Faculty of Mechanical Science and Engineering Institute of Power Engineering Chair of Imaging Techniques in Energy and Process Engineering

Electrochemical corrosion studies on zinc in boric acid containing electrolytes

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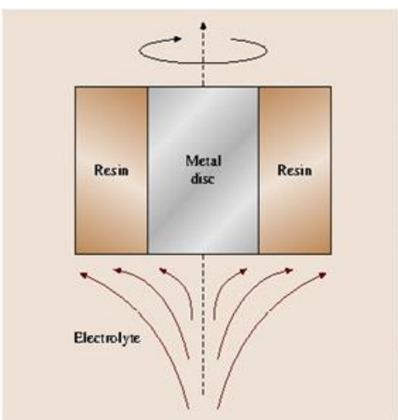
Background and Motivation

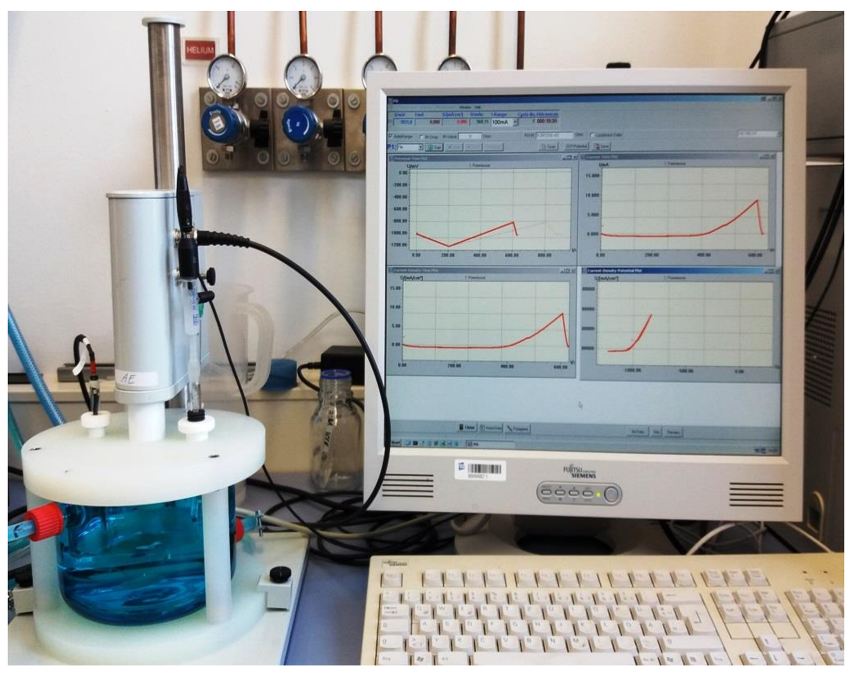
During the sump recirculation phase after a leak in the primary cooling circuit of a pressurized water reactor (PWR), corrosion of hot-dip galvanized containment internals in boric acid containing coolant could cause precipitation of formed zinc borates in hot regions of the reactor core.
Zinc dissolution studies in boric acid electrolytes were conducted to investigate the dependency of zinc corrosion rates in PWR coolants on different boundary conditions (fluid temperatures, pH, boric acid concentration, flow conditions).
Those had shown that moderate variations of the fluid temperatures or the boric acid content only cause small changes in resulting zinc corrosion rates, but an increase of flow rates or turbulences led to significant increased corrosion rates.

The main motivation for the realized electrochemical studies was to elucidate the underlying processes and mechanisms of the zinc corrosion under such boundary conditions (boric acid electrolytes, pH, fluid temperatures, flow conditions).

Experiments

Electrochemical investigations (rotating disc / zinc electrode) of different influencing parameters (temperatures, composition of electrolytes, flow conditions) on the corrosion rate in boric acid containing solutions were executed.



