Corrosion Potential Measurements in Boiler Water: The Influence of Oxygen Content*

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Summary

The corrosion potentials of AISI 304 stainless steel (SS), platinum, and 17MnMoV6.4 steel were measured in boiler water. The measurements were performed in a refreshing autoclave system at 200 °C in ammoniated water of pH 8.5. The oxygen content of the water was varied. The corrosion potential of the SS increased trom -400 to + 200 mV normal hydrogen electrode (NHE) in the oxygen range of 1 to 10 ppb.

Introduction

Oxidation reactions play an important role in various corrosion processes. The corrosion potential of a metal depends highly on the oxygen content in the water. The potential value determines which corrosion reactions can occur thermodynamically. Examples are stress corrosion cracking (SCC) of sensitized stainless steel (SS) under boiling water reactor (BWR) conditions[1-3] , rippling in boiler tubes [4.5] and erosioncorrosion of unalloyed steels[6] .

In water-steam circuits of conventional and nuclear boilers (pressurized water reactors (PWRs)), the oxygen content is kept to a minimum. In connection with intergranular stress assisted corrosion of sensitized SSs in BWRs, corrosion potentials have been measured over a wide range of oxygen values (0 to 10,000 ppb).

For example, the corrosion potential data of Indig and Lee [1,7] are shown in Figures 1 and 2, and are compared with those of Leibovitz in Figure 3. The results of the three authors are not fully identical; Lee observed a gradual increase in corrosion potential between 5 and 1000 ppb O_2, whereas the results of Indig show a more rapid increase in the corrosion potential in the oxygen range between 5 and 100 ppb.

