Arsenic resistant SCR catalysts

by:

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Summary

Gaseous arsenic trioxide (As$_2$O$_3$) is known as one of the most severe catalyst poisons in Selective Catalytic Reaction (SCR) applications. The vanadium/tungsten based SCR catalyst from Haldor Topsøe A/S has proven exceptionally tolerant towards poisoning by arsenic deposition. The Haldor Topsøe DNX® type catalyst has an optimized, trimodal pore structure which serves the purpose of distributing arsenic in the entire catalyst structure without blocking the pore system and impeding the diffusion of NO$_x$ and NH$_3$ to the active sites. This allows the arsenic uptake in the catalyst to exceed one weight percent before any effect is observed in catalyst activity. The result is a virtually arsenic proof catalyst with a very high tolerance towards arsenic poisoning.

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Gaseous arsenic and SCR performance

Arsenic in gaseous form is usually regarded as one of the main contributors to deactivation of catalysts in SCR DeNOx units on coal-fired boilers. Deactivation rates exceeding 50%/10000 hours have been observed in SCR’s installed on wet bottom boilers [1,2]. The effect is normally less severe but in many cases arsenic also contributes significantly to SCR deactivation on dry bottom boilers.

Arsenic (As) is a component found in most of the world’s coal supply. As the coal is burned, arsenic is released in the furnace as a gaseous oxide, As$_2$O$_3$(g). If the concentration of gaseous As$_2$O$_3$ exceeds the vapor pressure equilibrium in the SCR catalyst, As$_2$O$_3$ condenses in the porous catalyst structure, which may block access to the catalytically active sites. The rate of arsenic accumulation in SCR catalysts is proportional to the gaseous As$_2$O$_3$ concentration. Arsenic accumulation progresses until equilibrium of arsenic saturation is obtained in the catalyst pore system. The amount of arsenic at saturation is determined by flue gas temperature and As$_2$O$_3$ concentration. There is unfortunately no simple correlation between coal arsenic content and the arsenic gas phase concentration. The gas phase concentration depends on boiler configuration and the chemical composition of the coal. In dry bottom boilers normally 95-99% of the arsenic ends up in the ESP fly ash and in the bottom ash [3]. However, this is strongly influenced by the amount of reactive calcium oxide (CaO) present in the fly ash. As$_2$O$_3$(g) formed in the boiler reacts with CaO in the ash to form calcium arsenate Ca$_3$(AsO$_4$)$_2$. In alternative boiler configurations such as wet bottom boilers (cyclone boilers) and wet bottom boilers with ash recirculation the fraction of arsenic present in gas phase may increase significantly. Arsenic levels in flue gases are found to range from 10 µg/Nm$^3$ up to 1000 µg/Nm$^3$[1], a rather large span. The reason for the difficulty in estimating the arsenic gas phase concentration is that it is difficult to establish mass balances from coal chemical analyses and fly ash analyses due to the uncertainty of coal analyses. Arsenic is quite heterogeneously distributed in coal. There have also been difficulties with arsenic analysis procedures. Some of the standard analysis procedures caused arsenic to sublimate during sample preparation.

A better determination of the average gaseous As$_2$O$_3$ concentration can be obtained by arsenic analysis of successive catalyst layers. Unlike other SCR catalyst poisons, that are present as particles that distribute evenly throughout the catalyst, a clear gradient can be found for arsenic through the SCR catalyst layers due to the higher diffusion rate into the catalyst for gaseous As$_2$O$_3$. The analysis should be carried out after sufficient operation time but before the catalyst is saturated. At Stigsnaes power plant in Denmark the first catalyst layer (single layer NHSV = 16000 h$^{-1}$) had accumulated 2190 ppm arsenic whereas the second layer had accumulated 1874 ppm. Since the accumulation is proportional to the gas phase As$_2$O$_3$ concentration gas phase arsenic has decreased by 14% across the first catalyst layer to the second layer. The 2190 ppm arsenic accumulated in the first layer therefore account for 14% of the total gas phase concentration, which means that the gas phase arsenic concentration has been 23
µg/Nm$^3$. At Avedore power plant in Denmark a similar calculation yields 10 µg/Nm$^3$. Fly ash or coal arsenic and calcium contents gives an indication whether there is a risk of high gaseous As$_2$O$_3$ levels. The combination of an arsenic content in the coal above approximately 5 ppm and calcium content in the ash below 3% potentially leads to high gaseous arsenic content in the boiler flue gas [4,5].

