Measurement of corrosion in power plant boilers.

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Background of the corrosion sensor

Incinerators are these days commonly used for big scale handling of biomass and wastes, but such plants work at rather moderate efficiencies. The efficiency is normally limited by the thickness of corrosion layers formed on the internal boiler surfaces, especially when the boiler temperature is higher than 520 ^{o}C. On the other hand an enhanced efficiency leads to lower fuel consumption and a better boiler economy. In this connection an understanding of the causality and the control of the processes forming the corrosive layers constitute important steps towards a higher applicable boiler temperature. In two newer plants operated Danish power plant companies (the Masnedø boiler and the SH-bioboiler), the superheated steam temperature has been increased, according to two different principles. In the Masnedø boiler the steam temperature is increased up to 520 ^{o}C following the implementation of several constructive improvements, primarily aimed at the establishment of a self-cleaning superheating system. In the SH-bio boiler the straw incinerator steam temperature is only 470 ^{o}C where there are very few corrosion problems. The steam output from the straw boiler is subsequently fed into a high efficiency coal-fired boiler.

The electric power plant staff have tried to determine the rate of high temperature corrosion for many years. The rate of corrosion was measured in big central plants as well as in delocalised small power plants by use of sensors and with material samples inserted into the boiler chambers. These methods have given valuable information on the extent of corrosive environments in the different types of plants. By use of an instantaneous method such at the so-called electrochemical noise analysis method (ENM) for in-situ watching of the corrosion rate, it will be possible to correlate the operational parameters and similar features with the corrosion rate.

Electrochemical noise analysis method (ENM)

The electrochemical noise analysis method (ENM) is a new method under development for the studying of corrosion rates. It is well suited for remote surveying purposes, because it is possible to sense a local attack (pitting corrosion, stress crack corrosion, grain boundary corrosion, etc.). The purpose of these measurements are to demonstrate that ENM can give reliable information on the rate of corrosion and the corrosion morphology, making it possible to identify a local attack between grain boundaries. During this project new equipment has been developed especially designed for the analysis of electrochemical noise, originating from corroding electrodes. If our hopes the great prospects of this experimental technique will be fulfilled the big potential of the on-line method of measuring corrosion rate in an industrial furnace will be realised. An obvious advantage of the ENM method is the low price of the equipment and the possibility of automation.

Electrochemical noise analysis (ENM) on local corrosion

One obvious advantage by ENM is that it is not necessary to polarise the electrodes. This means that a disturbance of the material that is measured is not necessary. In this way a more true result is obtained than what is normally done by the polarising techniques. ENM can be a difficult technique to handle for non-specialists because the concept "noise" cannot be easily defined. It is necessary to eliminate contributions that have nothing to do with the corrosion processes. Electrochemical noise is made up by small variation in current and voltage caused by (electrochemical) processes at the surface of the metal (the electrode). These variations are of a stochastical (unpredictable) nature. There will be different characteristic features relating to the different kinds of corrosion. Figure 1 below gives an indication of an example based on active corrosion caused by chlorine gas under the formation of volatile $FeCl_2$.

In Figure 1A the formation of $FeCl_2$ at the corrosive front between the metal and the oxide layer (corrosion products). The diagrams to the right show the appearance of the corresponding electrochemical noise diagrams. The noise in measured current is not uniform because the corrosion is local but the overall situation is relatively stable.

In Figure 1B the oxide layer is broken down because of the volatility of the $FeCl_2$ and the unprotected metal is directly open to the corrosive environment. This leads to a change in the corrosion rate, which now will be faster. A big transient in the diagram to the right indicates this behaviour.

In Figure 1C it is shown that the current levels off together with the reformation of the protective layer of the final corrosion products (oxides).

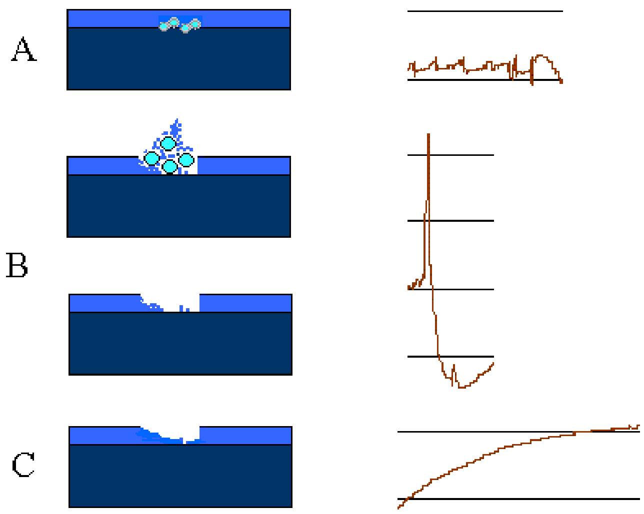

Figure 1: The correspondence between the events on the corroding electrode and the noise in the current. The noise shown in the diagrams to the right originate from real measurements on the steel type 15Mo3 in our laboratory.