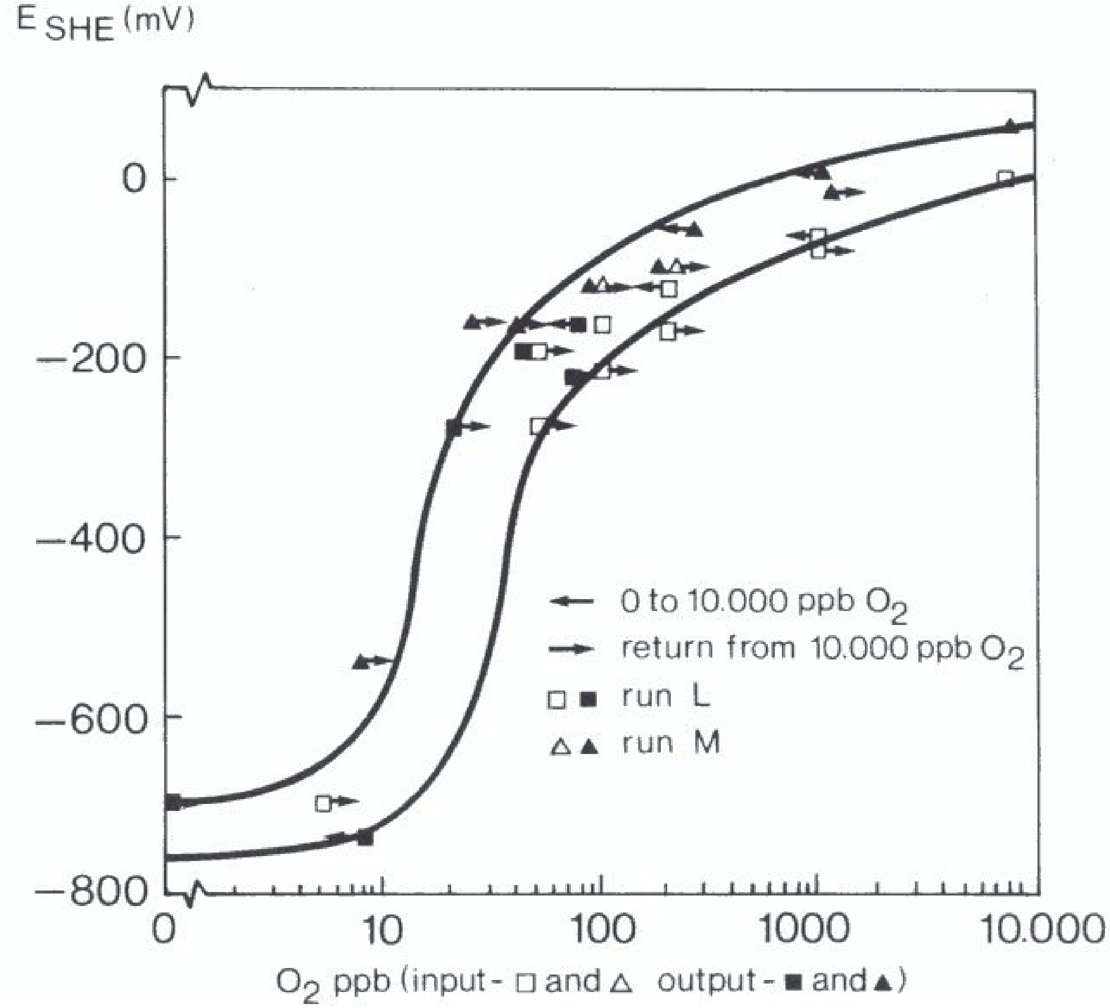

FIGURE 1 -Corrosion potentials of AISI 304 SS in high purity water (measurements of Indig1).

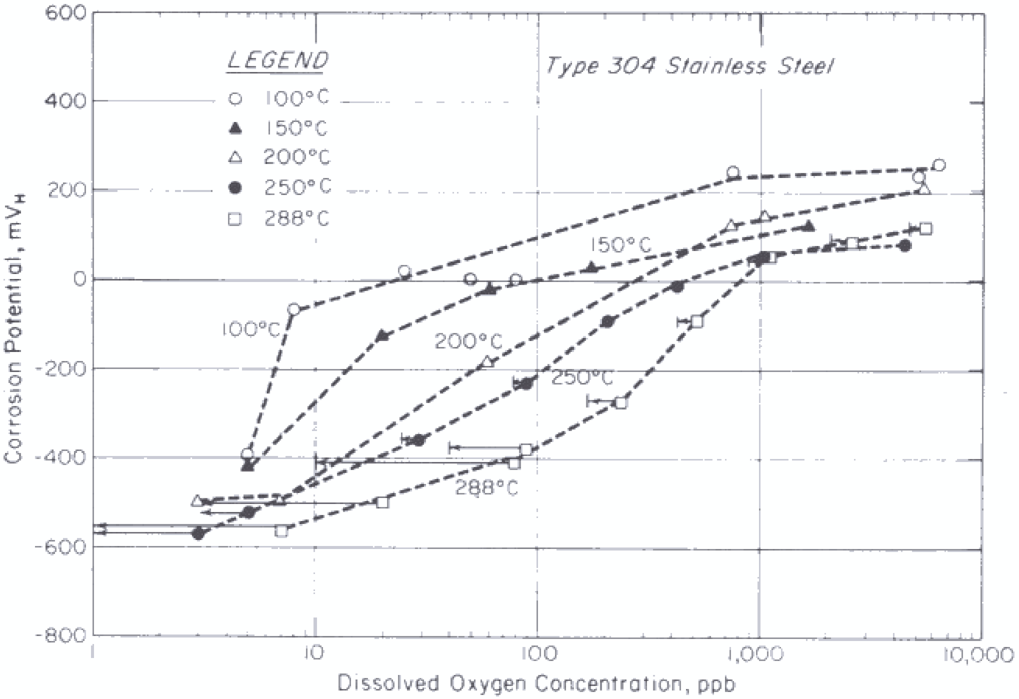

FIGURE 2 -Corrosion potentials of AISI 304 SS as a function of oxygen concentration at 100, 150, 200, 250, and 288 °C in high-purity water (measurements of Lee[7]).

