

LIMESTONE INJECTION FOR PROTECTION OF SCR CATALYST

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ABSTRACT

Gaseous arsenic is one of the predominant catalyst deactivation mechanisms in coal fired SCR applications. The arsenic resistance of the catalyst is one of many properties to be considered when selecting a catalyst design. Introducing CaO by adding limestone to the fuel reduces the gaseous arsenic in the flue gas and decreases its harmful effect on the catalyst. Limestone addition may be used in conjunction with an optimized catalyst design to increase the range of acceptable fuels or to permit selecting a lower volume of catalyst.

In this paper, we discuss the influence of fuel properties on catalyst selection, the effect of gaseous arsenic as a function of fuel CaO, the design of limestone addition systems, and SCR operating experience with limestone systems.

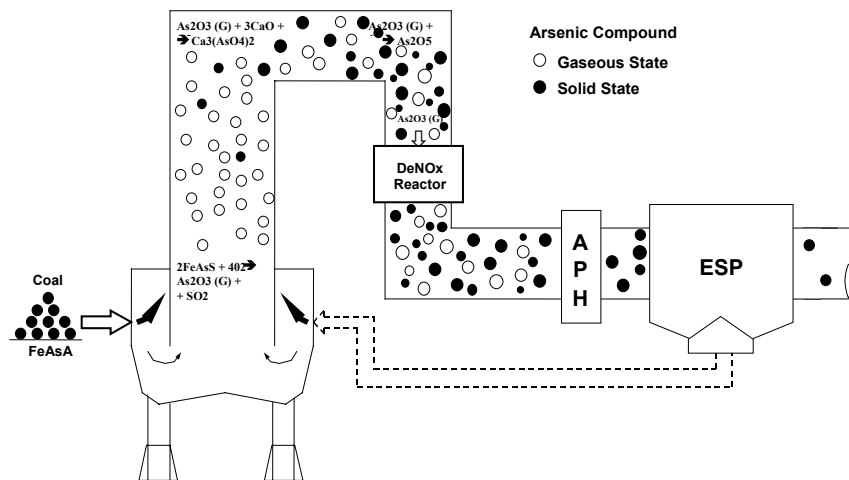
INTRODUCTION

The long term, reliable operation of a Selective Catalytic Reduction (SCR) system for high dust coal operation requires the careful integration of the system and the catalyst. An important aspect of this integration is the effect of coal properties on the catalyst. In the units discussed in this paper, arsenic in the coal is the predominant catalyst deactivation mechanism. It is the gaseous arsenic concentration in the flue gas stream that determines the rate of catalyst deactivation and the amount of catalyst needed to achieve a specified catalyst life and, therefore, economical SCR operation. One system countermeasure incorporates the use of limestone as a fuel additive to lower the arsenic levels in the flue gas stream. The addition of small amounts of calcium to the fuel has been shown to be an effective method of controlling arsenic poisoning. Limestone addition allows for greater flexibility in coal purchasing and saves costs. It should be recognized that CaO can also be a catalyst poison via formation of CaSO₄ in the catalyst pores effectively blocking the catalyst reactive sites. Therefore a good understanding of all interactions of fuels and catalyst is required.

EUROPEAN AND JAPANESE EXPERIENCE

The earliest SCR experience in Japan was with low sulfur coals from Australia and South Africa fired in dry bottom boilers. These systems experienced no appreciable catalyst deterioration from arsenic¹. German and European coals have also relatively low arsenic concentrations, however when fired in wet bottom boilers the catalyst experienced significant arsenic poisoning. Work with experimental SCR plants behind wet bottom boilers in Germany showed that a high proportion of gaseous arsenic in the flue gas caused the catalyst deactivation. In another case, a Japanese catalyst manufacturer expected a 35% loss in activity after 16,000 hours of operation based on dry bottom boiler experience². However, tests in a VKR pilot plant resulted in a similar loss in catalyst activity after only 400 hours of operation. The Japanese catalyst manufacturer expected this loss in activity after 16,000 hours of operation based on dry bottom boiler experience². The high gaseous arsenic concentration in the flue gas, which ranged from 500 to 1000 µg/ m³, were attributed to 100% ash recirculation from the ESP's into the wet bottom furnace. This was a standard operating method in these plants due to high carbon content of the flyash³. Field tests showed that the recirculation of the fly ash to the boiler dramatically increased the gaseous (As₂O₃) form of arsenic. The arsenic brought into the boiler with the coal is vaporized into arsenic trioxide at about 2,500 F. As the flue gas leaves the furnace in a temperature range of 1,800 to 2,000 F, the gaseous form of arsenic quickly reacts with the flue gas dust to form stable solid compounds. These solid compounds do not harm the catalyst. However, if there is fly ash recirculation, the solid compounds of arsenic in the fly ash reenter the boiler where the arsenic is re-vaporized into the gaseous form (Figure 1). Fly ash recirculation at Datteln Power plant in Germany resulted in an estimated increase of 6.5 times of the total arsenic concentration before the air preheater².

