

## Study on Application of Oxygenated Water Chemistry For Suppression of Flow Assisted Corrosion in Secondary System of PWRs

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The electrochemical model for oxygen consumption with hydrazine at 180 °C is developed based on the results of a series of loop experiments for the application of Oxygenated Water Chemistry (OWC) to secondary system of Pressurized Water Reactors (PWRs). The integrity and performance of Steam Generators (SGs) in PWR is greatly affected by the input of corrosion product which is generated in secondary system due to Flow Assisted Corrosion (FAC) of carbon steel used as a main structural material. While OWC has been successfully adopted in Boiling Water Reactors (BWRs) and fossil units to suppress the FAC in feed water system, in case of OWC application to PWRs, further attention should be paid to remaining oxygen in final feed water, which could affect integrity of SGs and has to be eliminated with hydrazine addition. The model is essential for this purpose, because it is difficult to monitor the oxygen concentration under coexistence of hydrazine using the existing sampling line.

### 1. Introduction

An important contributing factor to the degradation of steam generators in Pressurized Water Reactors (PWRs) is deposition of corrosion products from the feed-water train. To ensure steam generator integrity it is important to minimize the influx of corrosion products. It is known from boiling water reactors that an oxygen level of the order of 10 ppb in the water has a very beneficial effect on Carbon Steel (CS) corrosion in the feed-water train and effectively reduces Flow Assisted Corrosion (FAC).

PWRs have generally relied on deoxygenated, alkalized water chemistry to reduce corrosion on the secondary side. A very low oxygen level is normally achieved by means of hydrazine injection. However, it is likely that an oxygen level of a few ppb in the feed-water would further reduce CS corrosion in PWRs and would be beneficial with respect to input of corrosion products to the steam generators. On the other hand, oxygenated water in the steam generators might give rise to oxygen concentration cells that could potentially enhance crevice corrosion. It is therefore important to assure that the oxygen reacts essentially completely with the added hydrazine before the feed-water reaches the steam generators. This situation can be achieved by the right combination of hydrazine injection and

oxygen injection into the feed-water (or condensate). The concept has been called Oxygenated Water Chemistry (OWC) and is illustrated in Fig. 1.

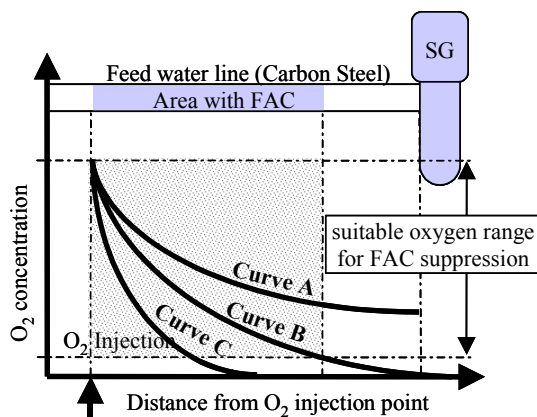


Fig. 1. Oxygenated Water Chemistry in PWR secondary circuit.

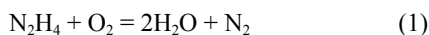
Curve A indicates a situation with too much oxygen and curve C one with too little. The ideal situation is that of curve B. In practice, this situation means that oxygen is fully consumed in the final feed-water heater. This condition is possible to establish since the rate of reaction of oxygen with hydrazine increases sharply with both

temperature and with the ratio of surface area to volume (the reaction is at least partly heterogeneous). However, the desired oxygenated water chemistry is difficult to monitor directly, since oxygen levels in the sampling points are affected by oxygen-hydrazine reaction in the sampling lines. A model is needed, showing how the oxygen level and the electrochemical potential (ECP) change along the feed-water train. The present paper describes the initial development of a mechanistic model, based on electrochemical kinetics, for describing oxygen and hydrazine behavior in the secondary side of PWRs. Basic input parameters of the model are pipe diameter and length, flow rate, temperature, pH, and the levels of hydrazine and oxygen, respectively. The main outputs from the model, called OWC Simulator, are the oxygen level and the corresponding ECP along the CS pipe.

