazine, pressurized at about 15 MPa and heated to 225°C. Flowing through a converging nozzle the jet of water speeds up to 60 m/s and impinges the flat surface of the test specimen at an angle of incidence of 45°. Four similar nozzles are set up one after another so that four samples can be tested at the same time under reasonably comparable conditions. After cooling, the full water flow is polished in a mixed bed ion exchanger, so that any complexing agents (chloride, sulfate) and iron compounds (oxides, hydroxides, etc.) are removed as far as possible. It is then necessary to adjust the pH with ammonia or morpholine as required.

The rig tubing and the main components are made of stainless steel or Inconel 600.

TABLE I : Ratio between corrosion at various pH under steam generator conditions of a graphite-gaz reactor (250°C – 90% steam) and in water at 250°C and that obtained at neutral pH (réf. 12-13).

pH at 25°C	8.5	8.8	9.0	9.1	9.2	9.3	9.4	9.5	9.6
With ammonia									
(steam quality 90%)	0.88	0.77	0.64	0.58	0.50	0.43	0.37	0.31	0.27
(steam quality 0%)	0.55	0.50	0.39	0.34	0.29	0.25	0.22	0.20	0.18
With morpholine (in water or wet steam *)	0.50	0.31	0.23	0.20	0.17	0.16	0.14	0.13	0.13

* The partition coefficient of morpholine in water and steam being taken as 1.

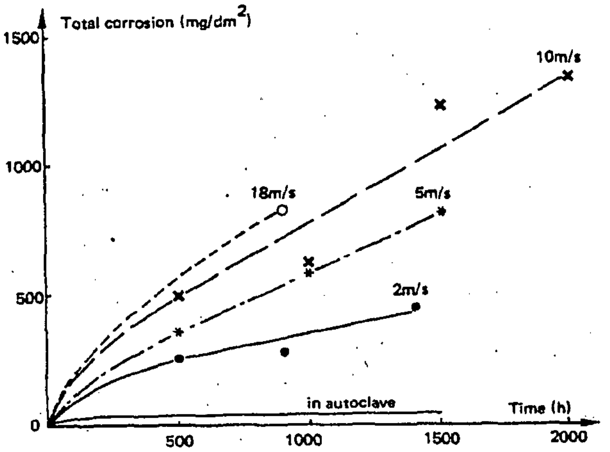
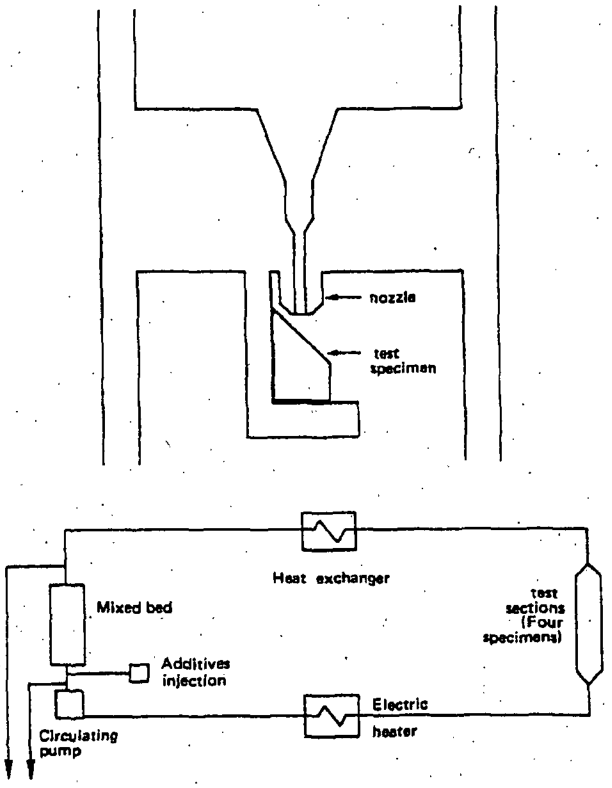


Figure 1 : Effect of flow rate on corrosion in circulating 300°C water of low alloyed Mn Mo steel [4]



Measures of pH, conductivity, O_2, H_2, N_2H_4, Fe, Cl^-, SO_4^{--}

Figure 3 : Scheme of CIROCO LOOP and test section.