Figure 1.: Wet bottom boiler with fly ash recirculation (From Reference 4)



The German experience with high gaseous arsenic levels prompted the reformulation of catalyst making it more resistant to arsenic. In addition to this, system countermeasures were employed to lower the gaseous arsenic levels in the process stream.

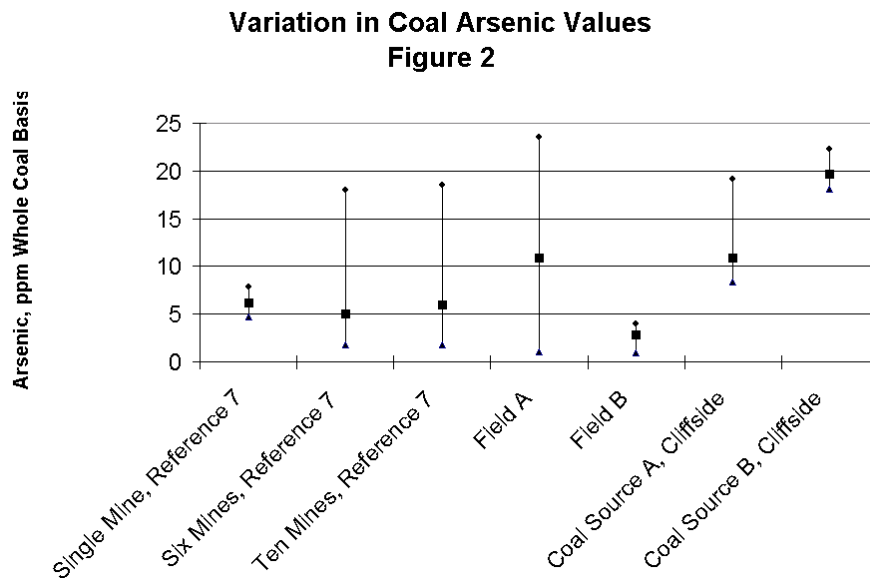
Of the various methods available to reduce gaseous arsenic in the flue gas from wet bottom boilers, BBP in Europe decided in favor of ash extraction. They had good experience with this method in the high dust SCR plants at Walheim and Oberhavel³. Approximately ten percent (10%) of the precipitator fly ash is removed from the ash handling system and discarded. This resulted in catalyst deactivation that was only slightly poorer than that shown with dry bottom furnaces.

Another European method of protecting the catalyst utilized the introduction of CaO through addition of limestone to the coal to reduce gaseous arsenic in the flue gas. If there is adequate free calcium oxide (CaO) in the flue gas from the coal or limestone, then most of the As_2O_3 in the flue gas reacts with the CaO to form solid calcium arsenide ($Ca_3(AsO_4)_2$). The calcium arsenide then collects in the bottom ash or fly ash. Testing at the Datteln Power Plant in Germany demonstrated that an addition of 1 % calcium carbonate ($CaCO_3$) to the coal in the form of limestone reduced gaseous arsenic before the airheater from 0.5 to 1.0 mg/m^3 to about 0.1 mg/m^3 ².

UNITED STATES COALS

U.S. Geological Survey data shows that United States Appalachian Basin coal has a mean arsenic value of 22 ppm⁵. Conventional commercial coal cleaning reduces this concentration from between 35% to 83% depending on the fuel type and cleaning process⁶. Further examination found that several coals contain high elemental arsenic with corresponding low calcium which could lead to rapid deactivation of the catalyst due to the resultant high gaseous arsenic concentration. Some coals had over 100 ppm of arsenic and less than 1% CaO³ in the ash.