Model development has involved laboratory loop experiments to generate input data, creation of an electrochemical model for the oxygen-hydrazine reaction, and implementation of the electrochemical model as a computer code with a Graphical User Interface (GUI). The paper is organized as follows. First, a very brief background is given on the chemistry of hydrazine and the modeling of electrochemical kinetics. The loop and the test results are presented next. The implications of the test results are then discussed and the fit of the calibrated model to the data explored. Finally, conclusions are given and future model development outlined.

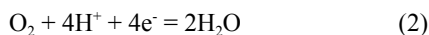
## 2. Chemistry of hydrazine and modeling of electrochemical kinetics

Hydrazine reacts with oxygen according to the following formula.

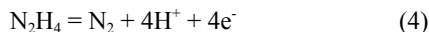


Analysis of experimental data has indicated that the reaction rate is first order in  $\text{O}_2$  and  $\frac{1}{2}$  order in  $\text{N}_2\text{H}_4$  [1]. An activation energy of 25.5 kJ/mol has also been given [1].

Oxygen is well known to react electrochemically with hydrogen on metal (oxide) surfaces in BWRs, producing water. This reaction is electrochemical in nature and due to the following separate reduction and oxidation reactions.



Hydrazine has an oxidation reaction analogous to that of hydrogen.



It is therefore natural to assume that the reaction of oxygen with hydrazine is the result of simultaneous reduction of oxygen according to reaction (2) and oxidation of hydrazine according to reaction (4) (or the corresponding reactions in an alkaline environment).

The reaction of oxygen and hydrogen in BWRs is well modeled using a Mixed Potential Model (MPM) and the Butler-Volmer equation; see e.g. [2]. It is natural to assume that the reaction of oxygen and hydrazine may be modeled using the same method. Once the surface reaction has been modeled, the total reduction of oxygen in any given pipe may be calculated as the integral of the surface reaction, using the finite difference method. The present work explores this hypothesis to create a model for the reaction of oxygen with hydrazine. Next comes the experimental section.

## 3. Experimental

The first aim of the experimental investigation was to measure ECP as a function of the oxygen level at a few different hydrazine levels. The test conditions are given in Table 1.

Table 1. Test matrix for the experimental investigation. Numbers in parenthesis indicate that only limited data were collected.

Inlet Oxygen conc.	0.5 – 50 ppb
Inlet Hydrazine conc.	(0), 100, 300, 1000, (5000) ppb
Temperature	180, (220) °C
Flow rate	0.1 m/s
pH	9.2

The number of different oxygen levels varied with the hydrazine level (highest at 100 ppb of  $\text{N}_2\text{H}_4$ ) and the temperature level. The pH was controlled by addition of 0.5 ppm of ammonia.

A schematic of the test loop is shown in Fig. 2. The loop basically consists of five 500 mm long carbon steel pipe segments with 22 mm outer diameter and 2 mm wall thickness. In each pipe segment, there is an electrode. The first four segments are equipped with Ag/AgCl reference electrodes. In the fifth segment there is a Pt electrode. The Ag/AgCl electrodes have their “tips”

in the cylindrical wall, opposite to the pipe wall, to ensure a well-defined flow rate and calculable mass transfer rate.

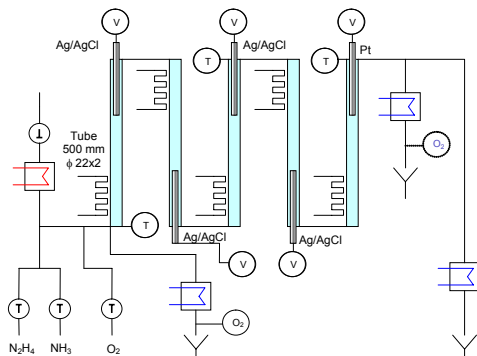


Fig. 2. Schematic of the test loop.

The loop is also equipped with thermo-couples, electric heaters to compensate for heat loss, coolers, and injection pumps for aerated water, hydrazine and ammonia. For oxygen measurement, there is an Orbisphere instrument that is normally connected to the loop inlet but may be connected also to the loop outlet in order to measure oxygen consumption in the loop. Measurement of the oxygen consumption rate was the second aim of the experiment. Simultaneous data on ECP and oxygen reaction rate are required for model calibration.