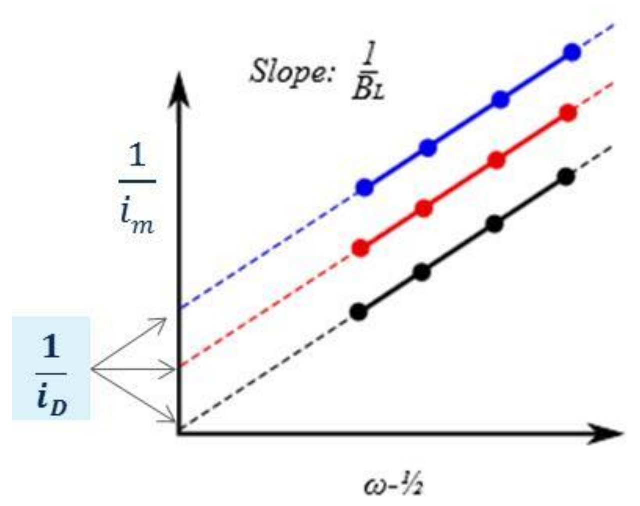


Levich equation (Rotating disc electrode) :

$$I = \underbrace{(0.620)\, n\, F\, A\, D^{2/3}\, \nu^{-1/6}\, C}_{\text{const.}}\, \sqrt{\omega} = B\, \sqrt{\omega}$$

Fig. 1: Investigations with the rotating disc measurement system

- Differentiation between mass transport control and electric charge transfer control (Butler-Volmer eq.)
- Test series under variation of rotation speed and with subsequent Levich extrapolations (ω ⟶ ∞; see fig. 2, 3)



Koutecky-Levich-Plot (Rotating disc) :

$$\frac{1}{i_m} = \frac{1}{i_D} + \frac{1}{B_L\sqrt{\omega}}$$

i_m = measured current density
i_D = current only controlled by el. charge transfer (Butler-Vollmer equation)
B_L = constant from Levich equation

Fig. 2: Levich extrapolation to calculate current densities for infinite flow rates (ω ⟶ ∞ / only charge transfer control / Butler-Volmer eq.)

General parameters of the electrochemical measurements :

- Platinum counter electrode in tempered boric acid solution
- Addition of 0.1 M Na_2SO_4 as conducting salt
- Linear anodic and cathodic polarization up to 200 mV vs. free corrosion potential (v = 1 mV/s)
- Temperature range: 20 … 60 °C
- Boric acid content: 1000 … 3000 ppm boron
- pH values: 4.7 … 7 (addition of LiOH)

Results

- Changes in boric acid content or pH (pH 4.7 … 7) did not lead to significant differences in current (or corrosion rates)
- Plateau in current density at high cathodic overpotentials (see fig. 3) indicates that mass transport controlled oxygen reduction is main limitation of overall reaction rate / corrosion process (pH 5 … 7)
- Strong increase of current density was observed at high rotation speed/ flow rate as consequence of accelerated transport of oxygen to zinc surface (see fig. 3, 4)
- Moderate increase of fluid temperature (20 °C → 60 °C) only led to small increase of current density / corrosion rate (see fig. 5)

Fig. 3 : Series of polarisation curves with tafel plots and Levich extrapolation (2000 ppm boron, pH 5.4, T = 30 °C)

