Perspective

# Clean Coal Technologies: OSCAR and CARBONOX Commercial Demonstrations

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## Introduction

The total world energy consumption will increase by approximately 50% by the year 2020 (EIA, 2002). Much of this energy will be used to meet the increasing demand in developing countries for transportation, heating and cooling services, and electricity. All indications are that this future energy demand, as in the past, will be met mostly with fossil fuels such as oil, natural gas, and coal. The continued reliance on fossil fuels is due primarily to their low cost of energy generation as compared to nonfossil fuels, such as biomass, wind, geothermal, and solar power. It is projected that oil will remain the dominant energy fuel, in response to increased demand in the transportation sector. The remainder of the world's energy demand will be provided primarily by natural gas and coal, in that order (EIA, 2002).

The core element of the U.S. Department of Energy's (DOE) Vision 21 plan is clean coal technology. Before the plan becomes a reality, an array of enabling technologies needs to be developed. *Opportunities abound for chemical engineering to develop innovative processes to reduce or eliminate gaseous and particulate pollutants*. The challenges, however, lie in the cost-effectiveness of the processes developed. This Perspective is intended to describe the overall energy outlook using coal. It addresses the intricate issues of the chemistry, processes, regulation and economics surrounding clean coal technology in connection with coal combustion. Two promising clean coal processes, OSCAR and CARBONOX, which were developed in the authors' laboratory from initial fundamental research to the current stage of pilot demonstration, are highlighted.

## Coal for electricity generation and environmental Regulations

Coal has provided the bulk of electricity generation for many decades. Almost two-thirds of the coal produced worldwide is used for electricity generation. Currently, more than a third of electricity generated worldwide comes from coal, and in the U.S., the contribution of coal to electricity generation is more than half. The dominance of coal in electricity production is expected to continue well into the 21st century (EIA, 2002).

Several facts render coal essential to current and future world energy needs. Coal represents over 80% of the world's proven recoverable fossil fuel (by heat content), and the U.S. has one-fourth of the world's supply. In addition, the world's growing energy demand cannot be satisfied by the relatively scarce reserves of natural gas or petroleum. Solar power is still too expensive, and nuclear power is viewed as expensive and risky by much of the world.

The use of coal for energy production, however, poses considerable environmental concerns. Combustion of coal results in emission of sulfur dioxide ($SO_2$), nitrogen oxides (NO and $NO_2$, together known as $NO_x$), fine particulate matter (PM), and trace heavy metals such as mercury (Hg). Sulfur dioxide and $NO_x$ are both precursors to acid rain, and especially $NO_x$ has been identified as a contributor to the formation of smog. Fine particulate matter is responsible for serious health effects in addition to visibility impairment due to the formation of smog. In recent years, attention has focused on Hg emissions from coal-fired power because of its bioaccumulation in the aquatic environment that causes neurotoxicity in fish-eating populations.

Since 1980, emissions of pollutants ($SO_x$, $NO_x$, and PM) from coal-fired power plants have been significantly reduced due to regulatory programs that set limits on the emissions of pollutants. For example, in the U.S., due to the Acid Rain $SO_2$ Reduction Program established under Title IV of the Clean Air Act Amendments (CAAA) of 1990, annual $SO_2$ emissions in the U.S. have been reduced from 17.3 million ton in 1980 to 13.5 million ton in 1999. In the case of particulate matter, the annual emissions of PM10 (particulate matter less than 10 μm) in the U.S. decreased from 1.6 million ton in 1970 to less than 260,000 ton in 1996. Particulate control devices (PCDs), such as the baghouse and the electrostatic precipitator, capture more than 99% of particulates in the flue-gas stream.

Emissions regulations are expected to become more stringent in the future. For example, Phase II of the Acid Rain $SO_2$ Reduction Program, which began in 2000 with a nationwide cap for annual $SO_2$ emissions at 9.48 million ton will be reduced further to 8.95 million ton by 2009. In the U.S., the State Implementation Plan is designed to reduce $NO_x$ emissions by 85% from 1990 levels or limit $NO_x$ emission to 0.15 lb/million Btu from utility sources in 22 Eastern states and the District of Columbia. Plans are also under development to provide additional control requirements for PM2.5 (particulate matter less than 2.5 μm) as a means to control regional haze.

The percentage of coal use in electricity generation is projected to decline in the future because of these environmental regulations. In addition, new regulations for mercury are on the horizon. Growing concerns with global climate change associated with $CO_2$ emissions are also likely to affect the use of coal in electricity genera-

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tion. The decrease in coal use will be offset by the use of cleaner natural gas that has a higher H/C ratio. It is anticipated that as many as 900 of the next 1,000 power plants to be built in the U.S. will be based on natural gas. However, because of the uncertainty in the price and supply of natural gas, many nations (including the U.S.) may still have to rely on domestic coal reserves for the majority of their electricity generation, provided technologies are available at affordable costs to alleviate pollutant emissions.

In the past, as environmental regulations became more stringent, improved clean coal technologies (CCTs) were developed. However, many CCTs are not ready to meet the impending more stringent regulations. Much more technological innovation will be needed to effectively address new issues (e.g., mercury, global warming), to reduce the implementation cost and to provide integrated abatement strategies that achieve multifunctional effects. *Chemical engineering is expected to play a critical role in the development of CCTs*. Research is underway to develop the technology for next-generation power plants. A fundamental understanding of the reaction mechanisms and rate processes will form the basis for cost-effective technologies. The challenge is to take the findings out of the laboratory and successfully demonstrate the technology at a commercial level.

