Electrochemical Noise Measurements of Steels in the Molten NaCl-K_2SO_4 System

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Electrochemical Noise Measurements (ENM) is a term used for the registration of small fluctuations in current and potential around a mean value (the steady state), typically at the corrosion potential. The relationship between these current and potential variations is determined by the processes occurring on the electrode. An electrode undergoing localized corrosion will display low-frequency, stochastic transients originating from occurrence of events on the electrode surface. While being random in nature it still makes intuitive sense to expect a jump in current to be accompanied by a change in potential and visa versa. One application of the ENM technique is to describe this relation between current and potential in terms of a polarization resistance which can be related to the corrosion rate using the procedures developed for potential sweep techniques like steady state voltammetry.

In the present work a series of laboratory experiments are designed to demonstrate whether ENM measurements can be used in a combustion environment where sulfur containing coal is co-fired with chlorine containing biomass (e.g. straw). The eutectic NaCl-K_2SO_4 (40% NaCl by weight) is a model melt for the molten film expected to be formed at superheater tubes at high temperatures. ENM is potentially a very strong tool for monitoring the corrosion as the technique is well suited for *in situ* real time measurements. The main goal is to monitor the occurrence of localized corrosion, a main parameter for life-time assessment of process equipment.

Electrochemical noise measurements (ENM) have been carried out on the steels AISI347, 10CrMo910, 15Mo3 and X20CrMoV121 in molten NaCl-K_2SO_4 at 630°C. Different types of current noise has been identified for pitting, intergranular and peeling corrosion. The corrosion mechanism was the so-called “active” corrosion, characterized by the formation of volatile metal chlorides as a primary corrosion product. A quantitative separation of general and intergranular corrosion based on the kurtosis (a statistical parameter calculated from the electrochemical noise data) was possible based on an average of at least 10 time records. The use of the kurtosis parameter has been suggested previously by Eden[1]. Average kurtosis values above 6 indicating intergranular corrosion and average values below 6 indicating general corrosion. The response time for localized corrosion detection in in-plant monitoring would be approximately 90 minutes on this basis. Reliable determination of corrosion rates was not successful for all steels, partly due to the frequency range used, and partly due to the fact that pitting corrosion in particular would create differences in impedance between the individual electrodes. Both of these factors invalidate the calculations of polarization resistance on the basis of spectral noise resistances. However, polarization resistances of AISI347 and 15Mo3 steels were determined to be 250 $\Omega \cdot cm^2$ and app.100 $\Omega \cdot cm^2$, respectively.

A test at Masnedø Power Station near Vordingborg, Denmark was carried out using an electrochemical probe. The design of this probe was partly inspired from literature[2]. The plant is a biomass fired plant constructed in 1996 almost exclusively using straw as fuel. The capacity is 8.3 MW electricity and 21 MW heat. Slag and ash from the combustion is returned to fields as fertiliser and approximately 40000 tons of straw are burned annually.

The electrochemical noise data were measured with equipment identical to what was used in the laboratory. Corrosion noise from this probe contained the same type of transients as found in the laboratory case of intergranular corrosion. This is an important observation because it shows that localised corrosion can be described qualitatively. This is also indicated in statistical parameters such as the kurtosis.

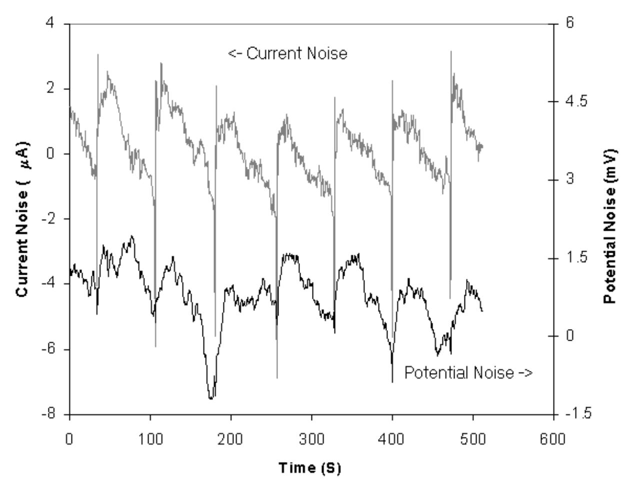

FIG 1: Example of laboratory ENM data from AISI 347 steel electrodes in the eutectic NaCl-K_2SO_4 melt in air at 630°C

REFERENCES

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