

SCR Deactivation Mechanisms Related to Alkali and Alkaline Earth Elements

C. Senior

Reaction Engineering International, 77 West 200 South, Suite 210, Salt Lake City, UT 84101
Email: senior@reaction-eng.com; Telephone: (801) 364-6925; Fax: (801) 364-6977

K. Davis

Reaction Engineering International, 77 West 200 South, Suite 210, Salt Lake City, UT 84101
Email: davis@reaction-eng.com; Telephone: (801) 364-6925; Fax: (801) 364-6977

M. Bockelie

Reaction Engineering International, 77 West 200 South, Suite 210, Salt Lake City, UT 84101
Email: bockelie@reaction-eng.com; Telephone: (801) 364-6925; Fax: (801) 364-6977

L. Baxter

Brigham Young University, 350 Clyde Building, Provo, UT 84602
Email: larry_baxter@byu.edu; Telephone: (801) 422-8616; Fax: (801) 422-0151

C. Bartholomew

Brigham Young University, 350 Clyde Building, Provo, UT 84602
Email: bartc@et.byu.edu; Telephone: (801) 378-4162; Fax: (801) 378-7799

K. Whitty

University of Utah, 1495 East 100 South, Salt Lake City, UT 84112
Email: whitty@eng.utah.edu; Telephone: (801) 585-9388; Fax: (801) 585-5607

E. Eddings

University of Utah, 1495 East 100 South, Salt Lake City, UT 84112
Email: eddings@che.utah.edu; Telephone: (801) 585-3931; Fax: (801) 585-5607

Summary

Reaction Engineering International (REI) has been funded by the US Department of Energy (under cooperative agreement DE-FC26-00NT40753) to carry out a program titled "NO_x Control Options and Integration for US Coal Fired Boilers." The overall goal of the program is to evaluate and demonstrate low cost NO_x control strategies and to study the potential impact of these NO_x control technologies on overall electric utility boiler performance. One of the tasks in this program is called "SCR Performance Under Co-firing Conditions." The objective of this task is to develop a deeper understanding of the operating costs of SCR with regard to catalyst deactivation from alkali and alkaline earth elements. The focus is on sub-bituminous fuels and coal-biomass co-firing, both instances in which the alkali or alkaline earth metals in the fuel may have a harmful effect on SCR catalysts. REI is working with Brigham Young University (BYU) and the University of Utah (UU) to carry out this work.

Loss of activity (or deactivation) of the catalyst with time has a significant impact on the amount of catalyst needed and on the frequency of catalyst replacement in SCRs. Both have a large effect on the operating costs of SCR units in coal-fired power plants. There are three mechanisms for deactivation of SCR catalyst in coal-fired power plants that have been identified: Fouling (surface deposition); Pore condensation (and/or pore blockage); Poisoning. For a given situation one or more of these mechanisms may be occurring. For PRB coals, there is a widely held belief that fouling by calcium sulfate deposits is the primary mechanism for catalyst deactivation [Siemens, 2000]. In some cases, sodium and potassium may be important. This may be due to poisoning (and perhaps pore-filling) when ash particles containing alkali sulfate come in contact with water if the catalyst drops below the dew point of the gas. This might be

poisoning from the alkali or pore condensation. Either way, water washing should regenerate the active sites. (This is in contrast to arsenic poisoning, which is irreversible.)

Limited information is available from Europe on the effect of biomass co-firing on SCR catalyst deactivation [Wieck-Hansen et al, 2000; Odenbrand et al, 2000]. Based on coupon testing in power plants and analysis of exposed catalyst, potassium has been implicated in the deactivation. With biomass, care must be taken to avoid being too general. The composition of biomass ash varies greatly with the type of plant material burned; there is much more variation in ash composition than found in different ranks of coal, for example. But, preliminary information suggests that masking seems to be the primary mechanism for deactivation of catalysts exposed to high-dust flue gas in plants firing biomass. Potassium has been implicated as an important element in certain cases, but it is not yet clear whether this is from pore condensation or blockage or from poisoning.

In this program, BYU is conducting a series of experiments designed to delineate the mechanisms and rates of SCR catalyst deactivation. These experiments include two general types: flow-reactor investigations and in-situ analyses of reactions on pellet surfaces. The former are conducted in temperature-programmed test cells that operated as differential reactors exposed to controlled concentrations of reactants. The data from these experiments include NO_x conversion, ammonia conversion, SO_2 and SO_3 conversion as a function of temperature, catalyst type and composition, and time. The latter include spectroscopic surface analyses of reacting and adsorbed species on surfaces during SCR reactions. The combination of experiments allows mechanisms and rates of NO_x formation to be definitively determined under a variety of conditions. Experimental work on regenerations methods for laboratory-tested and field-exposed catalyst will also be carried out at BYU.

Long-term testing in the field is also needed to confirm the information obtained in laboratory studies. In this program, UU has built a **Multi-catalyst Slipstream Reactor** to be deployed at a power plant for approximately six (6) months. Six catalysts will be exposed to flue gas in parallel and activity measurements will be made in the field. The first field test is planned for summer of 2002.

Development has started on a deactivation model that can be incorporated into REI's existing suite of boiler modeling tools. The basic SCR model is based on the work of Dumesic and coworkers [Dumesic et al, 1996] and involves a reaction scheme for adsorption of ammonia on Brønsted acid sites of vanadium oxide followed by activation of ammonia via redox sites ($\text{V}=\text{O}$). The activated ammonia is then assumed to react with gaseous or weakly adsorbed NO , producing N_2 and H_2O ; this reaction cycle also partially reduces the catalyst. The reduced sites react with O_2 in the gas stream and the catalytic cycle is complete. The reaction scheme has been shown to describe the kinetics of the SCR reaction under conditions that are relevant to field applications of SCR in the utility industry. The REI model is a one-dimensional model that uses the number of active sites per unit surface area as the chief parameter. The model has been shown to reproduce literature data well.

In summary, deactivation of SCR-based catalysts can occur by chemical poisoning, fouling of catalyst by deposition of inorganic (or organic) material on its surface, or surface area decreases associated with plugging pores on the catalyst surface. All of these mechanisms are observed to some extent in commercial installations, but catalysts deployed in high-dust applications using high-rank coals have established commercial success for long lifetimes. Low-rank coals and biomass pose potentially greater deactivation threats because they contain relatively high amounts of alkali and alkaline earth materials that are more active in all of the above-cited deactivation mechanisms.

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