**4. Results**

ECP data are shown in Fig. 3 as a function of the loop inlet O<sub>2</sub>-level at 100 ppb N<sub>2</sub>H<sub>2</sub> and a pH of 9.2.

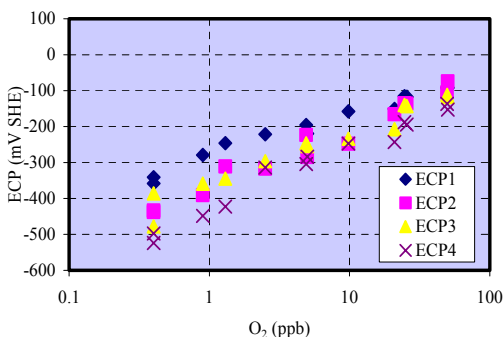


Fig. 3. ECP of CS as a function of loop inlet O<sub>2</sub> level in water with 100 ppb N<sub>2</sub>H<sub>4</sub> and 0.5 ppm NH<sub>3</sub>.

The span between the first and the last ECP measuring points in the loop (ECP 1 and ECP 4) increases below an inlet oxygen level of about 2.5 ppb. This is due to oxygen consumption in the loop becoming more significant at low inlet O<sub>2</sub>-levels.

Another way to present the data is to plot ECP 1 against the loop inlet oxygen concentration together with ECP4 against the loop outlet oxygen concentration, see Fig. 4. This figure indicates a more rapid decay of the ECP value below approx. 1 ppb of oxygen.

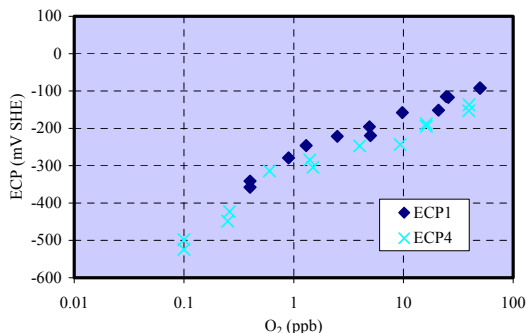


Fig. 4. ECP of CS as a function of loop inlet O<sub>2</sub> level (ECP 1) and loop outlet O<sub>2</sub> level (ECP 4), respectively, in water with 100 ppb N<sub>2</sub>H<sub>4</sub> and 0.5 ppm NH<sub>3</sub>.

Besides 100 ppb of hydrazine, experiments were also carried out at 300 ppb, 1000 ppb, and 5000 ppb of hydrazine. The data at 300 ppb N<sub>2</sub>H<sub>4</sub> are shown in Fig. 5 and the data at 1000 ppb N<sub>2</sub>H<sub>4</sub> and 5000 ppb N<sub>2</sub>H<sub>4</sub>, respectively, in Fig. 6.

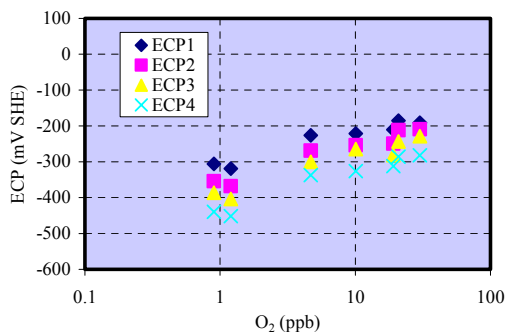


Fig. 5. ECP of CS as a function of loop inlet O<sub>2</sub> level in water with 300 ppb N<sub>2</sub>H<sub>4</sub> and 0.5 ppm NH<sub>3</sub>.

The data on oxygen consumption will be treated in the next section.