Numerous clean coal technologies have been developed and demonstrated that permit the effective use of coal for fuel, as well as chemical production and power generation. These include the technologies for pollution control systems, advanced combustion (e.g., atmospheric and pressurized fluidized-bed combustion) and gasification (e.g., Integrated Gasification Combined Cycle or IGCC), and direct or indirect coal liquefaction (to produce clean liquid fuels or chemicals) (U.S. DOE, 1999). At the authors' laboratory, two commercial demonstrations of CCTs in connection with atmospheric coal combustion have been initiated. These are the OSCAR (Ohio State Carbonation Ash Reactivation) process (Fan et al., 1998) and the CARBONOX (CARBON-based $NO_x$ reduction) process (Fan and Gupta, 2001). These processes represent two of the most comprehensive examples of the application of particle science and technology in environmental systems. The following sections give general background and the specific research that lead to the commercial demonstration of these processes.

## $SO_2$ Emission Control

Control of $SO_2$ emissions can be achieved by precombustion techniques such as fuel switching, blending of high and low sulfur coals, coal cleaning, and/or post-combustion installation of flue-gas desulfurization (FGD) equipment. Although only about 25% of the existing U.S. coal-fired power generating capacity has FGD equipment, as regulations tighten, most of the new and existing power plants will be required to install some form of post-combustion FGD equipment.

Post-combustion removal of $SO_2$ in flue gas can be achieved by contacting acidic $SO_2$ with alkaline sorbents such as limestone ($CaCO_3$), lime (CaO), hydrated lime ($Ca(OH)_2$), dolomite ($CaMg(CO_3)_2$), sodium bicarbonate ($NaHCO_3$), and sodium sulfite ($Na_2SO_3$). Sulfur dioxide reacts with the sorbent chemically either in the presence or in the absence of water to form reaction products, which can be either disposed of or further utilized (for flowable fill, structural fill, or animal pads). FGD processes are broadly classified as wet and dry processes, depending on whether wet or dry products are formed.

*Wet FGD*. In the wet FGD process, flue gas containing $SO_2$ is contacted with alkaline slurry in a scrubber. Wet scrubbers employing limestone as a sorbent represent the technology of choice around the world (Coal Power3, 1998).

The chemistry of the wet FGD process is quite complex and involves gas-liquid-solid equilibrium relationships, dissolution of limestone and $SO_2$ in water, ionic reactions, and the precipitation of reaction products (Chang and Rochelle, 1981; Gage and Rochelle, 1992). The overall reactions involved in the absorption of $SO_2$ by limestone slurry can be summarized as (Srivastava, 2000)

$$SO_2+CaCO_3+1/2H_2O \rightarrow CaSO_3\cdot 1/2H_2O+CO_2 \tag{1}$$

$$SO_2+CaCO_3+2H_2O+1/2O_2 \rightarrow CaSO_4\cdot 2H_2O+CO_2 \tag{2}$$

Normally, Ca/S molar ratios (indicating the number of moles of Ca added per mole of $SO_2$ removed) are in the range 1.01 to 1.1 with a corresponding slurry pH in the range 5 to 6. Well-designed FGD systems capture more than 95% of incoming $SO_2$ by properly controlling operating parameters such as flue-gas flow rate, liquid-to-gas ratio, Ca/S ratio, and residence time (Srivastava, 2000). However, the capital cost associated with the dedicated scrubber and its ancillary equipment can amount to 20% of the overall plant cost. In addition, the sludge wastewater stream requires additional disposal measures.

*Dry FGD*. In dry FGD processes, dry sorbent ($CaCO_3$ or $Ca(OH)_2$) particles can be injected in the upper furnace region (*furnace sorbent injection* process or FSI), or in the duct region between the air preheater and the PCD (*duct sorbent injection* process, or DSI) in a pulverized combustor, or they are introduced directly to a fluidized-bed combustor [e.g., *circulating fluidized bed* (CFB) combustor]. The majority of the bed materials in a fluidized-bed combustor are the sorbent particles. A CFB can also be used as a reactor for post-combustion desulfurization. Another dry FGD process, known as *lime spray drying* (LSD), involves the introduction of an aqueous lime slurry to an absorber (located in the region between the air preheater and the PCD) where it contacts $SO_2$ in the flue-gas stream. The sorbent injection processes, FSI and DSI, do not require a dedicated absorber vessel, as in the case with LSD. Because injection processes can be easily retrofitted to an existing combustor, their capital costs are lower than those for wet scrubbers or LSDs. This is particularly advantageous for existing power plants where large scrubbers cannot be installed because of space limitations.

Of the two injection technologies, FSI uses the higher residence time and favorable reaction kinetics in the higher temperature region of 900–1,100°C. The reaction between $SO_2$ and $CaCO_3$ is extremely fast in this temperature range. The reactions taking place in a FSI process are

$$\text{Calcination:} \quad CaCO_3 \rightarrow CaO+CO_2 \tag{3}$$

$$\text{Sulfation:} \quad CaO+SO_2+1/2O_2 \rightarrow CaSO_4 \tag{4}$$

In the first step, the calcination reaction (Reaction 3) drives off $CO_2$ at high temperatures encountered in the upper furnace regions and generates highly porous, high surface area CaO, which reacts in the second step with $SO_2$ in the presence of $O_2$ to form solid $CaSO_4$ (Reaction 4). The sulfation reaction is most favored in the temperature window of 800–1,100°C. At higher temperatures, the sulfur capture is reduced because of the thermal decomposition of

$CaSO_4$, whereas, at lower temperatures, the sulfation reaction is slower. In addition to the sulfation reaction, porous CaO particles undergo thermal sintering at high temperatures. Sintering results from the coalescence of small CaO grains into larger grains, effectively reducing the overall surface area and porosity of reactive CaO particles.