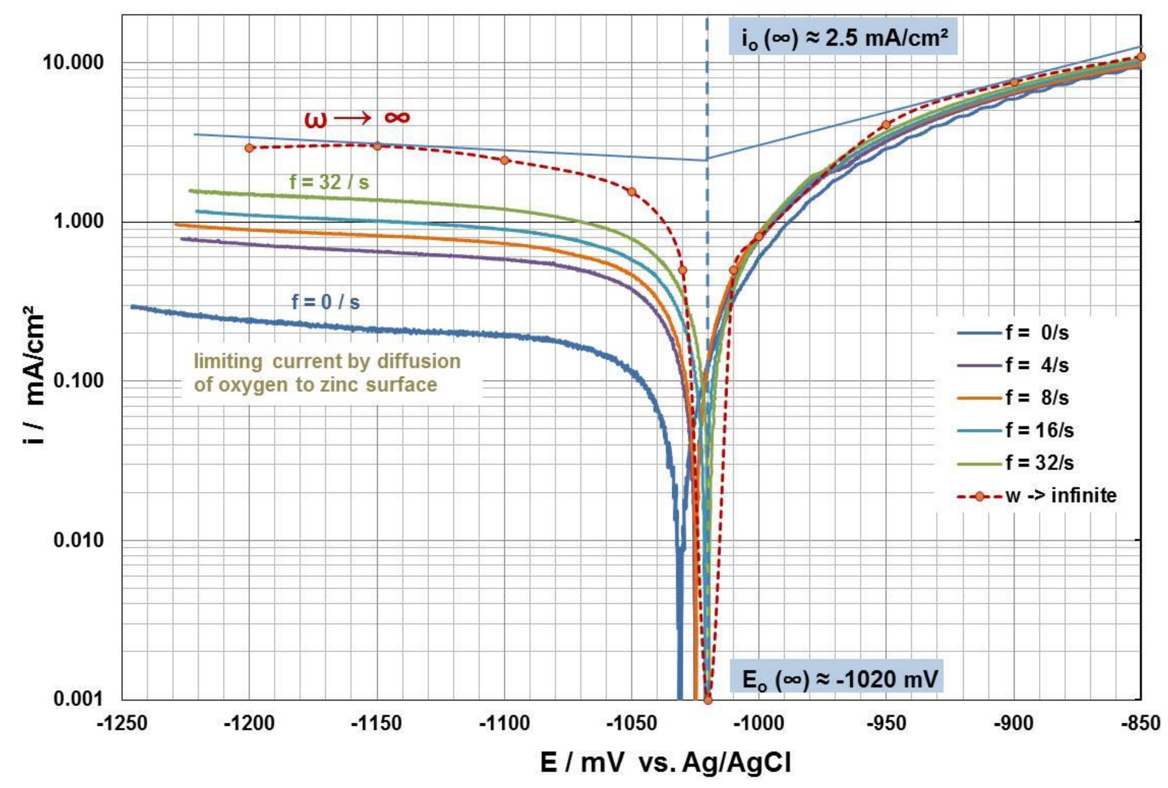


Fig. 4 : Dependency of zinc corrosion rates on flow conditions (rotation speed); System: 2000 ppm boron, (pH 5.4), T = 30 °C