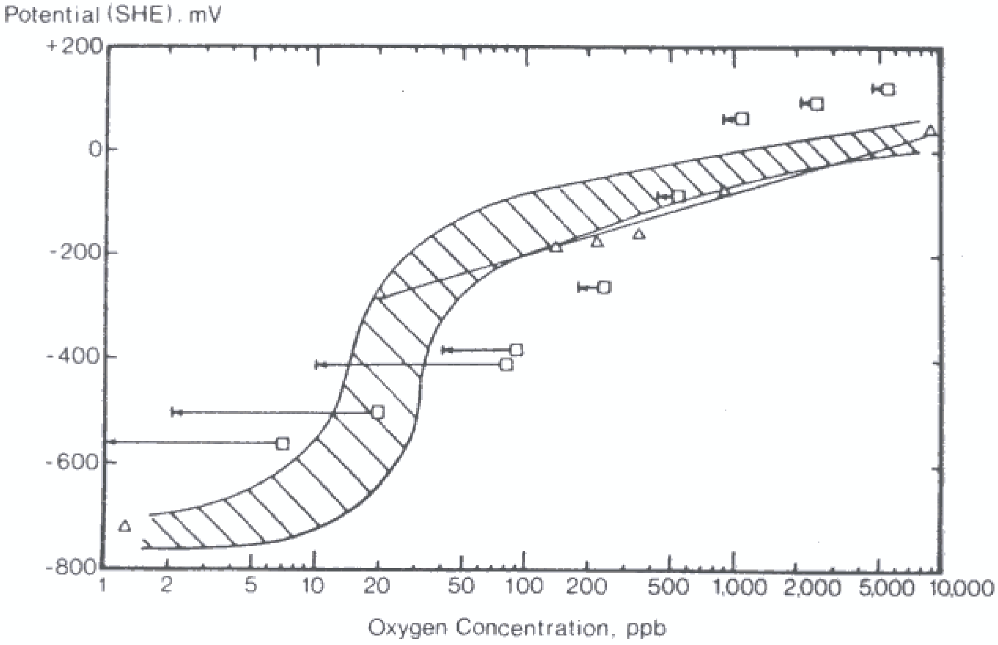

FIGURE 3 -AISI 304 SS potential at high temperature:
measurements of Indig[1] 274°C , arced
measurements of Lee[7] , 288°C, □
measurements of Leibovitz[8] , 288°C, Δ

Leibovitz did not observe such a rapid increase in the oxygen/potential curve, probably because the test ran only from 20 to 10,000 ppb O_2. It can be concluded, therefore, that the oxygen/corrosion potential relationship is not well characterized. However, progressively more researchers are using the results of Figures 1 through 3 to interpret their test results.[2,9] At KEMA, it was decided to expand on the earlier investigations, with the initial emphasis being placed on the dissolved oxygen/corrosion potential relationship for various materials in ammoniated water at 200 C.

Experimental

The measurements were performed at 200 °C in a continuously refreshed system (Figure 4).