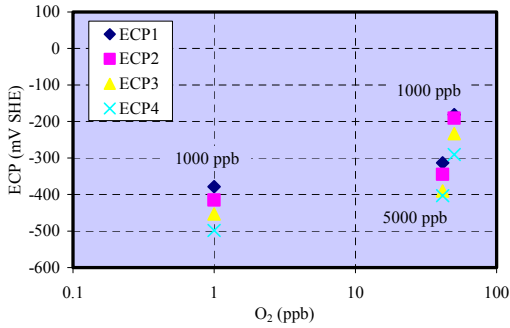
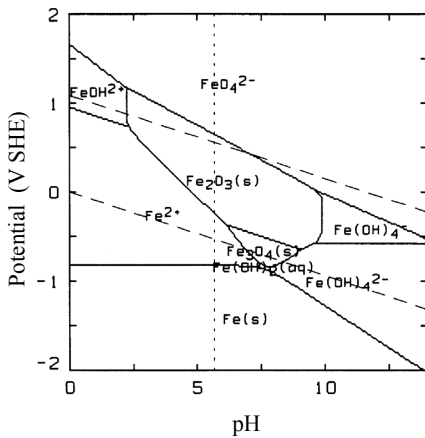


Fig. 6. ECP of CS in water with 1000 and 5000 ppb  $N_2H_4$ , respectively, and 0.5 ppm  $NH_3$

**5. Discussion**

It is interesting to note that the OWC concept is supported by thermodynamics. Figure 7 shows a potential-pH diagram for iron at 200 °C. Potential-pH diagrams are normally constructed for a level of dissolved species of  $10^{-6}$  mol/kg, which is too high for nuclear applications. The diagram of Fig. 7 was constructed for a dissolved species concentration of  $10^{-8}$  mol/kg.

Fig. 7. Potential-pH diagram for iron at 200 °C. The concentration of dissolved species is  $10^{-8}$  mol/kg.



The dotted line indicates neutral pH [3].

Half a ppm of ammonia gives a pH of 6.2 at 200 °C. The diagram of Fig. 7 indicates that at this pH hematite is not converted to magnetite as the potential is lowered. Instead, the hematite dissolves below a potential of around -300 mV SHE. The exact potential where dissolution starts depends, of course, on the iron level in the water.

The potential-pH diagram indicates that OWC has the potential to stabilize the oxide layer and to reduce the iron level in the water.

An important question is how one can determine from the data whether it supports the basic hypothesis that the reaction between oxygen and hydrazine is a heterogeneous, electrochemical reaction. One way is to use the criterion that a characteristic of an electrochemical reaction is that the rate constant depends on the potential. The reaction may be assumed to be first order in oxygen. The loop oxygen inlet to outlet ratio,  $C_{in}/C_{out}$ , is then a measure of the mean rate constant of the reaction along the pipe. The plot of  $\ln(C_{in}/C_{out})$  against the first reference electrode (ECP 1) is shown in Fig. 8.

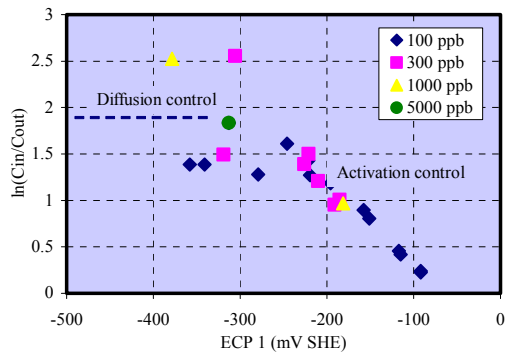


Fig. 8. The “rate constant” for the oxygen-hydrazine reaction at 180 °C plotted against ECP at four different hydrazine levels.

The figure shows an increasing trend down to -250 mV SHE and scattered data points at lower ECP values. The scattered data to the left in Fig. 8 are explained by the fact that in these cases the outlet oxygen levels are very low and therefore inaccurately known. In conclusion: The variation of the rate of oxygen reduction with the ECP supports an electrochemical mechanism for the reaction at 180 °C.

The oxygen consumption in the loop was found to be much higher at 220 °C, compared to 180 °C. This is apparent from Table 2. Note that at 220 °C the measured loop inlet oxygen concentration is reduced appreciably as the hydrazine level is increased, even though the  $O_2$  injection rate remains constant. This effect was very much smaller at 180 °C. Only at 5000 ppb of hydrazine was there a significant reduction of the injected oxygen level, from 51 to 42 ppb, at the measuring point.