The SCR design is further complicated because of a difference in the values of arsenic in coal from different test methods⁷ and natural variation of arsenic in coal. Figure 2 shows the range of variability in arsenic concentration that has been found in the open literature as well as recent Riley Power Inc. design experience⁸. It is a rare commercial plant that gets its coal from only one coal mine over the entire life of the plant. Operating an SCR with a fuel that is not included in the catalyst specification can result in a costly unanticipated early catalyst replacement⁹. Including every possible coal that could be burned with suitable design margin, however, can result in a very expensive SCR reactor design with an excessive amount of catalyst. It is under this array of uncertainty that adding a limestone addition system can be an economically favorable choice.



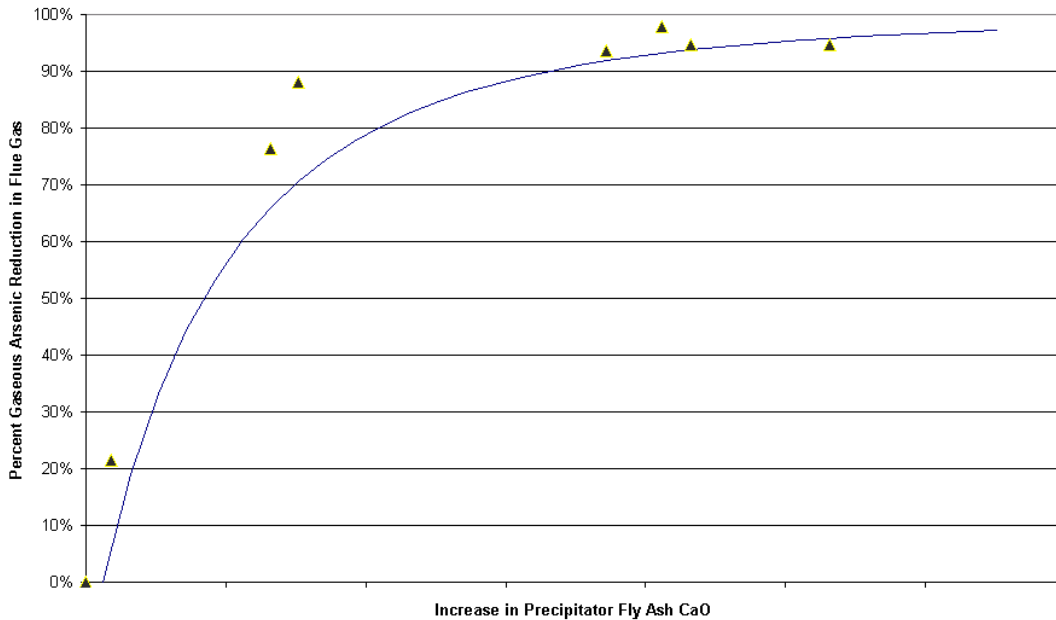
RILEY POWER INC. EXPERIENCE

First US Riley Power Inc. Limestone Units

Riley Power Inc. designed and manufactured high dust SCR systems for two units that fired any Eastern Bituminous coal as defined in ASTM-D-388 as Class II, medium volatile and high volatile A, B and C bituminous coal. There are no specific restrictions to any coal from any mine within the above category. The variation of arsenic levels for the first year of SCR operation for these systems is included in Figure 2 as 'Field A' and 'Field B'. Riley Power Inc.'s

scope of supply included the reactor, all associated support steel, ductwork, isolation/bypass dampers, expansion joints, access and testing provisions, platforms and stairs, initial catalyst charge, reagent unloading, storage and injection system. Before the catalyst was selected, an extensive testing program was completed that evaluated adding limestone to the coal to control arsenic poisoning. The customer was concerned that adding limestone could aggravate an existing boiler slagging tendency. A temporary belt system was installed to test the effect of limestone addition on gaseous arsenic and boiler performance. Gaseous arsenic reduction as a function of CaO in fly ash is displayed in Figure 3 below.