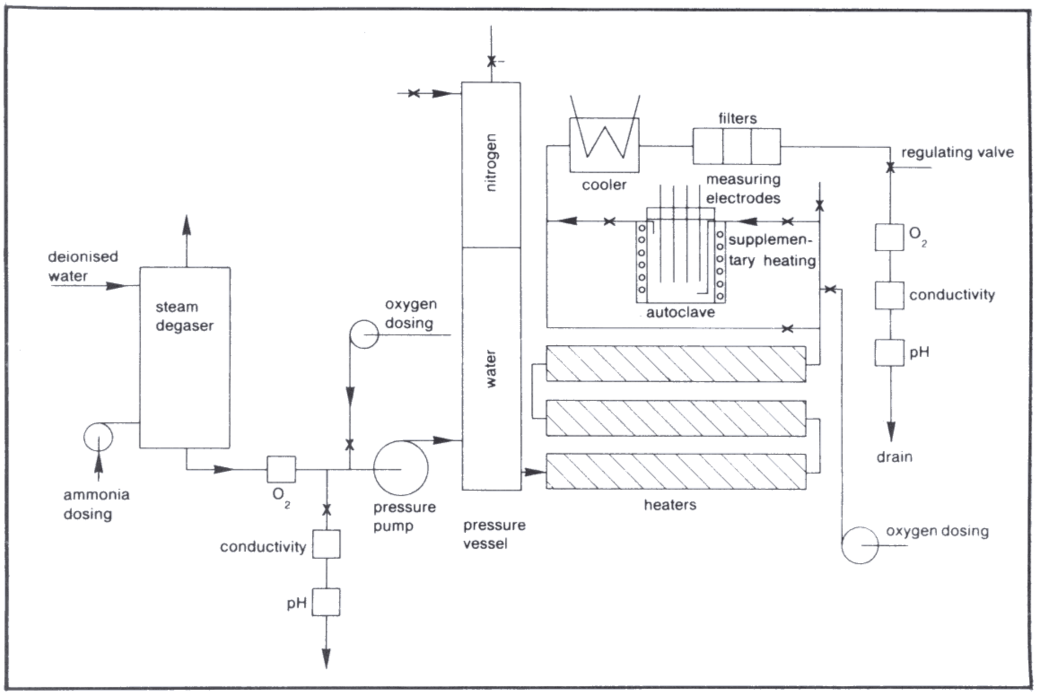

FIGURE 4 -Schematic diagram of the KEMA refreshing autoclave.

The linear flow speed of the water was 10^{-3} ms^{-1} (8.5 L/h). Demineralized water was thermally degassed in a reflux steam generator. Ammonia was dosed into the feed water to give a pH value of 8.5 at the high pressure inlet. The dissolved oxygen concentration in the autoclave was regulated by dosing the
degassed water with aerated CO_2-free water either before the high-pressure pump or before the autoclave. The dissolved oxygen content, pH, and conductivity were measured at the inlet and outlet to the system. The inlet and outlet conductivities were both ca 7 10^{-4} Sm $^{-1}$. A pressure of 50 bar was maintained in the buffer vessel by nitrogen.

The refreshing system contained an AISI 304 SS autoclave for electrochemical measurements. The cover of this autoclave was equipped with a Conax(1) fitting with a PTFE pressure sealing for four measuring wires. Two idential Ag-AgCl reference electrodes were used, one of platinum and one of a 17MnMoV6.4 steel sample. The autoclave was electrically isolated from the system by means of Frenzelite(2) and PTFE, seals and served as the third measuring electrode. Inlet and outlet water flow tubes and a thermocouple were also mounted in the autoclave cover.

((1) (2) : Registered trade names).

The Ag-AgCl-0.001 M KCl half-cell was chosen as a reference electrode. Indig and Leibovitz thoroughly tested this system, and it proved to work satisfactorily[1,8]. The potential values with reference to the normal hydrogen electrode (NHE) were calculated (Figure 5). Leibovitz calculated the solubility of AgCl as a function of temperature. The reference electrode capsules were filled with pure water because some of the molten AgCl on the Ag wire would dissolve to saturation. The potentials of such electrodes with respect to NHE are also given in Figure 5.