Calcination, sintering and sulfation reactions of fine particles essentially take place within a very short time of sorbent injection. For example, the calcination rate of fine calcium hydrate ($Ca(OH)_2$) sorbent particles is very high, and nearly 70% of calcination completes within 50 ms at 700°C (Bortz and Flament, 1985). Because of the ultrafast nature of these reactions, it is a challenge to accurately obtain kinetic data. Development of novel laboratory reactor systems has provided a better understanding of the reaction kinetics of these ultrafast reactions (Gullett et al., 1986; Raghunathan et al., 1992, 1993).

The initial rate of the sulfation reaction is fast, but subsequently the rate decreases drastically. This is due to the formation of a high molar volume of $CaSO_4$, which causes pore filling or pore-mouth closure and subsequent loss of internal porosity and surface area of the reacting CaO particles. This deactivation process results in the increased resistance to pore diffusion of gaseous $SO_2$. Furthermore, the presence of $CaSO_4$ on the CaO surface yields a significant product-layer diffusion resistance. Experimental evidence of high values of activation energy for the product-layer, diffusion-controlled sulfation reaction suggests that the reaction involves solid-state diffusion of ionic species through the nonporous product layer (Bhatia and Perlmutter, 1981; Borgwardt and Bruce, 1986). Earlier, it had been assumed that $SO_4^{2-}$ ions form at the $CaSO_4$/gas interface and then migrate inward through the $CaSO_4$ product layer to the CaO/$CaSO_4$ interface to react with $Ca^{2+}$ ions. However, recent findings of Hsia et al. (1993, 1995) based on inert Pt-marker and reactive isotopic marker experiments revealed physical evidence as to the nature and migration route of these ionic species. These findings determine that, contrary to earlier belief, $Ca^{2+}$ and $O^{2-}$ ions diffuse outward in a coupled manner through the $CaSO_4$ product layer to the $CaSO_4$/gas interface. This mechanism is also supported by the crystal geometry of $CaSO_4$. The rhombohedral crystal structure of $CaSO_4$ has a large tetrahedra of complex $SO_4^{2-}$ ions with $Ca^{2+}$ wedged in-between. Furthermore, the size of $SO_4^{2-}$ ions is larger than the $Ca^{2+}$ ions, roughly 4.5 Å vs. 1.8 Å. As a result, the $Ca^{2+}$ ions should inherently possess higher mobility than the $SO_4^{2-}$ ions.

The phenomena noted above, along with the short contact times available (<1 s), yield relatively low sorbent conversions (~20–30%) in the FSI process. Flue gas $SO_2$ reduction levels of only 50–60% are obtained in FSI processes even when a sorbent is injected at twice the stoichiometric amount (i.e., a Ca/S molar ratio of 2). Thus, much higher amounts of sorbent are required to achieve higher $SO_2$ reduction in flue gas, adversely affecting the performance of PCD.

## Sorbent Utilization Enhancement

The economics of the FSI process can be improved through the enhancement of sorbent utilization. Two paths to this end are the development of a highly reactive sorbent that undergoes nearly 100% utilization, and regeneration and reinjection of the spent sorbent. Recent research in both approaches is discussed in the next section. Sorbents prepared/regenerated by these techniques form the basis for the OSCAR process.

*High Reactivity Sorbent.* Conventional sorbents have a low surface area (SA) (2–18 $m^2/g$) and pore volume (PV) (0–0.18 $cm^3/g$), and are not effective in $SO_2$ removal in the sorbent injection process for the reasons given earlier. The development of a class of highly reactive and cost-effective $CaCO_3$ sorbents is the key to improved sorbent utilization. Such sorbents would calcine to produce CaO having an optimum pore structure with pore sizes predominantly in the 100–200 Å range and provide sufficient surface area for the sulfation reaction (Gullett and Bruce, 1987). Pores in this size range are not susceptible to the rapid pore-mouth plugging that is the major reason for reduced reaction rates and premature reaction termination found in sorbents with smaller size pores. It is also disadvantageous to have a sorbent with a majority of pores larger than 200 Å, as the surface area to pore volume ratio is reduced.

A highly reactive sorbent particle possessing high surface area and a favorable mesoporous structure can be prepared from Ca-based sorbents using surface-active agents or surfactants (Kirchgessner and Lorrain, 1987; Kirchgessner and Jozewicz, 1989; Wei et al., 1997). Specifically, calcium hydrate ($Ca(OH)_2$) particles can be modified during hydration of CaO by adding an anionic surfactant (e.g., calcium lignosulfonate). The resultant sorbent improves sulfation of up to 20% over conventional unmodified hydrated lime sorbent (Kirchgessner and Lorrain, 1987). The increase in reactivity is postulated to be due to a reduction in particle size of the modified hydroxide primarily through prevention of particle agglomeration and, secondarily, through crystal-size reduction.

Hydrated lime sorbent can also be modified during hydration of CaO by adding clay-based additives. These additives also reduce the fundamental crystal size of the hydrates and reduce the tendency of the sorbent to agglomerate and sinter. Clay-modified sorbents are reported to remove 89–99% $SO_2$ with inlet Ca/S molar ratios of about 1.5 to 3 for boilers firing bituminous coal with sulfur content in the range 1.7–3.2% (Benthamite Corp., 2002).