Effect of Limestone Addition For Control of Flue Gas Gaseous Arsenic
Figure 3

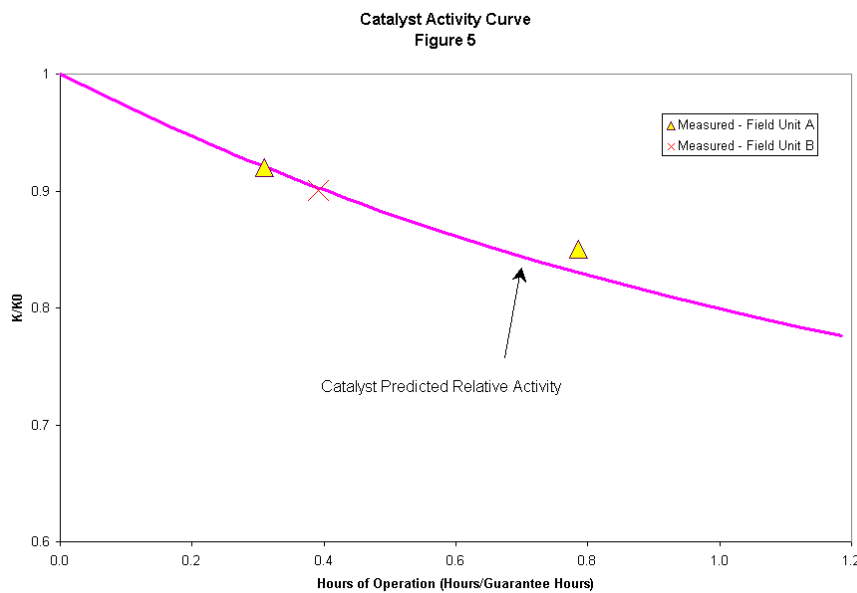
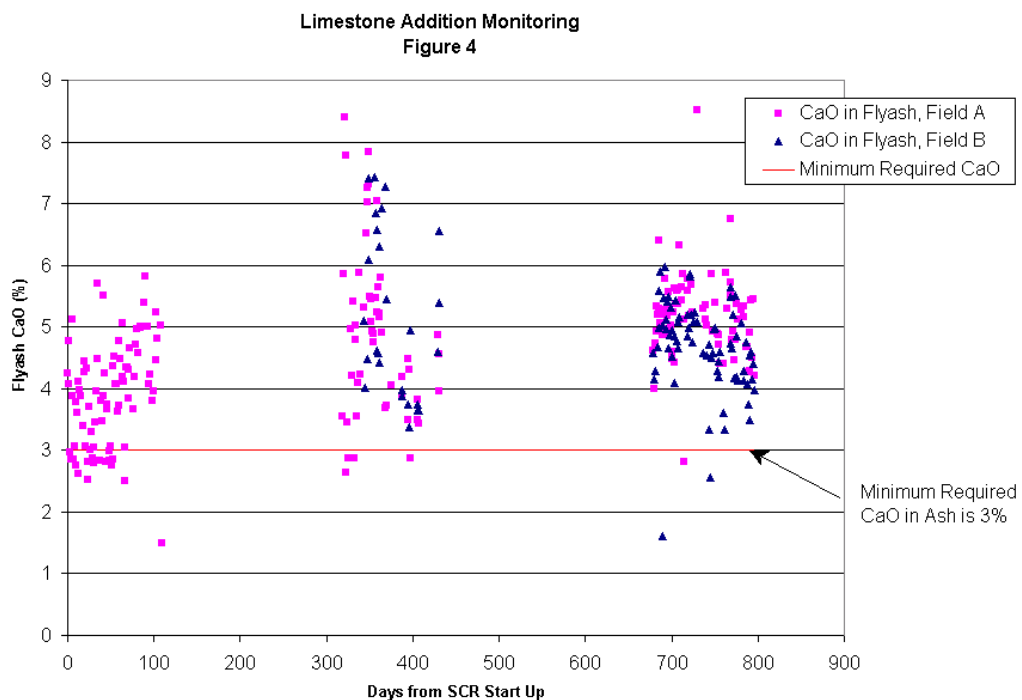


This test program determined the required limestone feed rate to mitigate gaseous arsenic while keeping boiler slagging within acceptable limits. Based on this study, a minimum level of 3% calcium oxide in the fly ash was established and a temporary limestone feeding system was installed for the first summer of operation of the Field Unit A SCR system. A separate limestone feed rate was selected for each fuel group ('Field A' or 'Field B').