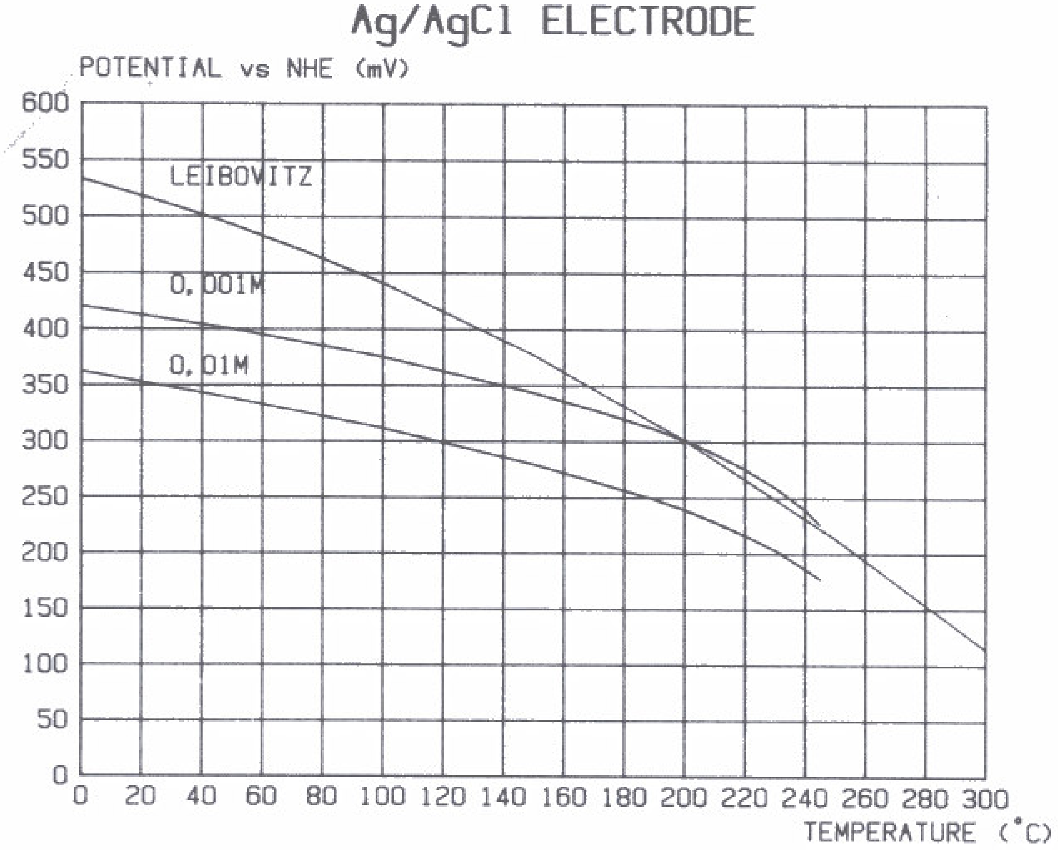

FIGURE 5 -Calculated potentials for the Ag.AgCl-KCl electrode with reference to NHE.

According to Leibovitz, the solubility of AgCl at 200 °C amounts to 0.001 M; the electrodes were thus filled with 0.001 M KCl before exposure. Minor leakage of this chloride into the water would be replenished by the dissolution of some AgCl. If the potential difference between the two reference electrodes was 0, it was assumed that both were functioning well.

The oxygen concentrations at the inlet and outlet of the system we re measured with a Weston and Stack(3) model 3400 analyzer. For reliable results, the electrolyte in the oxygen analysis cell was regularly refreshed, and the lead electrode was frequently cleaned.

(3)Registered trade name

Results

Five runs we re performed. Only the corrosion potential of the SS autoclave was measured in the first four runs; in the last run, the platinum and 17MnMoV6.4 steel were included. Figure 6 shows the measured corrosion potentials on SS for the five runs.

