Technical Bulletin

Number: 2006/02 January 2006

STEAM BOILER CLEANING: REMOVING MAGNETITE LAYERS

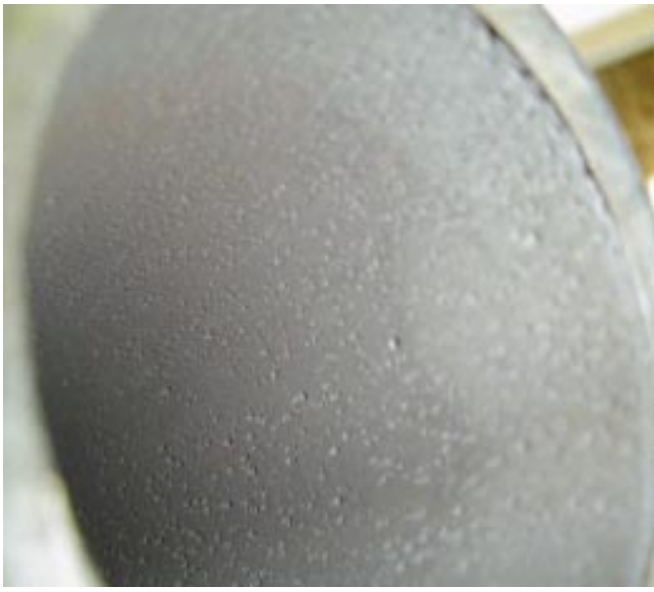
The steam boiler in a power station is made of carbon steel and the surface of the water side of the boiler must be kept free of undesirable deposits.

Deposits have a lower thermal conductivity than steel and make it necessary to raise the temperature on the combustion side of the boiler. Thus more fuel is needed to generate steam. The heat transfer efficiency (ratio of fuel consumed to steam generated) reduces.

Steam has the very important characteristic that at a specific elevated temperature it reacts with the iron ions on the boiler wall steel on the water side, to form a uniform layer of iron oxide (Fe_3O_4), known as magnetite. In a reducing atmosphere at temperatures above 100°C where the water acts as an oxidising agent, the electrochemical reaction takes place and a layer of magnetite is formed.
This magnetite layer is a typically black, extremely thin adherent film that passivates the steel surface and therefore protects it from corrosion. The layer of magnetite is thus a desirable deposit in a steam boiler and in an ideal situation the water side of a boiler would be coated with just this thin film of magnetite. This is often achieved by using a boiler water treatment programme. However, in time the magnetite ages, it can become porous or even detached.

Magnetite layer before cleaning
Top right: removed magnetite deposit

Then there is a chance of excessively thick localised deposits so that the film is no longer thin and strong. In addition to the negative effect on heat transfer, such irregularities also form a source of adhesion for other undesirable salt deposits such as calcium carbonate. When the efficiency of the steam boiler becomes too low or when there is a possibility of blockages and leaks, the decision is often made to clean the water side of the boiler chemically.
An inspection is carried out prior to chemical cleaning. This is usually done by sawing through a number of pipes at the point in the boiler pipes where the most deposits are expected. After an extensive metallurgical examination, the pieces of pipe with the deposits can be used for carrying out a cleaning test. The aim of such a test is to draw up the most suitable cleaning procedure. Firstly it is important that the composition and the quantity of the deposit is known, because only then can the most suitable chemical cleaning procedure be drawn up.



In December 2005 Vecom Industrial Services successfully chemically cleaned the evaporator at EPZ NV's coal-fired power station at Borssele. Prior to the cleaning, a laboratory examination was carried out so that the method and the cleaning agents required could be determined.
The chemical cleaning was carried out following the traditional method: degreasing, pickling with a mixture of hydrofluoric acid and hydrochloric acid, passivating with ammonium citrate and an oxidizing agent.

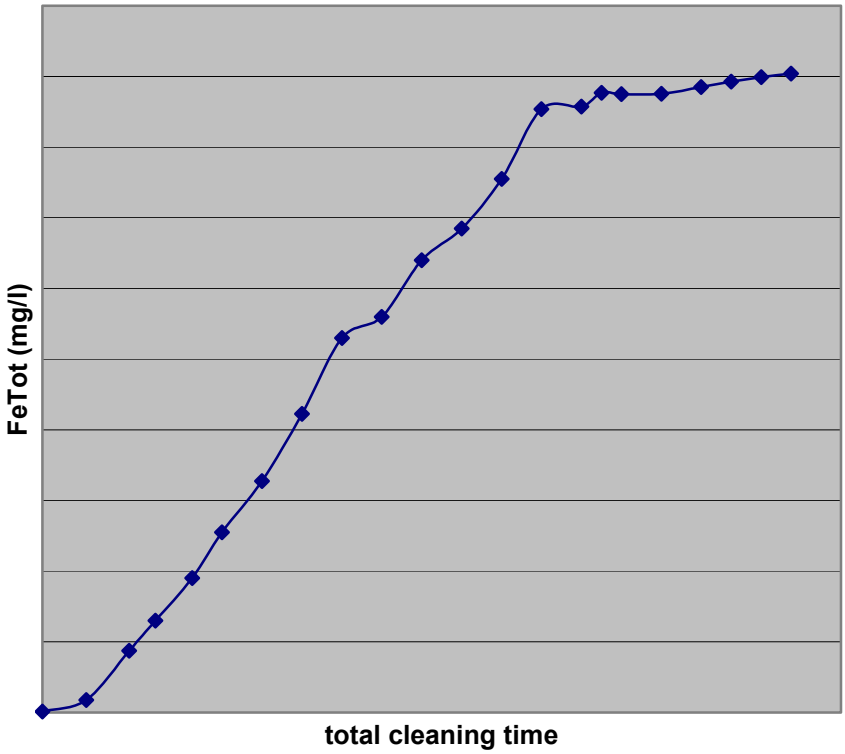
During the pickling phase, which is carried out by circulating a warm inhibiting hydrochloric acid/hydrofluoric acid solution, the magnetite (iron oxide) reacts with the acid. Thus the iron concentration in the cleaning fluid will increase and because the requirement is to dissolve the deposit and protect the bare steel against the corrosive action of acids, an inhibitor is added to the acidic solution. An inhibitor will reduce the corrosion rate to a value less than 50 mpy. The iron content in the cleaning fluid is therefore a parameter that is continuously determined and eventually gives a picture of how the cleaning is proceeding. When the iron content stabilises, all the magnetite has dissolved and the pickling phase is complete (see graph 1).

After the pickling phase, the steel surface will be very reactive and damp and oxygen will cause flash rust to form. Therefore the last phase of the boiler cleaning is the removal of this flash rust and the application of a passive iron oxide film. First a warm citric acid solution is used to remove the flash rust. Then the citric acid is neutralised with ammonia to form ammonium citrate with an alkaline pH.

Normally the dissolved iron would then precipitate as hydroxide, but because of the strong tendency of the ammonium citrate to form complexes, the iron remains in solution. A strong oxidising agent is added to this ammonium citrate to enable the ferrous ions to oxidise and therefore convert metallic iron into a uniform ferric state. This results in a thin, passive, cohesive iron oxide film (gamma Fe_2O_3). This passive film forms an excellent basis for the following boiler water treatment programme.

Standard set-up for chemical cleaning of a steam boiler

Graph: Typical curve of the total iron during chemical cleaning.



Author: T. van Os (Head Laboratory)
Reactions and/or questions: e-mail: tb@vecom.nl