The following summer a permanent limestone system was installed before the Field Unit B SCR system was placed in service. It is now supplying limestone for both units. The design of the limestone silo and feed system took into consideration the limestone quality and transport properties (pebble size, moisture, etc.). The limestone system consists of three basic components; a loading system, a storage system, and a feed system. In the loading system, a truck pneumatically unloads limestone into a hopper. Then the limestone is fed from the hopper through a rotary airlock and transported by a blower into a storage silo. The storage system consists of one bolted silo that stores up to six days of limestone. There are three outlets from the silo. The feed system consists of three volumetric screw feeders, one attached to each outlet, and one reversing screw feeder. Two primary volumetric screw feeders dump the limestone directly onto two coal conveyors. If one of the primary screw feeders fails, the third back-up

volumetric screw feeder and reversing screw feeder is energized. The back-up screw feeder dumps limestone onto the reversing screw feeder directing the limestone to the coal conveyor that was fed by the failed primary volumetric screw feeder. Ancillary systems consist of a water fog system to reduce limestone dusting on the coal conveyors and a backup truck silo loading system if the positive displacement blower fails.

Limestone has been injected into the Units A and B for three years. The limestone feed rate was increased after the first year of operation based on a review of the fuels, system performance, and catalyst activity. Figure 4 displays the calcium oxide levels in the fly ash showing that the minimum calcium oxide concentration in the fly ash has been maintained over that time. Figure 5 shows the catalyst activity curve for the field units. The measured catalyst deactivation is closely correlated to the predicted catalyst deactivation.



Duke Power Cliffside Station Unit 5

A permanent limestone addition system was included with the SCR system that Riley Power Inc. supplied for Unit 5 at the Duke Power Cliffside Station. The SCR system and the limestone system have operated for one OTAG season.

Cliffside Unit 5 is a balanced draft, sub-critical, natural circulation, single reheat boiler. The full load capability is nominally 590 MW gross with a steam flow rate of approximately 4,200,000 pounds per hour at 1005°F leaving the secondary superheater. The SCR system consists of two SCR reactors in parallel between the economizer and the air heater. The SCR reactors use anhydrous ammonia and provide 85% NO_x reduction with less than 2 ppm ammonia slip. When the reactors are not in service, the flue gas flows through a SCR bypass duct, and the reactor dampers are closed.

Cormetech supplied the initial two layers of honeycomb type catalyst for each reactor. There is room in each reactor for two additional layers of catalyst. A review of all the possible Cliffside coal sources resulted in the selection of a catalyst volume that could achieve guaranteed life burning about 50% of the fuels on a continuous basis without the addition of limestone. Two of the fuels could not achieve guaranteed life with the design catalyst volume if continuously burned even with the addition of limestone.

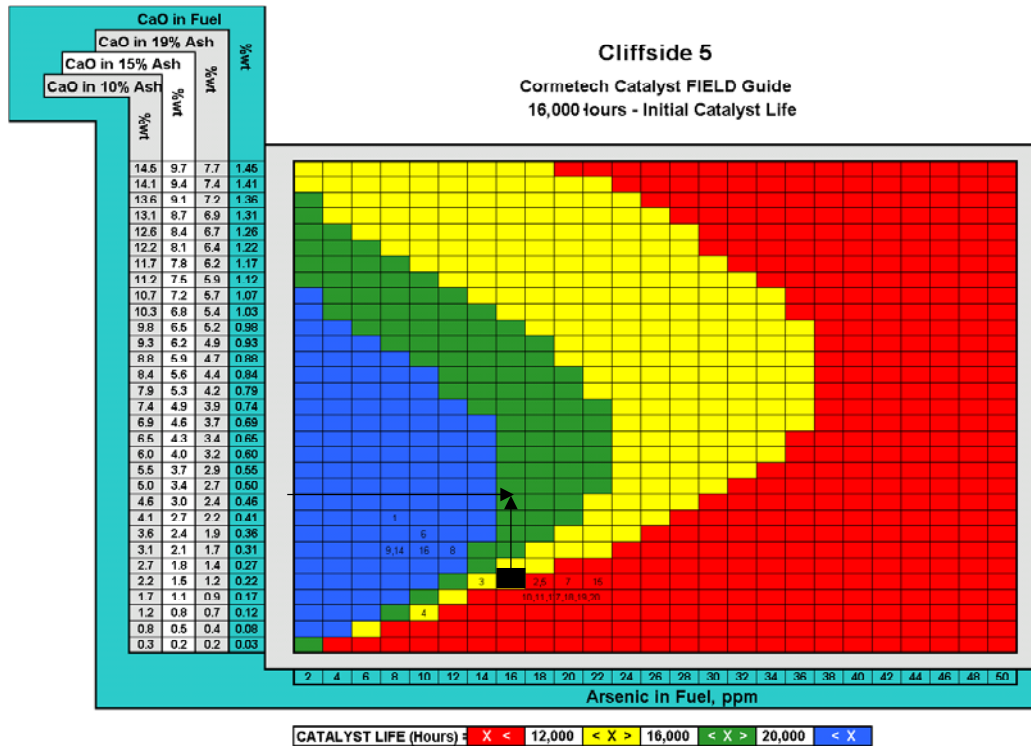
The limestone feed system is similar to the previously designed system. It consists of one limestone feed silo (7 day storage) with two limestone discharge outlets. The system includes two automatic slide gates (transition discharge valves), one bin vent filter for fugitive dust emissions, one air drier/filter and accumulator for silo bin vent, one silo fill line. There is a pneumatic truck unloading operator station for transferring limestone into the silo. The silo has two redundant limestone volumetric screw feeders with variable frequency drives (VFD) and two inclined belt conveyors. The limestone is fed to one (1) coal conveyor belt.