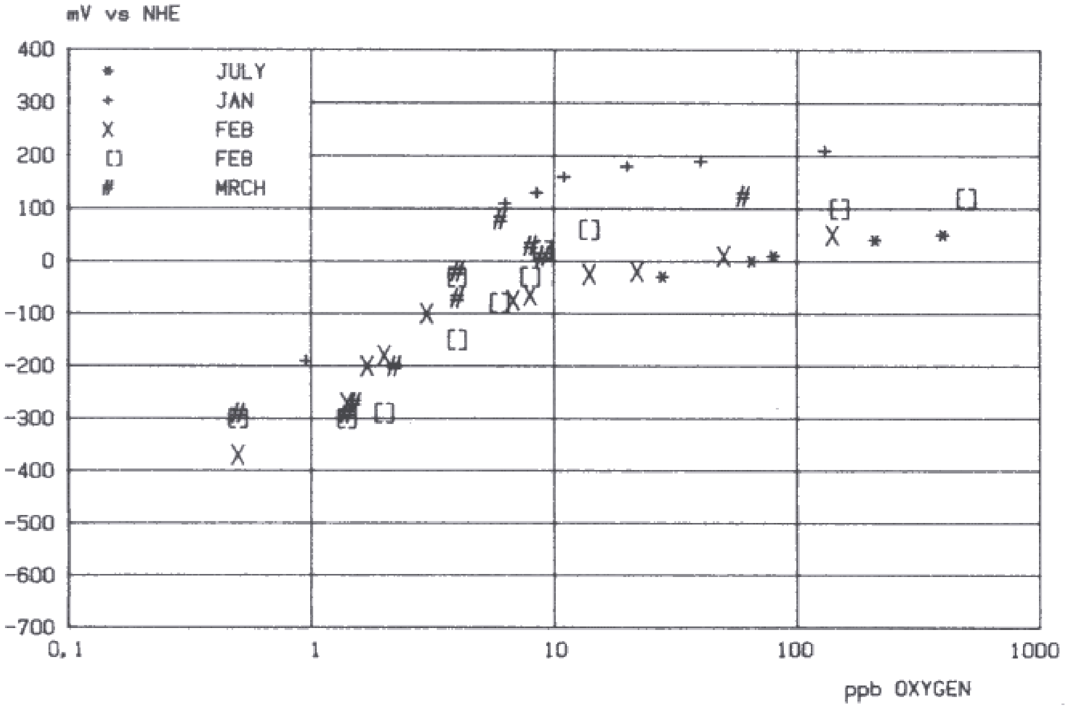

FIGURE 6- Corrosion potential of AISI 304 SS in 200 C water: the water was ammoniated to pH 8.5; linear flow velocity in the autoclave was 10-3 ms-1; and pressure was 50 bar.

During these experiments, the oxygen content was changed at intervals by dosing the initially degassed water with air-containing water ($C0_2$-free) before the highpressure pump or just at the autoclave inlet. When the increment in oxygen content was too large, particularly with low oxygen contents, it took several days for the corrosion potential on SS to become constant. When dosing oxygen just before the autoclave, an immediate response in corrosion potential was seen on the platinum electrode, even though the oxygen at the outlet remained low for several hours. The above effect may be explained by the oxidation of corrosion products in the high-pressure system. On the tubes and appendages, iron oxide (Fe_30_4) is formed that will oxidize to Fe_20_3 with increasing oxygen concentrations. Therefore, the oxygen content of the water was only changed af ter the potentials had become constant and an equilibrium had been established.

Figure 7 represents the results for SS, platinum, and 17MnMoV6.4 steel obtained in the last run. The latter steel was preoxidized for 7 days in water containing 200 ppb O_2. The potentials of this sample are clearly lower than those of SS and platinum.