The sorbent for the OSCAR process focuses on the synthesis of $CaCO_3$ particles by carbonating lime particles in aqueous slurry in the presence of small quantities of anionic surfactants or surface modifiers (Fan et al., 1998). Fine $CaCO_3$ particles with a surface area as high as 60 $m^2/g$ and highly porous structures (PV>0.18 $cm^3/g$) can be synthesized. By controlling the amount and type of surfactant and the carbonation-precipitation conditions, the particle-size distribution, pore-size distribution and surface area of the precipitated limestone can be tailored (Maruscak et al., 1971; Agnihotri et al., 1999). The amount of surfactant added to the slurry affects the particle structural properties by changing the surface charge of the precipitated and suspended $CaCO_3$ particles. Without any surfactant in the slurry, freshly precipitated $CaCO_3$ particles have a high positive charge with a zeta potential (indicative of surface charge) of over 30 mV (Agnihotri et al., 1999). The addition of anionic surfactants decreases the zeta potential as anions produced from dissociation of the surfactant are adsorbed on the particle surface. Near zero zeta potential, electrostatic repulsion is minimal, and nuclei form aggregates at an early stage during crystal growth. Under these optimized conditions, "fluffy" agglomerates are formed with highly open pore structure having high pore volume and surface area. Varying the surface modifier concentration away from the point of surface neutrality imparts either a positive or a negative charge to the surface and increases the repulsive forces, and an open pore structure is not obtained (Agnihotri et al., 1999).

The $CaCO_3$ prepared by the above procedure exhibits more than 70% sulfation conversion within 500 ms under laboratory conditions, much higher than the conversions obtained with other Ca-based sorbents (see Figure 1). The higher reactivity of the modified carbonate is due to the "open" pore structure of the CaO calcined from the carbonate. The CaO possesses most of its surface area in the range 50–200 Å (Mahuli et al., 1997). In contrast, CaO calcined from natural $CaCO_3$ has most of its pores smaller than 50 Å in size. Such an increase in sorbent utilization of more than twofold over conventional sorbents could sharply reduce operating costs associated with FSI processes.

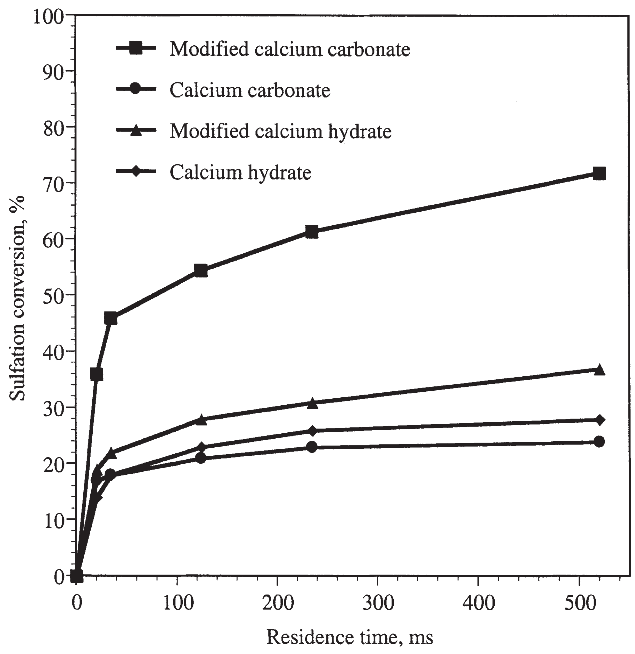

**Figure 1. Sulfation behavior of modified carbonate (SA=61 $m^2/g$), modified calcium hydrate (SA=62 $m^2/g$), calcium hydrate, and calcium carbonate (SA=1.9 $m^2/g$) particles.**
Particle size, 3.9 μm; $SO_2$ concentration, 3,900 ppm; temperature, 1,080°C.

*Spent Sorbent Reactivation*. Partially utilized Ca-based sorbents can be regenerated by slurry carbonation to increase the overall sorbent utilization. In the presence of water, unreacted CaO dissociates and generates $Ca^{2+}$ ions for $CaCO_3$ formation in the presence of bubbling $CO_2$ (Agnihotri et al., 1999; Fan et al., 2001). Unreacted calcium in the spent sorbent is, thus, redistributed, exposed, and converted back into $CaCO_3$ during the carbonation process. As shown in Figure 2, sorbents regenerated by the carbonation technique (Figure 2c) possess higher surface area and porosity as compared to the sorbents regenerated by the hydration technique (Figure 2b) and the spent sorbent (Figure 2a). The overall utilization of the reactivated sorbent can be significantly improved, increasing from less than 45% to nearly 100% (Agnihotri et al., 1999). Regeneration of spent sorbent, therefore, can reduce the fresh sorbent cost, as well as the spent sorbent disposal costs.

