

Corrosion of Steel in Relation with Hydrogen Activity of Concentrated HClO₄ Media: Realisation Sensor and Reference Electrode

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Abstract : Corrosion behaviour of carbon steel was studied in various concentrated HClO₄ solutions. To explain the acid attack in relation of H⁺ activity, new sensor was realised: two carbon paste electrodes (CPE) were constructed by incorporating ferrocene (Fc) and orthoquinone into the carbon paste matrix and crossed by weak current to stabilize potential difference. The potentiometric method at imposed weak current between these two electrodes permits the in situ determination of both concentration and acidity level of various concentrated HClO₄ solutions. The different factors affecting the potential at imposed current as current intensity, temperature and H⁺ ion concentration are studied. The potentials measured between ferrocene and chloranil electrodes are directly linked to the acid concentration. The acidity Ri(H) function defined represents the determination of the H⁺ activity and constitutes the extend of pH in concentrated acid solutions. Ri(H) has been determined and compared to Strehlow Ro(H), Janata HGF and Hammett Ho functions. The collected data permit to give a scale of strength of mineral concentrated acids at a given concentration. Ri(H) is numerically equal to the thermodynamic Ro(H), but deviated from Hammett functions based on indicator determination. The CPE electrode with inserted ferrocene in presence of ferricinium (Fc⁺) ion in concentrated HClO₄ at various concentrations is realized without junction potential and may play the role of a practical reference electrode (FRE) in concentrated acids. Fc⁺ was easily prepared in biphasic medium HClO₄-acid by the quantitative oxidation of ferrocene by the ortho-chloranil (oQ). Potential of FRE is stable with time. The variation of equilibrium potential of the interface Fc/ Fc⁺ at various concentrations of Fc⁺ (10⁻⁴ - 2 10⁻² M) obeyed to the Nernst equation with a slope 0.059 Volt per decade. Corrosion rates obtained by weight loss and electrochemical techniques were then easily linked to acidity level.

Keywords : ferrocene, strehlow, concentrated acid, corrosion, Generalised pH, sensor carbon paste electrode

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