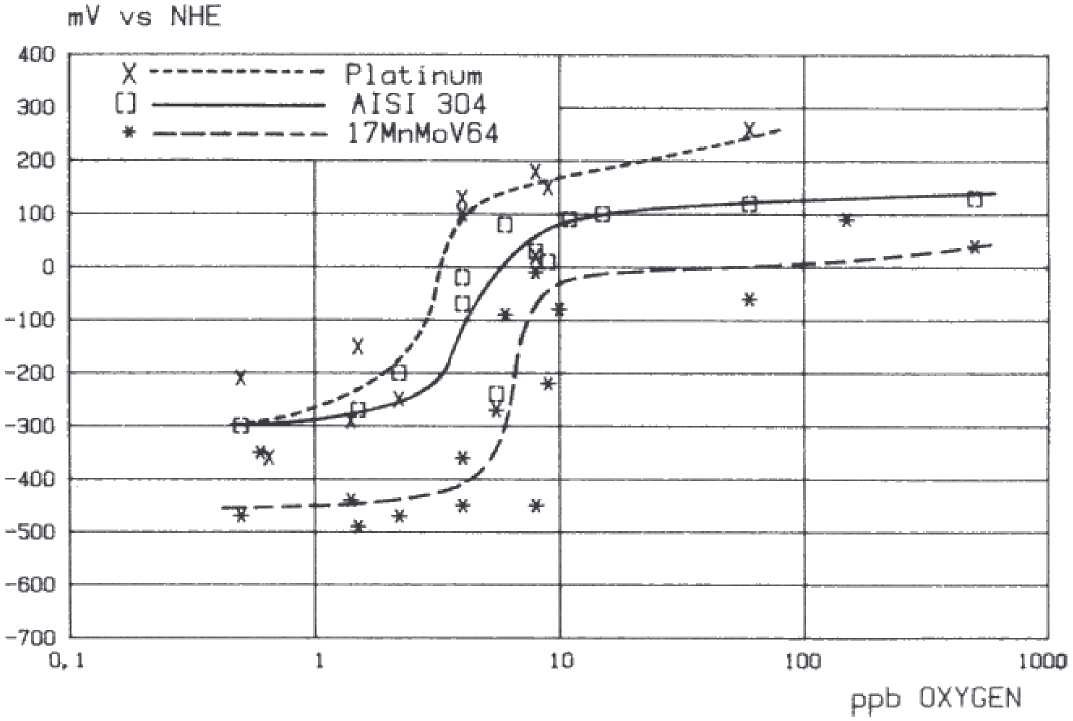

FIGURE 7 -Corrosion potential of platinum, AISI 304, and preoxidized 17MnMoV6.4 steel: the water was ammoniated to pH 8.5,200 C, 50 bar; linear water flow in the autoclave was 10-3 ms-1.

Discussion

The reported test conditions from the present and previoius [1,7,8] investigations are given in Table 1. The flow velocity in the present experiments was rather low: 10^{-3} ms^{-1}. Data concerning the flow velocities in the other research projects were not found. In all experiments, deionized water was used as make-up water with low conductivities. In the present experiments, some ammonia was dosed into the water so that conductivity and pH rose to 7.10^{-4} Sm^{-1} and 8.5, respectively. Conductivities, pH values, and oxygen contents were continuously measured at the inlet and outlet.

According to Murray, the pH values of pure and ammoniated water (0.07 mg/L NH_3) at 200 °C are 5.65 and 5.8, respectively [11] . It is suggested that this small difference in pH will have little effect on the corrosion potential values. Regarding the oxygen measurements, Indig and Lee used Beckman equipment, whereas the present investigation used the Weston and Stack type. For oxygen control, the desired amount of aerated water was injected, whereas Indig, Lee, and Leibovitz changed the oxygen content of the gas mixture above the water in the storage tank. Thus, it appears from Table 1 that a direct comparison of corrosion potential/oxygen content relationships may be ambiguous, either because the test conditions are reportedly different or because the data are incomplete.

TABLE 1 — Test Conditions of the Research Projects Cited

			Indig GE	Lee OSU	Leibovitz NWT	Present Authors KEMA
System	Type		Circulation	Circulation	Circulation	Once-Through Flow Autoclave
	Mass Flow	L/h	—	4	60	8.5
	Flow Velocity	ms^{-1}	—	—	—	10^{-3}
Autoclave	Volume	L	—	4	—	0.32
	Diameter	m	—	—	—	$5.5.10^{-2}$
	Material		Titanium	Inconel[4]	—	AISI 304
Temperature		C	274	100 to 288	288	200
Make-Up Water			Deionized	Deionized	Deionized	Deionized
	Conductivity	Sm^{-1}	$<10^{-5}$	$<10^{-5}$	—	$<10^{-5}$
Water in Autoclave			Pure	Pure	Pure	Ammoniated
	Conductivity	Sm^{-1}	—	—	—	7.10^{-4}
	pH at 25 C		Neutral	Neutral	Neutral	8.5
	pH at 200 C		5.65	5.65	5.65	5.8
	pH at 288 C		5.65	5.65	5.65	—
Oxygen						
	Measurement		Beckman[5] 7001	Beckman 735	—	Weston and Stack
	Dosing Method		Equilibrium	Equilibrium	Equilibrium	Injecting Aerated Water
	Gas Mixture		N_2-O_2	Ar-O_2	—	
Potential Measurement						
	Reference Electrode Ag-AgCl		0.01 M KCl	0.01 M KCl	Pure Water	0.001 M KCl
	Time to Steady Potential	Day	2 à 3	1	—	2 à 3