Figure 6 is the Cormetech catalyst FIELD Guide[®] for the Cliffside SCR system. It shows the expected catalyst life for a coal with a given amount of arsenic and calcium oxide concentration. The coals fired at the Cliffside station during the initial ozone season are plotted on the guide. There were two predominant coal sources at Cliffside; each fairly distinct with regards to CaO and arsenic variability. This is illustrated by the distinct groupings of fuels on the guide below. Note that one group of coals needed additional calcium oxide to shift the points into the green area to provide 16,000 hours of catalyst life. The black box on the guide represents the average of all fuel samples plotted.

As seen on Figure 6, the addition of approximately 0.3% CaO to the average fuel is required to optimize the catalyst life. It should be noted that CaO addition levels of greater than 3% could actually result in a decrease in catalyst life due to deactivation associated with CaO. Experimental tests at the plant focussed on balancing the optimization of catalyst life while controlling slagging in the boiler. This resulted in an initial limestone feed rate of 30% feeder speed.

Catalyst Field Guide Figure 6

Coal Sample analyses are from 5/5/02 through 7/18/02
Points are plotted using %CaO vs. As ppm



The limestone addition rate to provide a minimum calcium oxide concentration in the fuel is calculated by:

$$L = \frac{Y - Cc * Xa}{Cl - Y} \quad (1)$$

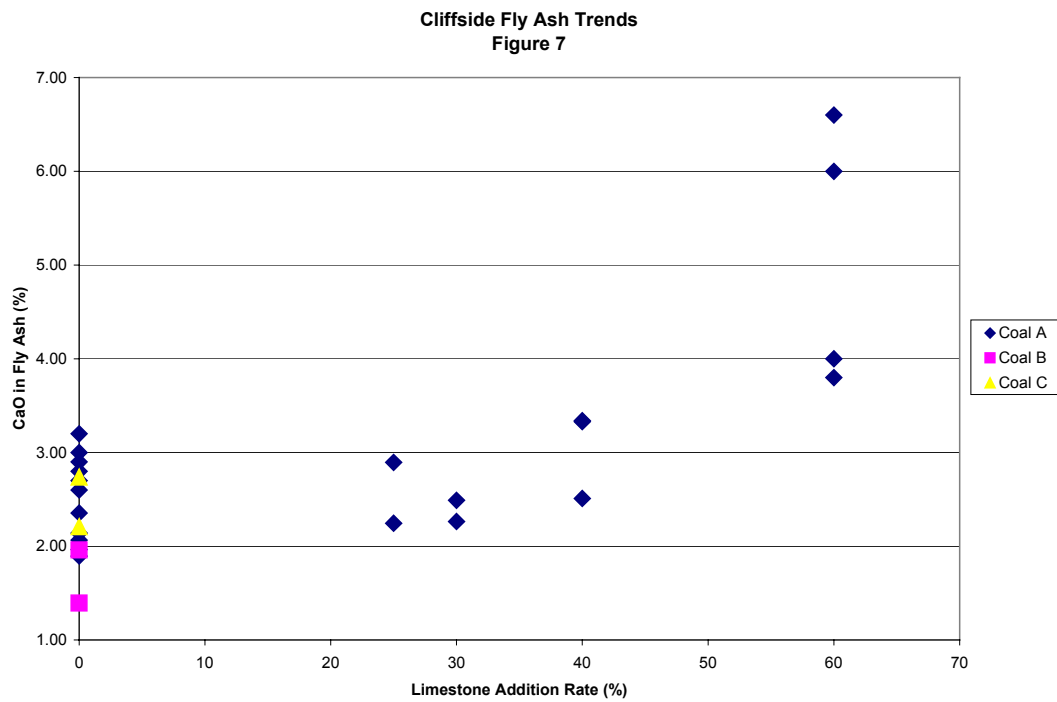
- where
- L = the limestone addition rate (lbs of limestone/lb of coal)
 - Y = the minimum required calcium oxide concentration (lbs CaO/lb fuel)
 - Cc = the calcium oxide concentration in the coal ash (lbs of CaO/lb ash)
 - Xa = the ash content in the coal (lbs of ash/lb of coal)
 - Cl = the calcium oxide concentration in the limestone (lbs of CaO/lb limestone)