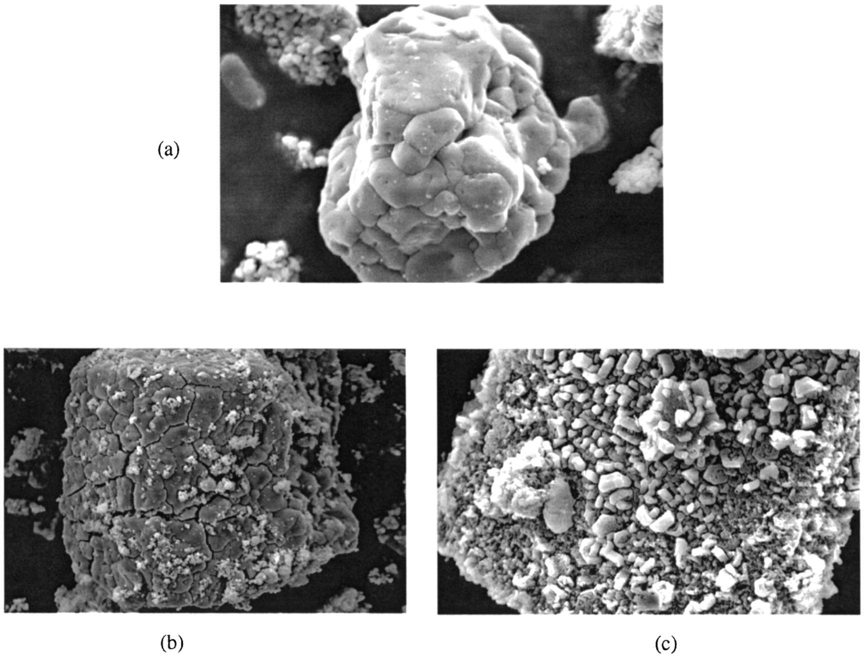

**Figure 2. Scanning electron micrographs of the reactivation effect on spent $CaCO_3$ sorbent.**
(a) $CaCO_3$ following sulfation; (b) sorbent regenerated by hydration method; (c) sorbent regenerated by carbonation method.

## Trace Element Control

Volatile elements such as mercury (Hg), arsenic (As), and selenium (Se) are present in coal in trace amounts and emitted in the gas phase along with other pollutants during combustion. Of these trace toxic elements, Hg is particularly notorious because of its toxicity and bioaccumulation potential, and has been identified in the U.S. for future regulation of coal-fired power plants. A significant amount of these toxic elements can be captured by Ca-based sorbents injected during the FSI process (Gullett and Raghunathan, 1994; MTI, 1999). Ca-based sorbents, thus, possess a multifunctional capability to capture both sulfur species and trace elements.

Ca-based sorbents capture the oxidized form of mercury ($HgCl_2$) in the lower temperature range by physical adsorption, and elemental mercury ($Hg^0$) by chemisorption on sulfur sites created on the sorbent surface in the presence of $SO_2$ (Ghorishi and Gullett, 1998; Ghorishi and Sedman, 1998). For As and Se, however, the capture takes place mainly by chemical reaction. Arsenic and selenium are present in the flue gas predominantly in the oxide form as $As_4O_6$ and $SeO_2$. Arsenic oxide ($As_4O_6$) reacts with CaO in the presence of oxygen to form tricalcium orthoarsenate ($Ca_3As_2O_8$) below 600°C and dicalcium pyroarsenate ($Ca_2As_2O_7$) between 700 and 900°C (Jadhav and Fan, 2001). Above 900°C, thermal decomposition of $Ca_2As_2O_7$ leads to the formation of $Ca_3As_2O_8$ (Shigematsu, 1986; Guerin et al., 1970). It has been shown that optimum capture of As by CaO takes place around 600°C (Jadhav and Fan, 2001). As with the sulfation reaction, the above reactions are facilitated by the diffusion of calcium and oxygen ions through the product arsenate layer (Yanagase et al., 1975). CaO also reacts with $SeO_2$ in the temperature range 400–600°C to form calcium selenite ($CaSeO_3$) (Ghosh-Dastidar et al., 1996). The optimum temperature for this reaction is 600°C, as $CaSeO_3$ thermally decomposes above 800°C.

## Nitrogen Oxides Control

Coal-fired power plants employ a variety of techniques to lower $NO_x$ emissions. Primary measures that target the reduction of $NO_x$ in the combustion unit itself involve lowering the combustion temperature by staged combustion, burner out of service (BOOS), lower air preheating, flue-gas recirculation, and the use of low-$NO_x$ burners (Muzio and Quartucy, 1997). These relatively inexpensive modifications achieve only 35–45% $NO_x$ reduction. Post-combustion secondary measures such as selective noncatalytic reduction (SNCR) and selective catalytic reduction (SCR) can achieve a higher degree of $NO_x$ reduction. The SNCR technique reduces NO to $N_2$ using reducing agents such as ammonia and urea at an optimum temperature in the 850–1,000°C range. The reaction can be stoichiometrically written as

$$6NO+4NH_3 \rightarrow 5N_2+6H_2O \quad (5)$$

This temperature-sensitive technique leads to ammonia slippage at lower temperatures and decomposition of ammonia to NO at higher temperatures (U.S. EPA, 1983). The SCR technique achieves a similar reduction by catalysis. While varieties of catalyst/catalyst supports have been investigated, vanadia on titania has emerged as the catalyst system of choice. The catalyst reduces the operating temperatures of the reduction processes from 850–1,000°C to 280–450°C. Among the available commercial technologies, SCR is the most effective and can reduce $NO_x$ by over 90% (Cho, 1994). Challenges to the SCR technology are reducing cost, and resolving problems such as catalyst poisoning by arsenic, formation of ammonium bisulfate/bisulfite, and oxidation of $SO_2$ to $SO_3$ with a resultant acid plume.