Table 2. Effect of N<sub>2</sub>H<sub>4</sub> on O<sub>2</sub> reduction in the loop at 220 and 180 °C, respectively.

Temp. (°C)	N <sub>2</sub> H <sub>4</sub> (ppb)	O <sub>2</sub> inject (ml/min)	O <sub>2</sub> inject (ppb)	O <sub>2</sub> in (ppb)	O <sub>2</sub> out (ppb)	Quotient
220	0	6	30	29.6	—	—
220	100	6	30	24.6	1.9	0.06
220	300	6	30	19.7	0.9	0.03
220	625	6	30	16.4	0.6	0.02
180	100	5	25	25.6	16.2	0.65
180	300	4	20	20.9	9.35	0.47
180	300	6	30	30.1	11.6	0.39

The quotient in the table is the measured outlet oxygen concentration divided by the nominal concentration at the injection point (5 ppb/ml/min)

The limited data at 220 °C seem to indicate that the reaction rate is above that of a mass transfer limited reaction, indicating also a homogeneous component at this temperature.

The MPM model constants were fitted to the experimental ECP and oxygen consumption data. In addition, input from an unpublished MPM for BWRs was used for the oxygen reduction reaction. The model constants were fitted assuming that due to additional turbulence the mass transfer rate in the loop was, on the average, 50 % higher compared to a straight pipe with no internal parts. The model fit to the ECP data is shown in Fig. 9.

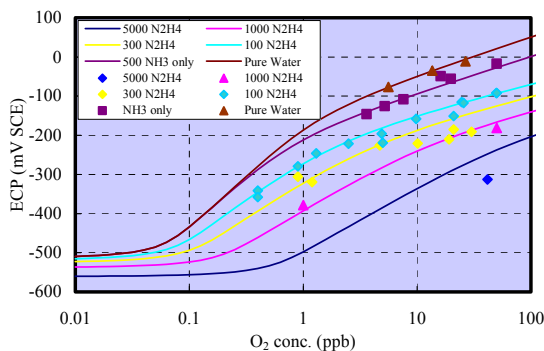


Fig. 9. Modeled ECP as a function of O<sub>2</sub> concentration at 180 °C and different levels of N<sub>2</sub>H<sub>4</sub>, pH 9.2, except for pure water. The data points are the measured ECP values at the position of the first reference electrode (ECP 1) and are given as functions of the measured inlet O<sub>2</sub> level.

Some data that were taken in pure water and in water with 500 ppb NH<sub>3</sub> only have been included in the figure. In general, the fitted model seems to represent the experimental ECP data well. This, also, can be taken as an indication of the

fundamental correctness of the electrochemical modeling of the oxygen-hydrazine reaction at 180 °C.

The shape of the curves in Fig. 9 has the following background. At oxygen levels above 10 ppb the ECP is determined by the intersection of the Tafel lines of hydrazine oxidation and oxygen reduction. Below an oxygen level of around 1 ppb, the Tafel line for hydrazine oxidation intersects instead the horizontal limiting current density line for oxygen reduction. This affects the slope of the curve of ECP as a function of potential and causes the ECP to decay more rapidly at low potentials. Even lower potentials will result if the metal oxidation current is higher at low ECP values.

Oxygen consumption is assumed to be due to the heterogeneous, electrochemical reaction with hydrazine, i.e. given by the oxygen reduction current in the MPM. Integrating this current density gives the oxygen consumption in any given pipe. To carry out the integration, the finite difference method is used.

The loop, including inlet/outlet pipes and sampling system on the outlet side, was modeled as a 4 m long 22x2 mm pipe with an average flow rate of 0.15 m/s. The flow rate is not critical for the oxygen consumption at low O<sub>2</sub> levels, since a higher flow rate will give a higher rate of mass transfer, but a shorter residence time in the pipe. These opposing factors nearly balance.

The modeling of the outlet O<sub>2</sub> levels is shown in Fig. 10. It is seen that a good fit is obtained, except at oxygen levels around 0.1 ppb. The latter may be due to the problems of accurately measuring such low oxygen levels.