**Arsenic deactivation mechanism**

Arsenic poisoning is caused by gaseous arsenic oxide. As$_2$O$_3$ has a melting point of 312°C and a reported vapor pressure of 66.1 mmHg at this temperature [6]. The observed gradients of arsenic accumulation rates going from the first layer to the succeeding layers actually prove that arsenic is deposited from the gas phase. Similar observations have been made by Schallert and Guterlet [7,8]. As$_2$O$_3$(g) diffuses into the catalyst and solidifies in the micro pore structure. The effect is at least to some extent reversible since it has been observed that the arsenic load in the catalyst decreases when switching to another coal source with lower arsenic content. As$_2$O$_3$(g) either adsorbs on specific sites on the catalyst surface or condenses due to capillary forces. Capillary condensation occurs when a condensing material, e.g. liquid As$_2$O$_3$, wets the surface of a porous material which creates a concave curvature in the liquid surface. This increases the coordination number for the condensed molecules in the interface and results in a lower vapor pressure. The equilibrium arsenic uptake, i.e. the level at which no further accumulation occurs, depends on As$_2$O$_3$ concentration in the gas phase, temperature and pore size distribution.

In order to investigate the distribution and mobility of arsenic inside a DNX catalyst wavelength and energy dispersive X-ray spectrometry (WDS and EDS respectively) were used to measure arsenic concentrations in the catalyst wall cross section. The analyzed sample has been installed at Allegheny Energy Supply’s Harrison station for 6,200 hours. The results reveal that arsenic during catalyst operation is distributed evenly throughout the entire cross section. In some cases, a minor gradient through the wall (cf. Figure 1) can be observed. The arsenic present on the catalyst examined does not contribute to its deactivation. In fact, the average As/V molar ratio is 1.63, which implies that arsenic is not a strong chemical poison. A transmission electron microscopy study with EDX analysis of the micro pore structure in the same sample shows that arsenic is distributed evenly on a 2 nm scale.
Figure 1 Typical As and V profiles in a DNX catalyst wall. The profile is obtained by WDS in a scanning electron microscope (SEM). The SEM image to the right shows where the profile was acquired.

These observations indicate that a catalyst with a homogeneous micro pore structure is susceptible to arsenic poisoning. As₂O₃ condensation in micro pores close to the catalyst surface may block the access to the interior part of the catalyst [4]. Earlier experience from Germany shows an enrichment of arsenic up to 7% by weight in the surface part of an arsenic deactivated catalyst compared to an average arsenic content of 9,700 ppm [8].

Countermeasures

Different approaches can be used for minimizing the effect of deactivation due to arsenic. Adding CaO to the fuel has been demonstrated to successfully minimize levels of gaseous arsenic [4,9,10,11]. An alternative and more economically feasible approach is to modify the catalyst either chemically or physically by optimizing the pore structure. One approach applied has been molybdenum addition to the catalyst which seemed to have some effect [4,12]. However, the Mo based catalysts also contained a modified pore volume distribution, i.e. larger pore volume and lower BET surface area [4]. It is now widely recognized that the key to abate arsenic poisoning is to modify the pore structure [4,9]. With this in mind Haldor Topsøe has optimized the arsenic tolerance of its DNX® vanadium/tungsten based catalyst.
HAldor Topsøe industrial experience

The Topsøe DNX® catalyst has been operated on various coals from all over the world. In all cases the DNX® catalyst has proved to be insensitive to the amount of arsenic accumulated in the catalyst. In the laboratory it has been shown that 10,000 ppm arsenic uptake from the gas phase results in only a 10% decrease in catalyst activity and even 5% arsenic uptake only reduces activity by 40%. The accumulation of arsenic and deactivation rates have been monitored in a number of high dust SCR units with DNX® catalyst and these results confirm the expected feature of the DNX® catalyst.

The performance of Topsøe’s DNX-362 on US high sulfur coal with up to 6 ppm arsenic was demonstrated at Southern Company Services pilot plant at Plant Crist, Pensacola, FL. The plant was in operation for approximately 10,000 hours burning US high sulfur coal. This coal often gives high gaseous arsenic levels because SO$_3$ and As$_2$O$_3$, both acidic gases, compete for the same reactive CaO sites in the fly ash. A very rapid accumulation of arsenic was observed in the catalyst test monoliths during the first approximately 3,000 hours. A slight decrease was observed after 3,000 hours which correlates with a switch to another coal type. The coals that were fired the first 3,000 hours was from Illinois (KerrMcGee #5 and #6 mines) blended with coals from Alabama (Taft, Walker and Jefferson Counties). From 3,000 run hours and onwards coals from Illinois #6 and Herin #6 mines were fired. The presence of 3,000 ppm arsenic in the catalyst has no effect on the catalyst activity as clearly shown by the graph in Figure 2. The deactivation was as expected for high dust operation with other bituminous coal types.