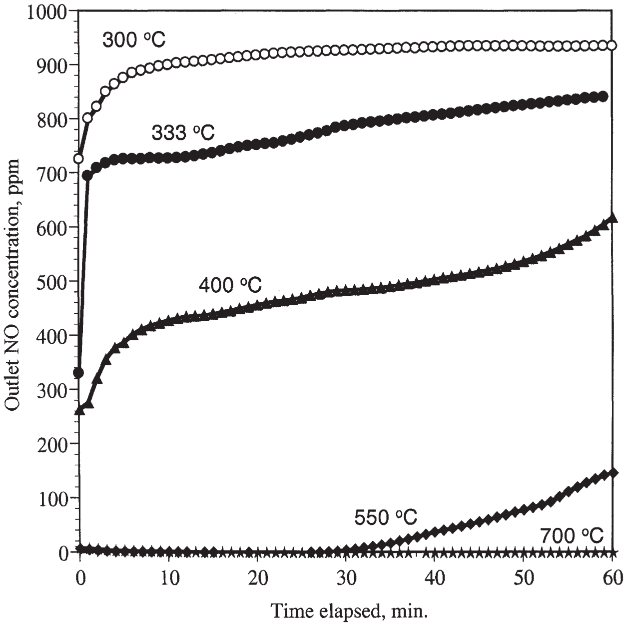

**Figure 3. Integral studies of the temperature effect on the reduction of NO by high-sodium lignite char.** Initial surface area, 250 $m^2/g$; flow, 1,000 mL/min; inlet NO concentration, 1,000 ppm; weight of carbon, 800 mg; oxygen concentration, 2%.

In another low-temperature process, NO is oxidized to $NO_2/N_2O_5$ by ozone or electron beams at 65–150°C. $N_2O_5$ can then be scrubbed by water (to form nitrous and nitric acid) or alkaline slurry (to form nitrite and nitrate salts) (Saxena et al., 1999).

Carbon-based technologies have also been employed for $NO_x$ reduction. In a reburning process, coal and/or natural gas are injected over the combustion zone to create a reducing atmosphere and react with NO to form $N_2$ and $CO/CO_2$ at about 1,100°C (Chen and Ma, 1996; Burch et al., 1994). Combined $SO_x/NO_x$ processes have been developed where carbon is used as a catalyst for the reduction of NO with ammonia at temperatures below 200°C (Hjalmarsson, 1990; Gangwal et al., 1993; Knoblauch et al., 1981).

Recent studies have spurred the development of another carbon-based technology, in which carbon in the form of coal char is used as a reducing agent for $NO_x$ reduction in the temperature range 300–700°C (Fan and Gupta, 2001). The carbon-NO reaction given below forms the central part of the carbon-based $NO_x$ reduction process known as the CARBONOX process

$$C+2NO \rightarrow N_2+CO_2 \quad (6)$$

The temperature range for the above reaction is substantially lower than that required for the reburning process. The lower reaction temperature is a result of the catalytic action of alkali metals (such as Na) in coal char (Gupta, 2001). Other alkali metals (such as K) and transition metals (such as Cr, Fe, Co, Ni and Cu) are also effective catalysts for the above reaction (Illan-Gomez et al., 1999). Figure 3 shows the effect of reaction temperature on the reduction of NO by high-sodium lignite char.

## OSCAR Process Demonstration

The OSCAR process, which is currently being commercially demonstrated at the Ohio McCracken Power Plant located on the campus of The Ohio State University, employs both techniques described earlier for maximizing sorbent utilization in FGD process. The purpose of the demonstration pilot plant is to quantify the effectiveness of the fresh and reactivated sorbent for $SO_2$ capture. The commercial demonstration facility is constructed on a slipstream (1 MW Equivalent) from the power plant. The simplified process flow diagram for the pilot plant is given in Figure 4. Photographs of different parts of the process are shown in Figure 5.

The process consists of two main parts. In the first part, a highly reactive $CaCO_3$ sorbent, also known as modified carbonate (MC) or precipitated calcium carbonate, is prepared. This part also involves reactivation of the spent FGD sorbent generated in the existing LSD of the power plant. The processes and chemistry involved in these sorbent generation/reactivation techniques have been described earlier. In the operation, a slurry of fresh or unreacted calcium sources is carbonated in the slurry reactor using power plant exhaust flue gas that contains nearly 15% $CO_2$. Calcium carbonate precipitates in the slurry, which is filtered and dried before it is sent to the second part of the process to react with $SO_2$ in the 700–850°C range in a riser reactor. The reactor provides up

