

Deactivation of SCR Catalyst

Prof.-Dr. Heinz Gutberlet, PreussenElektra Engineering

Andreas Schlüter, KWH

Anthony Licata, Technical Advisor, KWH

DEACTIVATION MECHANISMS

There are many factors that cause the catalyst to deactivate. Poisoning is a primary factor in deactivation with blockage and physical destruction of equal importance to catalyst life. When the surface or the pores of catalyst are blocked, flue gas/NO_x cannot contact the catalyst. This causes the same detrimental effects as if the catalyst was poisoned. Dr. Howard Franklin published an excellent analysis of these mechanisms and we have included some of his findings in this paper.

Sulfur

SO₃ formed during combustion and by catalytic reaction combines with ammonia to create ammonium bisulfate, which is a small sticky particle that causes major clogging problems in the air heater and on the catalyst surface. These formations are a function of SO₃ and NH₃ concentrations plus lower SCR operating temperatures. Vanadium in the catalyst cannot be entirely eliminated and oxidizes 1 to 2% of the SO₂ to SO₃, increasing the SO₃ concentration of the flue gas.

PreussenElektra developed an SO₃ control technology using limestone addition to the coal. This yields distinct reductions in SO₃ emissions and was an offshoot of limestone injection work to mitigate arsenic (As) poisoning of the catalyst.

Alkaline Metals

Alkaline metals chemically attach to active catalyst pore sites and cause blinding. Sodium (Na) and potassium (K) are of prime concern especially in their water-soluble forms which are mobile and penetrate into the catalyst pores. Certain U.S. PRB coals contain more than twice the water-soluble metals than German coals.

Earth Metals

Earth metals, especially calcium (Ca), react with SO₃ absorbed within the catalyst to form CaSO₄ and blind the catalyst. Calcium compounds in fly ash from PRB coals are bound to and finely distributed throughout the fuel resulting in the reaction with sulfur taking place on boiler tubes and the catalyst surface.

Vanadium

Vanadium in the fuel is deposited on the catalyst as vanadium sulfate and together with vanadium pentoxide in the catalyst increases the catalyst reactivity and increases the oxidation of SO₂ to SO₃. This is countered by reducing vanadium pentoxide in the catalyst and increasing catalyst volume.

Fly Ash Plugging

Plugging of catalyst channels occurs due to poor gas distribution in the SCR reactor or excess fly ash carryover. Modeling studies prior to designing the ductwork and SCR reactor are essential. KWH normally designs for about 5% plugging of the channels between cleanings/outages.

CATALYST DEACTIVATION BY ARSENIC

Deactivation of SCR catalysts by arsenic was observed in Germany during testing of SCR catalysts in slag tap furnaces with 100% ash recirculation. Japanese catalyst manufacturers anticipated an activity loss of 65% residual activity after 16,000 hours based on experience with dry bottom furnaces. In the PreussenElektra slag tap furnace pilot plant with ash recirculation, this occurred after only 400 hours of operation. It was immediately clear that a high-dust application under these preconditions is impossible.

Initial Measurements

In 1986, testing was performed before the air preheater of different furnace types to determine the cause of this activity loss. Initial testing indicated that in both dry bottom furnaces and slag tap furnaces without ash recirculation, the volatile arsenic in the flue gas was near the detection limit of 0.001 mg/m^3 while in a slag tap furnace with ash recirculation it was 1 mg/m^3 or 1000 times higher.

Ruhr District coal was used in both types of furnaces so these differences were not from the fuel. Therefore, the poisoning of SCR catalysts in slag tap furnaces with ash recirculation appeared to be due to the presence of higher levels of gaseous arsenic in the flue gas before the air preheater.

Measurements in Different Furnaces

Gaseous arsenic levels before the air preheater were studied by PreussenElektra Engineering and KWH in about 15 different furnaces, chiefly slag tap furnaces with ash recirculation. Widely varying concentration levels were found in the flue gases. Specifically, in slag tap furnaces with ash recirculation, the arsenic in the flue gas varies from 0.001 to 1 mg/m^3 with a similar degree of poisoning of the SCR catalysts. Even in the case of dry bottom furnaces, arsenic can contribute under unfavorable conditions to the deactivation of the catalysts. The arsenic content of coal was thus identified as the sole cause of these plant-specific differences; however, no correlation could be found.

Influence of Concentration

Arsenic in the furnace enters with the coal and with recirculated fly ash. A small portion of the arsenic is discharged with the bottom ash. Arsenic leaving the furnace with the flue gas is partly separated on the heating surfaces during its passage through the boiler. Two mechanisms should be differentiated here:

- The reaction with boiler tube deposits which are generally in the region of the high pressure bulkhead and of the preheater which leads to deposits containing arsenic, and
- Deposits of arsenic with the ash on the contact heating surfaces, i.e. in the wake of general boiler fouling between the soot-blowing intervals.

The arsenic cycle which is fed by coal thus has three natural deposit points; the bottom ash, the boiler, and the clean gas downstream of the electrostatic precipitator. The fourth point is represented by an arbitrarily

adjustable discharger of fly ash at the electrostatic precipitator. A fifth point could be a catalyst in the flue gas flow before the air preheater.

Soot blowing is a daily operational process in a boiler in which the arsenic cycle gets enriched from two sources, i.e. from the coal and the boiler deposits. In the case of recirculation operation, this has enormous consequences on the concentration factor in the cycle. Under identical conditions, a concentration factor of 18 is obtained during soot blowing instead of 7 at steady-state operation. The arsenic feed has a uniform concentration in the bottom ash, in the fly ash, and in the flue gas before the air preheater. The concentrations in all three material flows rise directly after soot blowing.

Influence of Ash Quality

The high furnace temperatures in the slag tap furnace cause fusion of a considerable quantity of minerals in the glass matrix. Although, there are some plant-specific differences, it can be ascertained that fly ash from slag tap furnaces contain a maximal crystalline amount of only about 5%. In the case of dry bottom furnaces, the percentage is about threefold of the above.

The influence of calcium oxide was demonstrated with a test at the Datteln Power Plant. This test determined that the main influence is due to the reactivity of flue gas particulate matter with the increase in the percentage of free and thus reactive CaO.

Certain components of ash, including the reactive CaO determine the reactivity vis-à-vis arsenic trioxide. The reactivity is greater, in proportion to the more reactive CaO the ash contains whether it is a component of the coal or is introduced by the addition of limestone. The increased fusion of these minerals in the glass matrix of the ash acts negatively on the reactivity in the case of slag tap furnaces as against the dry bottom furnaces, since the compounds bound in the glass matrix lose their reactivity.

A further influencing variable is the oxygen content of the flue gases. Increasing the excess air decreases the arsenic of the gas phase and reduction in excess air increases it.