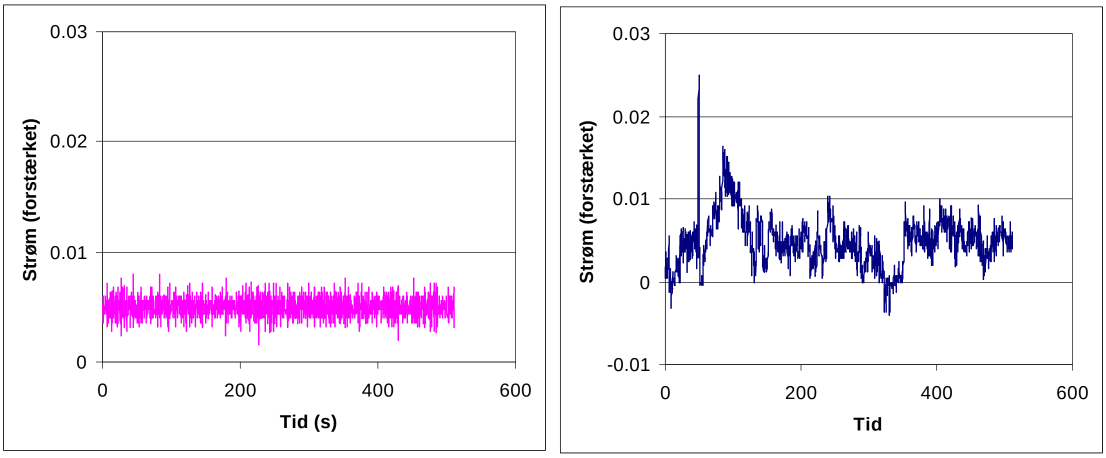

Figure 2: Examples of measured noise in the current. To the left: a situation without local corrosion (white noise). To the right: a situation with local corrosion. The noise shown was obtained with a remote sensor electrode introduced into Masnedø Kraftvarmeværk.

As seen in principle the electrochemical noise contains information on what goes on at the surface under corrosion. A complete noise picture without any characteristic features is seen in connection with general, non-local corrosion. This kind of noise is referred to as white noise and an example is shown to the left in Figure 2. As long as the appearance of the noise pattern can be related to types of corrosion behaviour, it is possible to detect the occurrence and frequency of localised corrosion events.

This determination of electrochemical noise takes place in practice by measuring the fluctuations in the current and voltage from two separate electrodes in relation to a reference electrode. It was chosen to use a system with three identical electrodes, letting one act as the reference. This so-called pseudo-reference electrode will lower the accuracy, because the measurement of delta V and delta I will be the sum of the noise from the two electrodes. Only if one assumes that these electrodes were exactly alike (i.e. same surface area, impedance and surface morphology) would it be possible to determine the contribution to the noise form a single electrode. The reason why it was decided to carry the measurements out with this set-up, was that the design of a measurement probe for use in a boiler would be relatively simple, and a true reference electrode would be really difficult to get to work reliably in practice.

Figure 3 shows a diagram of the practical set-up for the measurement of the electrochemical noise. Since the signal of the noise is very small it is necessary to use amplification. The electronic high-pass filter takes away all signals of low frequency. It will leave the signal of corrosion intact but will filter off any drift. Drift in the potential was a great problem until we installed this filter. The drift was caused by the development of small differences between the electrodes and the corrosion noise signal is very much buried in the overall signal. The set-up as it is now is highly sensitive and even when this kind of drift among the electrodes shows that the electrodes are not exactly alike, the potential difference between two electrodes were only a few millivolt in the worst cases. A low-pass filter was implemented to avoid contributions of frequencies higher than defined by the rate of sampling (a so-called anti-aliasing filter).

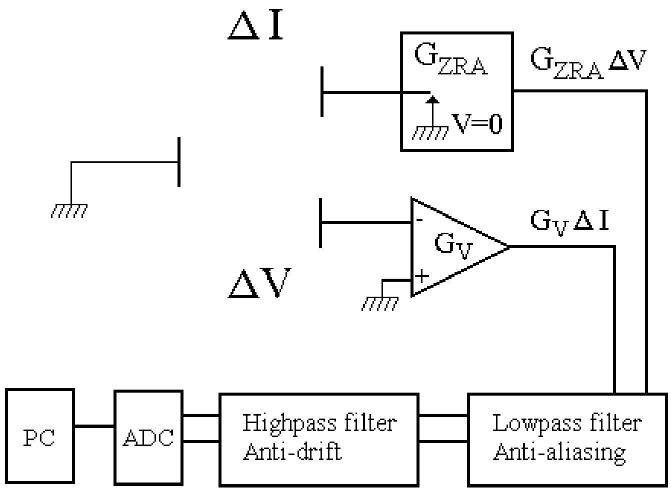

Figure 3: Principle of the ENM measurement circuit.