In the present experiments, the corrosion potentials on SS at a given oxygen content varied by as much as 200 mV over the whole range of oxygen contents. On the other hand, for each individual test run, the potential values are on a characteristic curve (Figure 6), similar to those found in the experiments of Indig and Lee. Figures 1 and 2 show that the scatter in these latter results is also rather high.

This scatter cannot be easily explained. However, the authors are of the opinion that the activity of the electrode surface is a primary factor for the reproducibility of the potential measurements. The passivity of the SS and the amount of the deposited oxide (magnetite and/or hematite) will influence the potential measurements.

An important difference between the measurements of Indig and Lee and those of the present is found in the oxygen value at which the corrosion potential increases rapidly for a given increment in dissolved oxygen content. From Figures 2, 6, and 7 it can be concluded that in the present measurements at 200 °C, the rapid increase in potential for an increment in dissolved oxygen content occurs at much lower oxygen concentrations (1 to 10 ppb) than those observed in Lee's measurements (5 to 1000 ppb) at 200 °C.

Conclusions

1. The Ag-AgGI electrode is readily applicable to electrochemical measurements in hightemperature high-pressure water.
2. The KEMA results show higher corrosion potentials with lower oxygen contents than the experiments in the US. The cause of this discrepancy is not yet clear.
3. A sudden increase in corrosion potential for a given increment in dissolved oxygen content was observed in 200 G water when the oxygen content was in the range of 1 to 10 p pb. This critical potential range was also found to be higher in the US measurements (5 to 1000 ppb).

References

1. M. E. Indig, A. R. Mcllree, Gorrosion, Vol. 35, No.7, p. 288, 1979.

2. M. J. Povich, D. E. Broecker, Materials Performance, Vol. 18, No.10, p. 41, 1979.

3. K. Agrawal, G. A. Welch, J. A. Begley, R. W. Staehle, CORROSION/78, Paper No.187, National Association of Corrosion Engineers, Houston, Texas, 1978.
4. W. Schoch, H. Wiehn, E. Richter, H. Schuster, VGB-Mitteilungen, Vol. 52, No.3, p. 228, 1972.
5. W. M. M. Huijbregts, KEMA Scientific and Technological Report, Vol. 3, No.2, p. 33, 1985.
6. W. Kastner, K. Riedle, H. Tratz, VGB Kraftwerktechnik, Vol. 64, No.5, p. 452, 1984.
7. J. B. Lee, A. K. Agrawal, R. W. Staehle, ..Corrosion and Corrosion Cracking of Materials for Water-Cooled Reactors," EPRI Report NP-1741, Ohio State University, Electric Power Research Institute, Palo Alto, California, March 1981.
8. J. Leibovitz, W. R. Kassen, W. L. Pearl, S. G, Sawochka, "Improved Electrodes for BWR In-Plant ECP Monitoring," EPRI Report NP-2524, Electric Power Research Institute, Palo Alto, California, July 1982.
9. G. Herbsleb, VGB Kraftwerkstechnik, Vol. 64, No.2, p. 138, 1984.
10. K. J. Vetter, Electrochemical Kinetics, Theoretical and Experimental Aspects, Academic Press, New York, New York, p. 642, 1967.
11. W. M. M. Huijbregts, '.Oxygen and Corrosion Potential Effects on Chloride Stress Corrosion Cracking," KEMA Report SO 359/85, to be published.
12. R. C. Murray, J. W. Cobble, Proc. Int. Water Conf., Chemical Equilibria in Aqueous Systems at High Temperatures, Pittsburgh, Pennsylvania, p. 295, 1980.