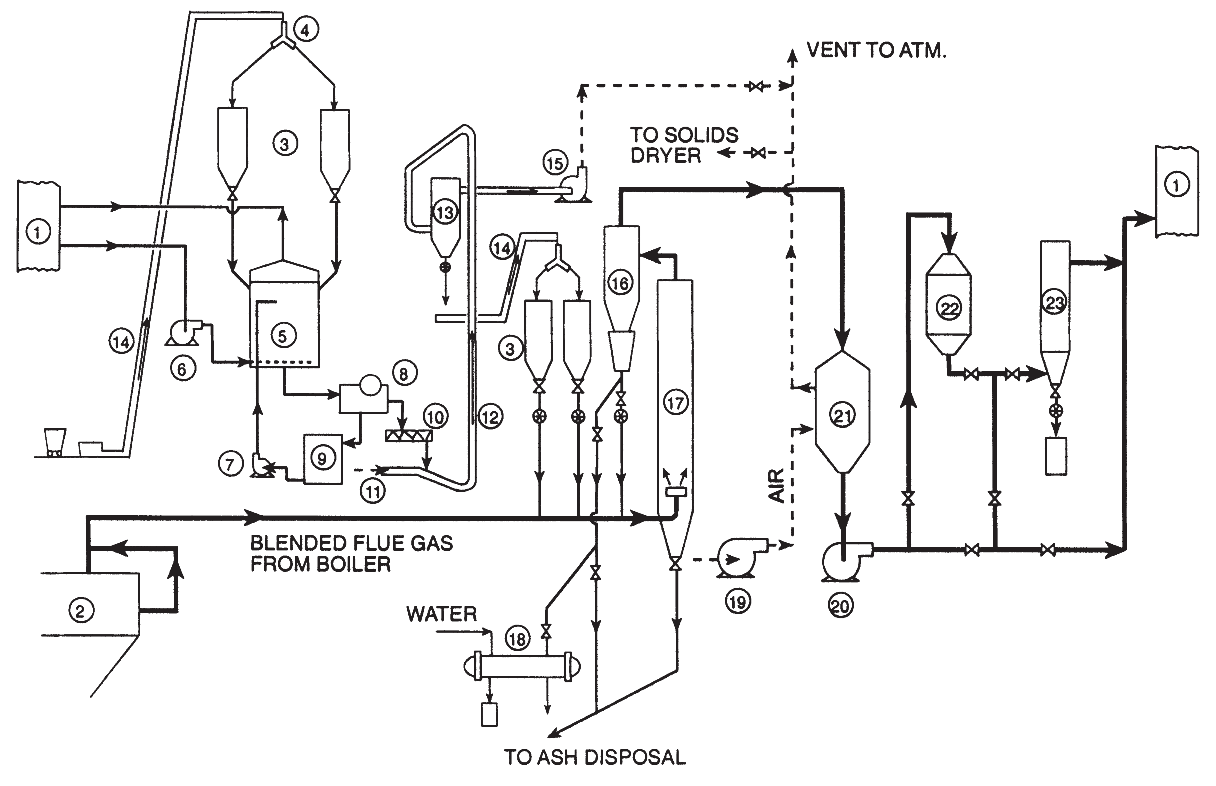

**Figure 4. Simplified OSCAR demonstration process.**
(1) Flue duct; (2) coal combustor; (3) hoppers; (4) diverter; (5) slurry reactor; (6) gas blower; (7) recycled water pump; (8) vacuum drum filtration unit; (9) drain tank; (10) screw conveyor; (11) air from heat exchanger, (12) flash dryer; (13) flash dryer baghouse; (14) conveyor; (15) exhaust fan, (16) cyclone, (17) riser reactor; (18) screw cooler; (19) air fan; (20) gas fan; (21) heat exchanger; (22) SCR reactor; (23) baghouse.

to 1.5 s of residence time to allow for calcination and sulfation reactions. The reactor can be used as either a once-through system or a CFB system. Depending on the configuration and the sorbent used, the particles collected in the cyclone can be recycled into the reactor, sent for ash disposal, or sent for regeneration. Characterization and utilization of the spent sorbent are also a part of this demonstration project. The flue gas from the cyclone passes through a heat exchanger, a SCR unit for $NO_x$ control, and a baghouse that removes fine particulates escaping the cyclone. The cleaned flue gas is then sent to the stack.

The OSCAR process demonstrates the multifunctional role of the sorbent in capturing trace elements (Hg, As, and Se) along with $SO_2$. This is particularly significant for Hg, as current Hg removal technologies focus on the injection of costly activated carbon in the flue-gas stream for plants not equipped with a FGD technology (U.S. EPA, 1997). The use of cheaper, multifunctional sorbent such as the OSCAR sorbent will be highly beneficial to pollution abatement operation. Furthermore, removal of As (a known poison for the SCR catalysts) in the higher temperature range extends the life of the catalyst utilized in the downstream SCR system (if installed).

## CARBONOX Process Demonstration

The CARBONOX process (Fan and Gupta, 2001) is currently being demonstrated at the University of North Dakota's Energy and Environmental Research Center (EERC) in a joint venture between the senior author and EERC with sponsorship from the U.S. DOE, the Lignite Energy Council, EPRI, and five industrial partners. The process consists of contacting $NO_x$-laden flue gas with activated carbonaceous materials, such as inexpensive high-sodium lignite coal char, for a sufficient time to reduce the outlet $NO_x$ concentration to a desired level. As described earlier, NO is converted to $CO_2$ and $N_2$ following Reaction 6. While the gas residence time required is of the order of tens to hundreds of milliseconds, the carbon particles require 10–180 min (solid residence time) for complete oxidation depending on the sorbent characteristics and reaction conditions. This carbon-based process has several advantages. Theoretically, 100% $NO_x$ reduction can be achieved by providing enough gas residence time and/or char loading in the reactor. The process can also adapt relatively easily to changing load conditions. At lower turndown ratios, a portion of the bed would be active and the rest of the bed can be bypassed (if a series of multiple beds were used) or it would remain inert. The process employs carbonaceous sorbents whose handling and storage are well known in the coal industry. The low-temperature oxidation of char by the remaining oxygen in the flue gas leads to significant heat liberation (5–8% of the entire power plant thermal output) that can be harnessed into steam or electricity.

