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Elemental selective dissolution of a silicon-rich austenitic stainless steel in acidic medium investigated through Atomic Emission Spectro Electrochemistry

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Austenitic stainless steels (SS) with silicon additions are used for some equipment containing nitric acid in the spent nuclear fuel reprocessing plant. This work aimed at studying the corrosion behavior of this SS in such acid media. Literature expects the passive layer's evolution to be related to the corrosion potential shifts, even within the passive state [1]. Based on electrical transient currents analysis and X-ray photoelectron spectroscopy, it is shown that its composition is deeply modified and the reversibility of these modifications is unknown [2]. To study these modifications, two kinds of electrochemical experiments were performed: linear polarizations from active to transpassive domains to study the oxidation/dissolution behavior as a function of potential (Fig 1.a.) and alternative polarizations between active and passive states to study the passive layer formation/dissolution kinetics (Fig 1.b.). In both cases, the measurement was followed using in-situ Atomic Emission Spectro ElectroChemistry (inductive coupled plasma atomic emission spectroscope real time connected to a potentiostat) and chemical surface evolution was characterized with ex-situ X-ray photoelectron spectroscopy.

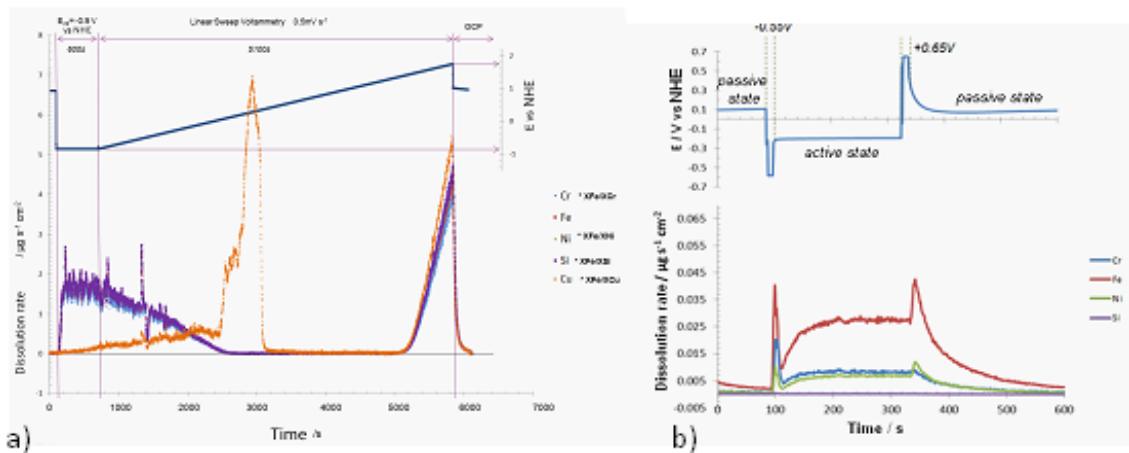


Figure 1.

- Dissolution signals of Fe, Cr, Ni, Si and Cu during a 0.5 mV s^{-1} polarization curve in nitric acid 4M at room temperature (Cr, Ni, Si, Cu signals have been divided by the ratios of each elements versus iron in the bulk)
- Dissolution signals of Fe, Cr, Ni and Si during a passive-active-passive cycle of silicon enriched steel in sulfuric acid 2M at room temperature

An accumulation on surface (resulting from a selective dissolution) of several elements was found as a function of potential. In the active domain, metallic copper accumulates on surface and dissolves intensely at the end of the active domain, which affects the cathodic reaction kinetics (Fig 1.a). In the passive domain, surface accumulation of chromium was found to be reversible when polarized again in the active domain (Fig 1.b). This phenomenon directly controls the SS global dissolution rate. Eventually, accumulation of silicon at the surface was found in both active and passive domains. Hence, this enrichment is more likely to be localized at the surface of the sample, hypothesis which is investigated by XPS.

- Plante, G., *Contributions à l'étude de la passivité d'aciers inoxydables en milieu nitrique bouillant*. 1969, Université de Paris.
- Robin, R., F. Miserque, and V. Spagnol, *Correlation between composition of passive layer and corrosion behavior of high Si-containing austenitic stainless steels in nitric acid*. Journal of Nuclear Materials, 2008. 375(1): p. 65-71.