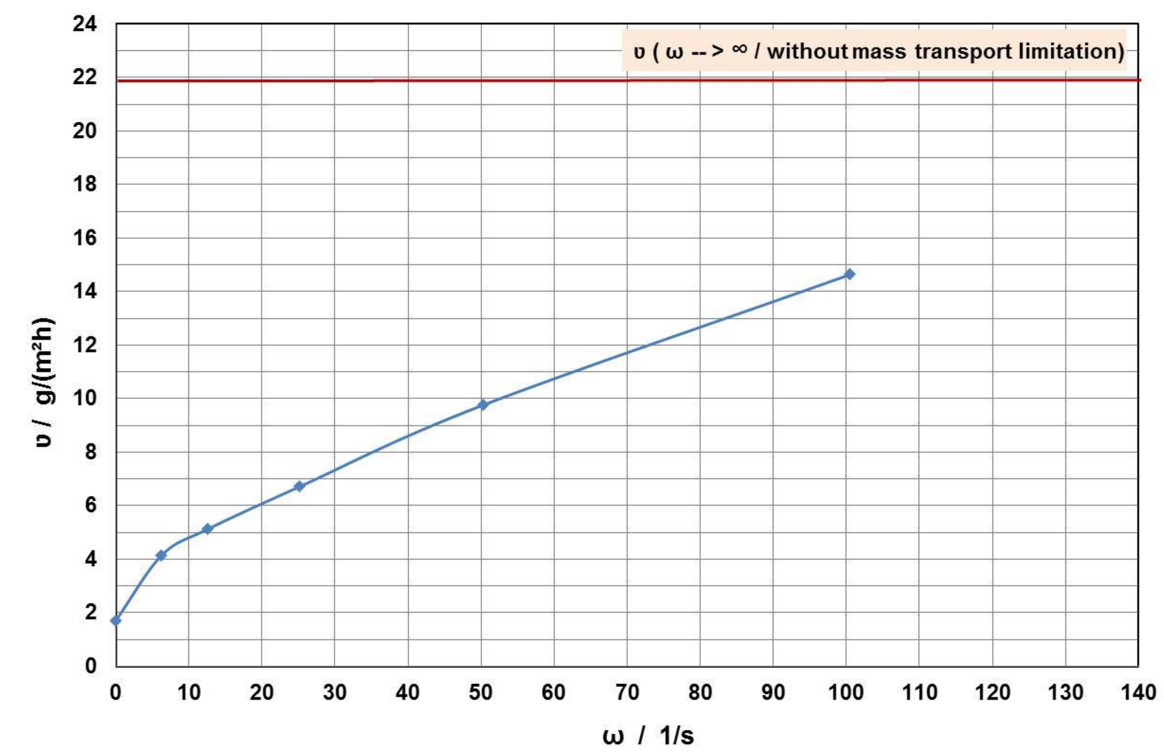
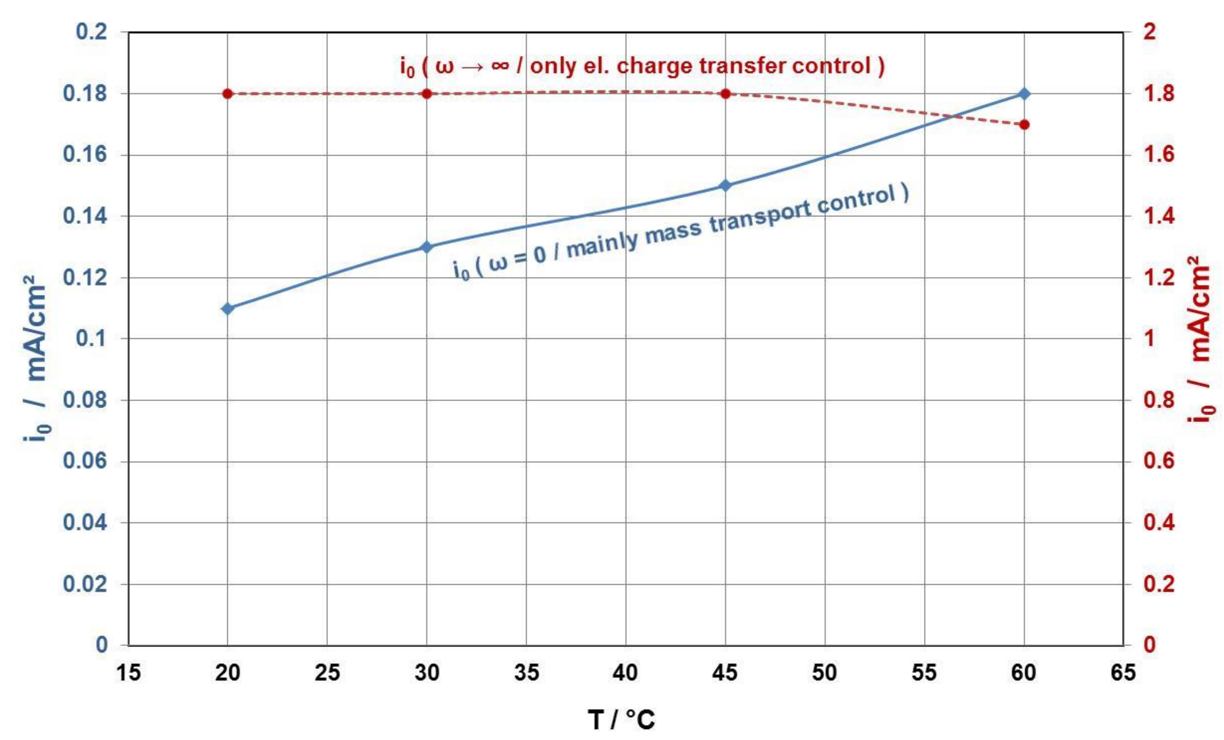


Fig. 5 : Dependency of current density on temperature of the electrolyte; System: 2000 ppm boron, (pH 5.4)



Outlook

Further investigations of the dependency of corrosion rates on flow parameters (flow rate, angel between flow direction and zinc surface, Re number) are to be realized for a better understanding of the mass transport effects and to predict corrosion rates at different flow conditions.

Mitglied im Netzwerk von: DRESDEN concept

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