## Future of Emissions Control Research

In light of the growing public and industry concerns regarding environmental pollution from coal-burning power plants, there is an urgent need to develop novel and efficient pollution control technologies. The challenges are numerous. The U.S. DOE's Vision 21 program, which envisages producing energy from coal and other fossil fuels with *zero emissions*, provides goals for the future of emissions control research. According to the plan, a 21st Century Energy Plant would use one or more fossil fuels to produce electric power, fuels, and chemicals at much higher efficiencies (U.S. DOE, 2002). The current efficiency of coal-fired power plants is in the range 33–35%, which would increase to over 60% under the plan. Advanced pulverized coal combustors, pressurized fluidized-bed combustors, and integrated gasification combined cycle (IGCC) systems are under development and/or demonstration that could achieve such efficiency. The IGCC system could gasify coal in the presence of steam to generate hydrogen-rich syngas that can be used as fuel (e.g., in fuel cell applications), for synthesis of chemicals (e.g., methanol and dimethyl ether) and for power generation. These advanced plants would be operated with *near-zero* emission of pollutants such as $SO_2$, $NO_x$, and Hg. Carbon dioxide emissions would also be reduced by 40–50% because of an increase in plant efficiency. Emerging technologies addressing carbon sequestration could reduce $CO_2$ emissions to a near-zero level. Economical separation of $CO_2$ from flue gas holds the key to successful deployment of carbon management schemes. Active efforts are ongoing to apply the modified sorbent used in the OSCAR Process to $CO_2$ removal from flue gas (Gupta and Fan, 2002).

Future research and development programs undertaken at the university, government and industrial levels need to address the issues of economical energy production and pollution control. Technological innovation will shape the future of fossil fuels in electricity and transportation fuels production. Established clean coal technologies and those under demonstration will serve as design guides and provide a cost basis for gauging future technology developments aimed at meeting increasingly stringent pollution emission regulations. Coal continues to be the cheapest source of fossil energy, and its ubiquitous and abundant availability will ensure its worldwide use without geo-political uncertainties. These emerging technologies will enable the continued widespread utilization of coal in an environmentally acceptable manner in the coming decades.

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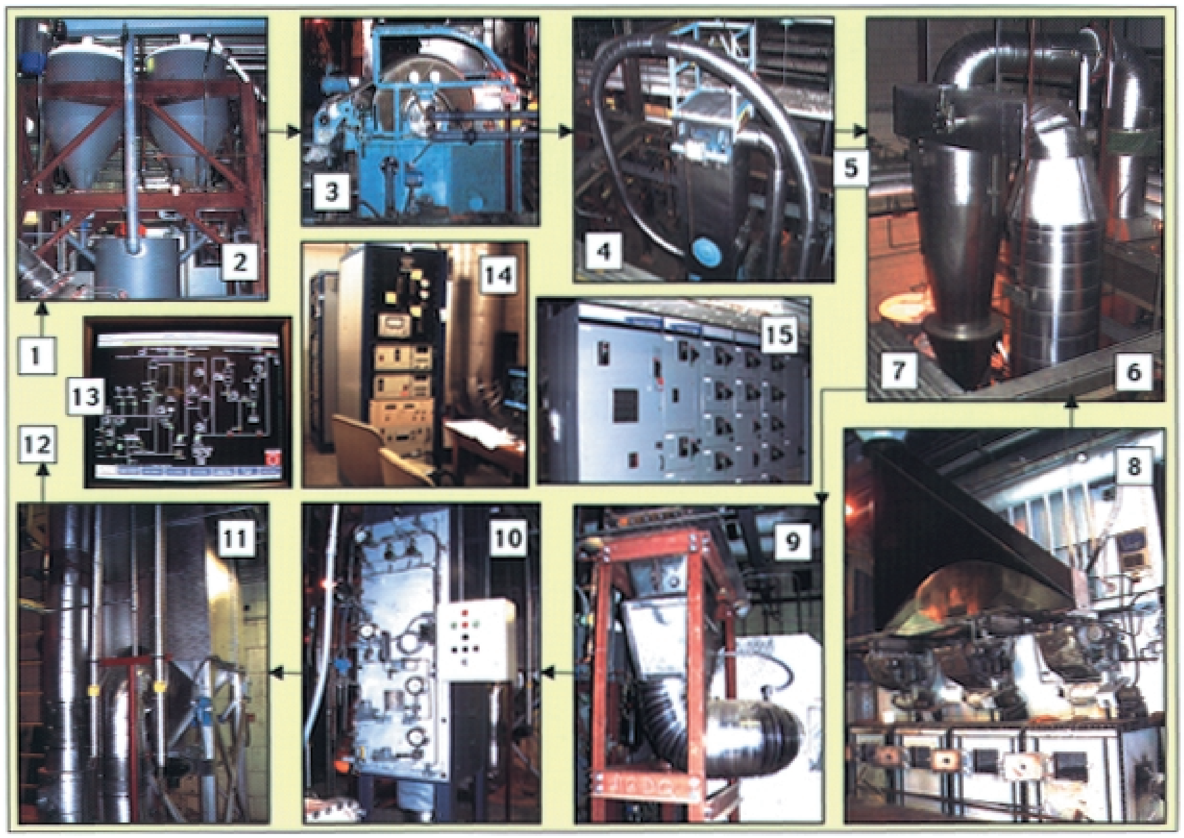

**Figure 5. OSCAR commercial demonstration process consisting of various parts, operations and ancillary equipment.** (1) Fresh/spent calcium; (2) slurry reactor; (3) vacuum drum filter; (4) Flash dryer; (5) modified/regenerated sorbent; (6) riser reactor; (7) cyclone; (8) coal combustor; (9) ID fan and heat exchanger; (10) SCR reactor; (11) baghouse; (12) cleaned flue gas; (13) control panel; (14) continuous emission monitors; (15) PLC buckets.

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