Typically a fuel analysis provides the calcium concentration in the ash rather than the calcium oxide concentration. The coal ash calcium oxide concentration is calculated as:

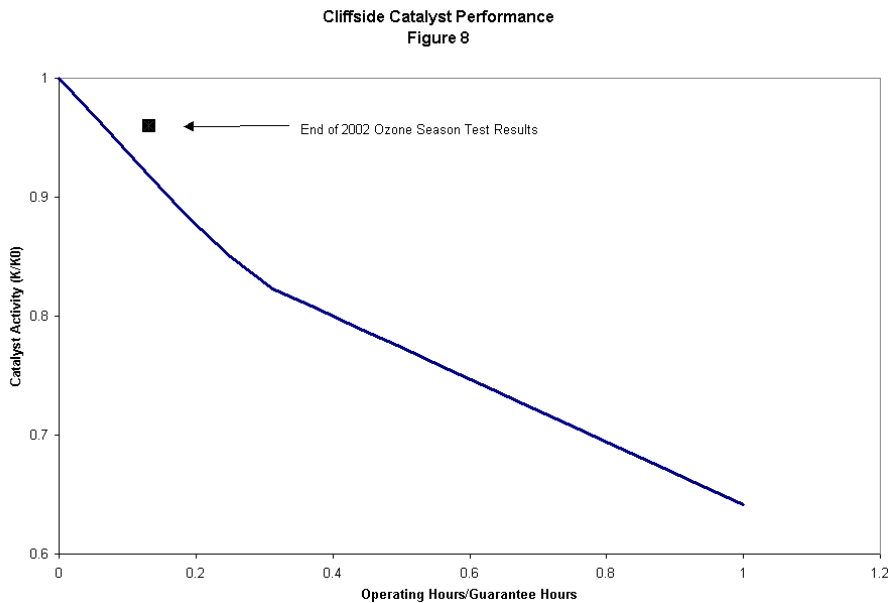
$$Cc = [Ca] * \frac{1 \text{bmol Ca}}{40 \text{ lb}} * \frac{1 \text{bmol CaO}}{1 \text{bmol Ca}} * \frac{56 \text{ lb CaO}}{1 \text{bmol CaO}} \quad (2)$$

where [Ca] = the concentration of calcium in coal ash (lbs of Ca/lb of ash)

The limestone equipment was sized to provide the limestone addition rates needed for the range of coals fired. Figure 7 displays the effect of limestone feed rate on calcium oxide in the fly ash.



The measured catalyst activity for Cliffside Unit 5 SCR system is compared to the design activity curve in Figure 8. It shows that the catalyst activity was maintained for the first operating season. The catalyst is expected to continue to meet the SCR system performance requirements over further operating seasons.



CONCLUSION

Adding limestone to coal is an effective way to protect catalyst from arsenic poisoning. This method is in use for the SCR systems supplied by Riley Power Inc. at two units for three years and the first season at the 590 MW Duke Power Cliffside Unit 5. The limestone systems have provided the minimum amount of calcium oxide in the fuel needed to protect the catalyst over that time. The catalyst activity has been maintained at the expected level.

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