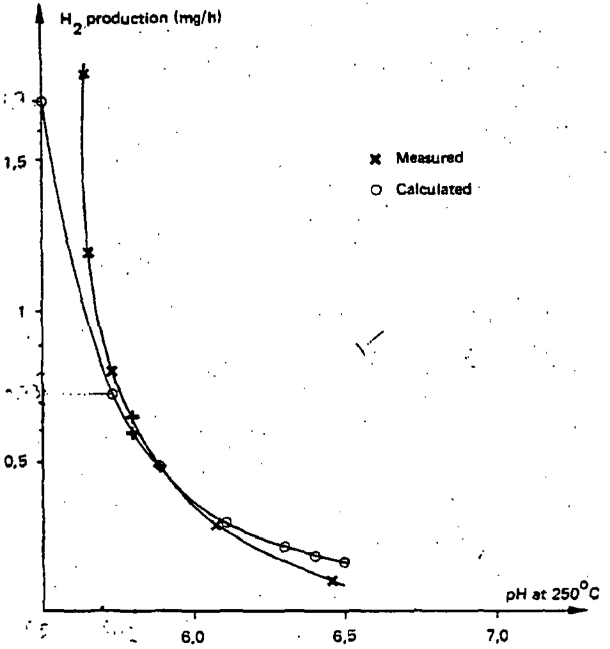


Figure 2 : Effect of pH on the H_2 production in a steam generator of a graphite-gaz reactor.

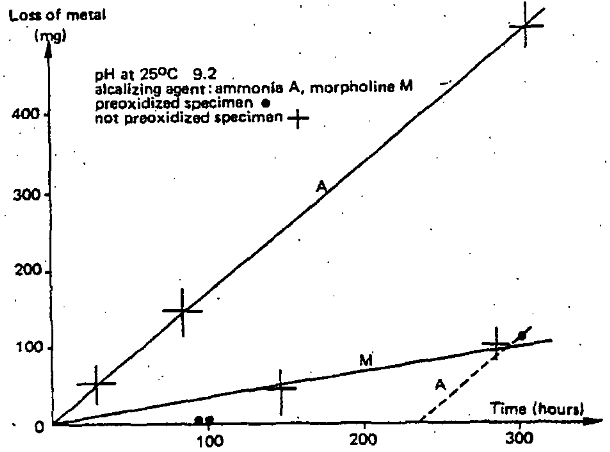


Figure 4 : CIROCO LOOP corrosion curves.

Under the above conditions, the loss of metal obtained during a few hundred hours by corrosion-erosion is easily measurable by weighing each steel specimen. By continuous or recurring water sampling, it is possible to check the variations of the following chemical parameters : pH, cationic conductivity, chloride, sulfate, iron, hydrazine, dissolved hydrogen and dissolved oxygen concentrations.

The steel surface preparation determines two different types of corrosion versus time curves (Fig. 4) : when the steel has not been preoxidized the loss of metal due to corrosion-erosion is proportional to the time ; in contrast when the steel has been preoxidized by exposure in high temperature static water, corrosion-erosion starts after some delay.

Taking into account the above theory, one can assume the rate of metal loss due to corrosion-erosion strongly depends on the pH. When the steel specimens have not been preoxidized, for a given temperature, hydraulics conditions and hydrogen concentration, when the water has not been contaminated by complexing agents, the corrosion-erosion rate depends linearly on the ferrous iron concentration at equilibrium, given by the pH (Fig. 5).