Arsenic accumulation and deactivation of DNX-362 has been monitored for almost 40,000 hours at Avedøre power plant in Denmark. The accumulation of arsenic in catalyst test coupons is shown in Figure 3. During the period from start of run to 10,000 hours the boiler was burning coal from Russia. The arsenic content in the coal was approximately 15 ppm whereas the arsenic content in the ESP fly ash was approximately 50 ppm. In the period between 10,000 hours and 27,000 hours coal from Poland with a lower arsenic content was burned in the boiler. During this period the As$_2$O$_3$ vapor pressure decreased and arsenic was released from the catalyst. After 27,000 hours the fuel was switched to US high sulfur coal and the arsenic content in the catalyst increased again. The arsenic content in the three layers stabilizes at approximately the same level, as expected. However, initially the uptake in the first layer was larger compared to the 2nd layer since approximately 30% of the gaseous As$_2$O$_3$ is captured in each layer (1 meter catalyst bed). The As$_2$O$_3$ concentration therefore is lower at the entrance to the succeeding layer. The accumulation of arsenic had no observed effect on the catalyst activity. The activity numbers shown in Figure 3 are the test coupon activities corrected to monolith activities - including a correction for the accelerated deactivation that is always observed in test coupons.
Figure 2: Arsenic accumulation and development in activity relative to the fresh catalyst activity at Plant Crist. The fuel is high sulfur eastern coal with an arsenic content of 6 ppm. The SCR temperature was approximately 370°C (634°F) (design flow conditions).

Figure 3: Arsenic accumulation and deactivation at Avedøre power plant. The fuel history is described in the text. The SCR temperature is 360°C (634°F).
**Figure 4:** Arsenic accumulation and SCR catalyst deactivation at Allegheny Energy Supply’s Harrison station. The fuel is high sulfur eastern bituminous coal. The SCR temperature has been approximately 350°C (598°F).

**Figure 5:** SCR catalyst activity as a function of arsenic content in a number of Haldor Topsøe SCR catalyst installations.
For the SCR unit at Allegheny Energy Supply’s Harrison station arsenic accumulation is shown for the first 6,200 hours of operation in Figure 4. The coal fired is high sulfur eastern bituminous coal. The arsenic accumulation is initially very rapid. However, the chemical analyses indicate that the arsenic accumulation has ceased after 6,200 hours. After 3,000 hours, there is a clear difference in the arsenic content between 1st and 3rd layer. After 6,200 hours, the arsenic content seems to have stabilized in all layers indicating that the arsenic uptake has stopped. The activity relative to the fresh catalyst activity of a catalyst element that was tested after 6,200 hours was 88% which corresponds to a projected deactivation rate of less than 15%/10000h over the service life of the catalyst.

By plotting catalyst activity as a function of accumulated arsenic for a number of Topsøe catalyst installations it is seen that there is no correlation between arsenic content in the DNX® catalyst and SCR activity (cf. Figure 5).

Optimised pore structure

The DNX® catalyst pore structure is optimized to provide arsenic resistance by introducing a trimodal pore structure, i.e. a pore structure that contains pores of three different sizes, in combination with a high porosity (cf. Figure 7). The catalyst elements are manufactured by fusing a corrugated glass fiber structure with titania. The primary particles of the titania have a diameter of 10-20 nanometers. The size and packing density of the primary particles determines the size of the micro pore structure. The micro pores provide the high specific surface area necessary for the catalyst intrinsic activity. During the manufacturing process, clusters of the primary TiO$_2$ particles are milled down to approximately 1 micron. The packing of these clusters, which is controlled by dispersing agents in the titania slurry, determines the size of the meso pores which are critical for arsenic resistance. Finally, the catalyst contains macro pores, which serves to enhance the diffusion of SCR reactants into the catalyst and thereby improve catalyst activity.

![Figure 6: Distribution of As (measured by EDS) in the matrix of micro pores and meso pores. The arrow on the scanning electron microscopy (SEM) image represents the path of the EDS scan.](image-url)
Figure 7: DNX pore size distribution. The three pore size regimes - A: Macro pores, B: Meso pores, C: Micro pores - are visualized by scanning electron microscopy (SEM).

A: Macro pores

B: Meso pores

C: Micro pores
Figure 6 shows how arsenic distributes evenly in the matrix of micro pores and meso pores during exposure in SCR installations. This distribution ensures that the active sites are accessible for the SCR reactants without any additional diffusion restriction caused by condensed As₂O₃. The fine distribution of arsenic combined with a high specific pore volume means that the Topsøe DNX® catalyst can maintain its activity even though fairly large amounts of arsenic have been accumulated in the catalyst.

**Conclusion**

Arsenic poisoning of SCR DeNOx catalysts is most effectively abated by optimizing the catalyst pore structure. The DNX® catalyst from Haldor Topsøe features a trimodal pore structure. The resistance towards arsenic poisoning has been demonstrated in a number of installations including units firing US eastern bituminous high sulfur coal resulting in high levels of gaseous arsenic. Even arsenic accumulations close to 10,000 ppmw in the catalyst do not seem to affect significantly the activity.

The full scale observations show that arsenic accumulates in the catalyst layers by deposition of gaseous As₂O₃(g). Initially the highest accumulation rate is seen in the first layer. After some operation time a saturation point is reached and the arsenic uptake ceases and the arsenic content stabilizes at the same level in all layers. The observed deactivations are as expected and is explained solely by usual alkali poisoning and pore plugging.
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