The model reproduces the 180 °C data well. However, it underestimates the reaction rate at 220 °C. As already stated, this is thought to be due to an additional homogeneous reaction at 220 °C in addition to the heterogeneous one.

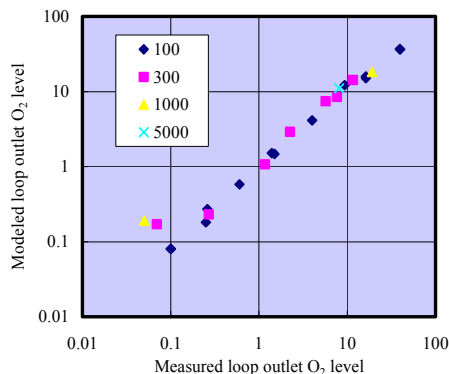


Fig. 10. Modeled loop outlet  $O_2$  level plotted against measured loop outlet  $O_2$  level. The  $N_2H_4$  levels are 0, 100, 300, 1000 and 5000 ppb, respectively, and the temperature 180 °C.

The model was implemented in a computer program called the OWC Simulator that calculates ECP and oxygen concentration along any given pipe. Simulation shows that the oxygen concentration decays very slowly in a large diameter feed-water line at 180 °C. On the other hand, the model predicts that the oxygen concentration decays rapidly in sampling lines. For example, an oxygen level of 5 ppb is reduced to essentially zero in 10 m of a sampling line with 10 mm diameter and a flow rate of 20 g/s; see Fig. 11.

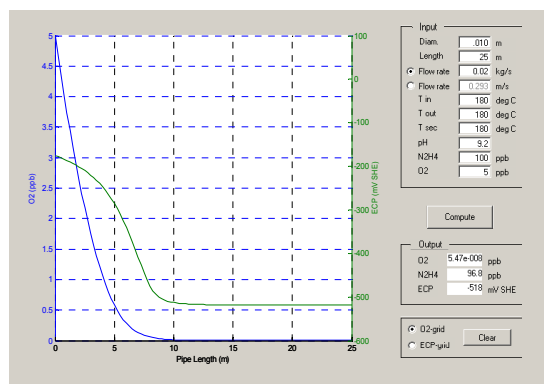


Fig. 11. The GUI of the OWC Simulator. The figure shows simulation of a 25 m long 10 mm sampling line at 180 °C with a flow rate of 20 g/s.

## 6. Conclusions

The present investigation has demonstrated that the reaction of oxygen with hydrazine in CS piping

is well described by electrochemical kinetics at 180 °C. The reaction is thus mainly heterogeneous under these conditions. This means that the reaction rate is greatly influenced by the ratio of surface area to volume. In particular, the reaction rate is very significant in a sampling line. Therefore, OWC is not possible to monitor using sampling lines. Instead, a modeling approach is needed. We have established a MPM that calculates the  $O_2$  decay profile and the ECP profile along a feed-water pipe at 180 °C under AVT conditions, 0.5 ppm  $NH_3$  and 0 - 1000 ppb  $N_2H_4$ .

Using the model it is possible to control the injection of oxygen and hydrazine, so that the goals of OWC are achieved. In practice this implies that oxygen is present in the feed-water lines upstream of the final feed-water heater. The reaction rate is low in this region due to the small ratio of surface area to volume. In the final feed-water heater itself, there is a large ratio of surface area to volume, an increasing temperature and a much increased rate of oxygen reduction. By quantifying this process with the OWC Simulator, it is possible control the oxygen and hydrazine injections to achieve the OWC goals:

- Protection of the CS surfaces upstream of the final feed-water heater.
- An oxygen-free final feed-water.

Further development of the model in three ways is considered.

- The kinetics of an electrochemical reaction is surface dependant and an in-plant surface may be somewhat different from an out-of-plant surface. The model should be checked and possibly recalibrated using an in-plant surface.
- The preliminary data at 220 °C indicate that a homogeneous reaction may be important at higher temperatures. Kinetic data at higher temperatures than 180 °C should be obtained.
- The model should be extended to higher temperatures and to vapor-liquid two phase systems.

## References

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