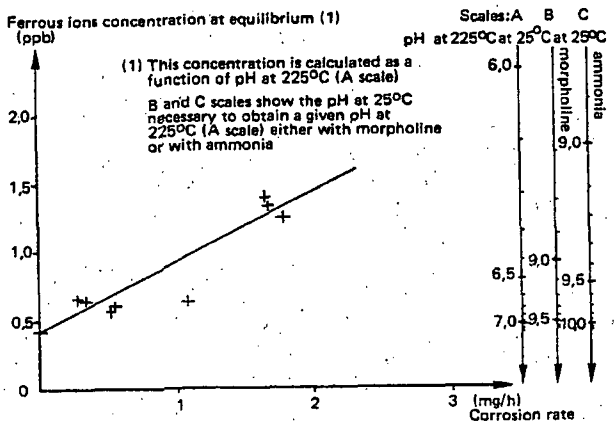


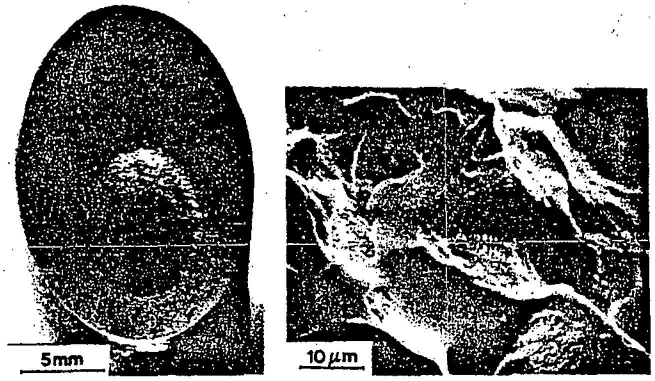
Figure 5 : CIROCO LOOP correlation between the corrosion rate and the soluble iron concentration at equilibrium.

Some steel specimens which have undergone corrosion-erosion either in the Ciroco test loop or in power plants during normal operations look very similar when observed with a Scanning Electron Microscope ; in some cases the perlite seems to corrode more rapidly than the ferrite (Fig. 6).

Furthermore it has been observed that if there is chloride or oxygen present in the water, the corrosion rate is modified as indicated above.

REMARKS

In order to verify that the phenomena observed in the Ciroco test loop under monophasic conditions are the same as those observed under diphasic conditions, a new program has been initiated. Another test loop in stainless steel giving wet steam at the required temperature and steam-quality, in under construction.



(a) (b)

Figure 6 : CIROCO LOOP specimen after testing
a - Macrograph (after 80 h at pH 8.5 with ammonia)
b - SEM examination (selection attack of the perlite).

Working conditions at the test section will be as follows :

- Wet steam quality	80 to 100 %
- Temperature	200 to 250°C
- Flow rate	50 to 100 kg/h
- Impingement velocity on target	50 to 70 m/s

The water will be demineralized, deaerated and conditioned before being turned into slightly superheated steam. Then the steam will be partially condensed and the emulsion sent into the test section, then drained off after cooling.

An ultrasonic device will make it possible to follow continuously the loss of metal.

CONCLUSION

The study undertaken has confirmed the very important part played by water chemistry on corrosion-erosion of steel.

The formula $\frac{dm}{dt} = \frac{2K\lambda}{2K+\lambda}(C_{eq} - C_o)$ which makes it possible to quantify the pH role on corrosion and which has been established taking into account certain hypotheses on the kinetic order of the Schikorr reaction, seems acceptable from the data obtained in the plant or in the laboratory.

REFERENCES

1. "Chimie de l'eau et corrosion dans les circuits eau-vapeur des centrales nucléaires". Colloque ADERP-EdF, Seillac, Mars 1980.
2. KELLER H. VGB, Kraftwerkstechnik 54, 1974, 5, 292-295.
3. SWEETON F.H. and BAES C.F. "The solubility of magnetite and hydrolysis of ferrous ions in aqueous solutions elevated temperatures". J. Chem. Thermodynamics, 1970, 2, 479-500.
4. BERGE Ph. Mécanisme de l'oxydation des aciers dans l'eau à haute température et de la formation de dépôts d'oxyde. Congrès d'Ermenonville, 13-17 Mars 1972.
5. STYRIKOVICH M.A., MARTYNOVA O.J. et al : Teploenergetika 19, 1972, H.9.S., 85-87.