Sensor testing at the Masnedø Plant.

A series of tests has been made near the Vordingborg town in the Masnedø plant, which burns straws. Electrochemical sensors were used and which were contemplated to be a basis for a system surveying corrosion. At fist the sensor design was in part inspired by designs in the literature. The Masnedø plant was built in 1996 and uses nearly exclusively straw as the fuel. The capacity of the plant is 8.3 MW of electric power and 21 MW of heat. Cinders, clinker and ashes from the plant are returned to the fields as fertilisers and about 40 ktons of straw are burned annually. The results of these tests have been encouraging. The phase of the project in which experiences are gained is still in operation, and new prototype sensors are still being tested.

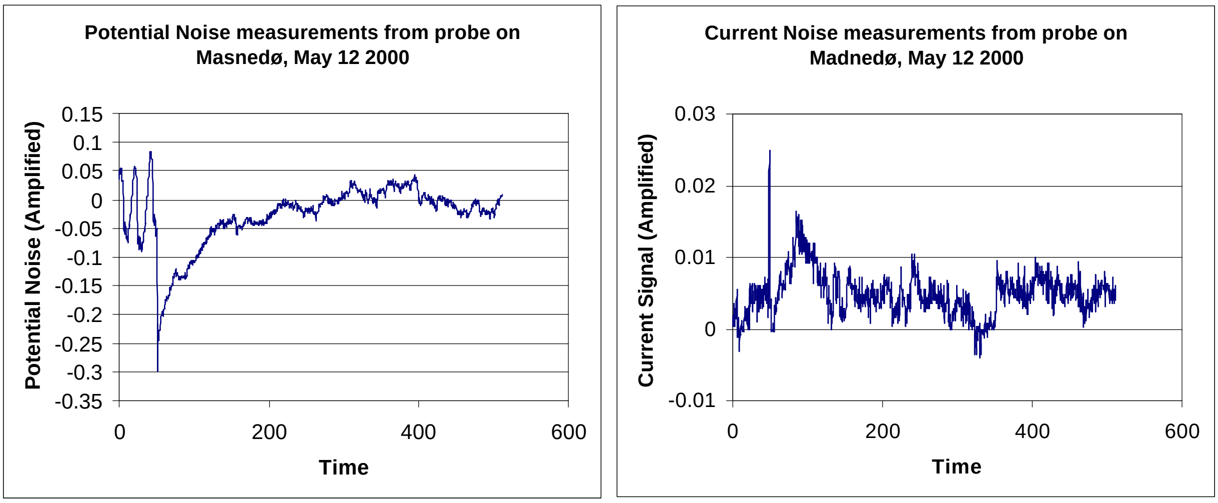

Figure 4: Typical measurement of noise from testing of an ENM sensor.

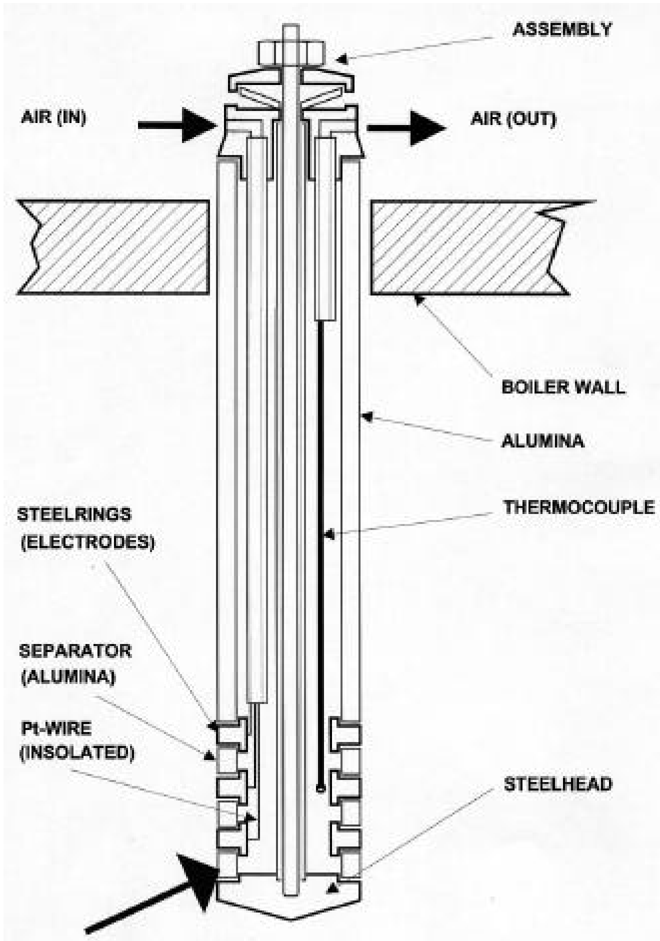

Figure 5: Design of an early type of sensor used for ENM tests.