6. STURLA P. S. Nationale Speisewasserkonferenz in Prag vom 2 bis 4, Oktober 1973.
7. BIGNOLD G.J., GARNSEY R. and MANN G.M.W. High temperature aqueous corrosion of iron development of theories of equilibrium solution phase transport through a porous oxide. Corrosion Science, 1972, Vol. 12, 325-332.
8. BERGE Ph., RIBON C. and SAINT-PAUL P. : "Effect of hydrogen on the corrosion of steels in high temperature water.Corrosion, 1976, 32, June, 223.
9. BOHNSACK G. Sonderheft VGB Speisewassertagung 1975, 15-19.
10. FREIER R.K. Wasser, Vol. 8, 1971, 443-458.
11. BRUSH E.G., PEARL W.L. Corrosion and corrosion product release in neutral feedwater. Corrosion, Vol. 28, 1972, 129-136.
12. POCOCK F.S. "Control of iron pickup on cycles utilizing carbon steel feedwater heaters". Proc. Amer. Power Conference, 28, 1966, 758-771.
13. MESMER R.E. No publied results.

Addendum to Paper 2

Mathematic study of diffusion and kinetic equations for different values of n, the order of reaction.

$$1/3\ Fe_3\ O4 + (2-b)\ H^+ + \frac{1}{3}\ H2 \rightleftarrows Fe\ (OH)_b^{(2-b)^+} + (\frac{4}{3} - b)\ H_2\ O$$

$b = 0,1,2,3$

Considering the predominant ferrous species at equilibrium (for instance Fe $(OH)_3^-$ in a basic medium according to the model of Sweaton and Baes) one can write down

$$(I)\quad \begin{aligned} \dot{m} &= \lambda\ (C - Co) \\ \dot{m} &= 2K\ (Ceq^n - C^n) \end{aligned}$$

or otherwise

$$(II)\quad \begin{aligned} \dot{m} &= \lambda\ (C - Co) \\ Ceq &= \left(C^n + \frac{(C-Co)}{2K}\right)^{1/n} \end{aligned}$$

Although the explicit function $\dot{m} = f\ (Ceq)$ can be calculated for $n = 1,2,3$, its study is not very easy for $n = 2$ and 3. One had better look for the shape of the curve $\dot{m} = f\ (Ceq)$ by studying the system (II) of parametric equations, $\dot{m}$ and Ceq being considered as functions of the same parameter C. One has then to calculate the first and second derivatives $\frac{d\dot{m}}{dc}$, $\frac{dCeq}{dc}$; $\frac{d^2Ceq}{dc^2}$ and deduce from them the concavity of the curve, the points of inflexion, and the behaviour at infinity.

The main results are summarized in the following diagrams (Fig.1).

The comparison between these theoretical results and the trend of experimental measurements may help us to determine the order of n of reaction.

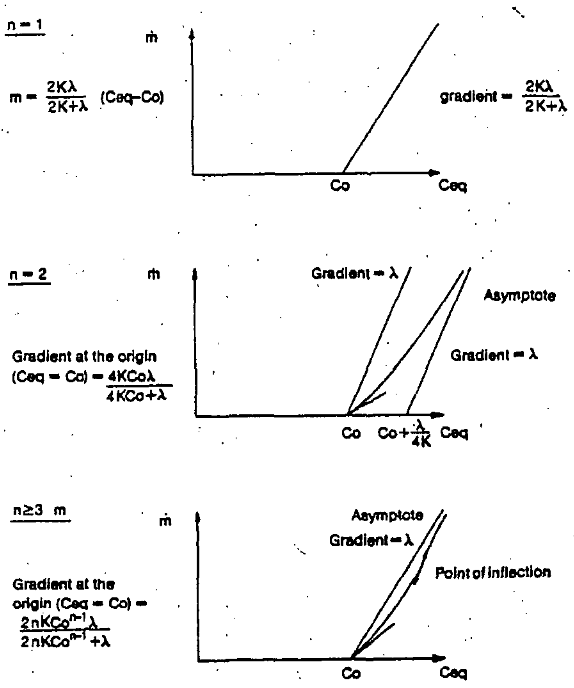


Fig.1