Hydrogen Peroxide Enhances Removal of NO$_x$ From Flue Gases

Radicals from homogeneous decomposition of H$_2$O$_2$ react with unscrubbable NO to produce scubbable gases.

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Pilot scale experiments have demonstrated a method of reducing the amounts of oxides of nitrogen (NO$_x$) emitted by industrial boilers and power-plant combustors that involves (1) injection of H$_2$O$_2$ into flue gases and (2) treatment of the flue gases by caustic wet scrubbing like that commonly used to remove SO$_2$ from combustion flue gases. Heretofore, the method most commonly used for removing NO$_x$ from flue gases has been selective catalytic reduction (SCR), in which the costs of both installation and operation are very high. After further development, the present method may prove to be an economically attractive alternative to SCR.

The primary constituent of NO$_x$ is NO. Although the nitrogen acid gases HNO$_2$ and HNO$_3$ (and, to a lesser extent, NO$_2$) can be removed from flue gas by caustic scrubbing, NO is almost completely insoluble and thus not scrubbable. If, however, the NO in NO$_x$ could be economically converted to HNO$_2$ and HNO$_3$, then scrubbing could be an effective means for removing NO$_x$.

NO can be oxidized to HNO$_2$, HNO$_3$, and NO$_2$ at low to moderate flue-gas temperatures by use of hydroxyl radicals (OH). In the present method, the OH needed for oxidation of NO is generated by thermal decomposition of the H$_2$O$_2$ injected into the flue gas.

For efficiency, it is necessary to maximize the proportion of OH and HO$_2$ radicals, relative to other products of decomposition of H$_2$O$_2$. In particular, it is necessary to suppress a competing reaction in which H$_2$O$_2$ decomposes into water and oxygen. This competing reaction occurs readily at surfaces. In general, peroxides are preserved at acidic surfaces and are decomposed at basic ones. Experiments have shown that the incidence of the competing decomposition into H$_2$O and O can be reduced by treating reactor surfaces with boric acid to render them acidic.

In one of several sets of experiments to demonstrate the feasibility of the method, the optimum temperature for conversion of NO to HNO$_2$, HNO$_3$, and NO$_2$ by use of injected H$_2$O$_2$ was found to be about 500 °C (see Figure 1).

A study performed under the guidelines of the EPA, EPRI comparing the economics of SCR and the experimental H$_2$O$_2$-injection/scrubbing method was conducted for a design base case and a variety of alternative cases. This study illustrated the tradeoff between capital and operating costs for the two methods. The single largest factor in determining the total cost of one method relative to the other method was found to be the H$_2$O$_2$:NO$_x$ molar ratio. At the H$_2$O$_2$:NO$_x$ molar ratio of 1.92, which was previously demonstrated in the laboratory, the H$_2$O$_2$-injection/scrubbing method was shown to be uneconomical. However, it was also concluded that the molar ratio in a full-size coal-fired power plant could be lower than that found in the laboratory, and that on the basis of all the assump-

Figure 1. The Conversion of NO by oxidation to other species was measured as a function of reactor temperature. The reactor inlet conditions for the points shown here were 400 ppm NO and 400 ppm H$_2$O$_2$ for an H$_2$O$_2$ :NO molar ration of 1.0:1.0.

Figure 2. The Outlet Concentration of NO was significantly reduced when H$_2$O$_2$ was injected. At 500 °C, 400 ppm NO, and various inlet concentrations of H$_2$O$_2$ (represented as H$_2$O$_2$:NO$_x$ molar ratios), 90-percent conversion of NO was achieved at the reactor outlet for a molar ratio of 1:1.
tions of the study, at an H₂O₂:NO molar ratio of 1.37, the H₂O₂-injection/scrubbing method could be an economically feasible alternative to SCR.

Pilot-scale tests run at Kennedy Space Center demonstrated the feasibility and competitiveness of this new technology. The H₂O₂ to NO molar ratio, at 500 °C shown to achieve a NO conversion efficiency of > 90 percent was 1:1, which is significantly lower than the required 1.37:1 (See Figure 2).

This work was done by Michelle M. Collins of Kennedy Space Center and C. David Cooper and Christian A. Clausen III of the University of Central Florida.

This invention is owned by NASA, and a patent application has been filed. Inquiries concerning nonexclusive or exclusive license for its commercial development should be addressed to the Technology Commercialization Office, Kennedy Space Center, (321) 867-1463. Refer to KSC-12056.

Subsurface Ice Probe
Small samples of ice would be melted and pumped to the surface for analysis.

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The subsurface ice probe (SIPR) is a proposed apparatus that would bore into ice to depths as great as hundreds of meters by melting the ice and pumping the samples of meltwater to the surface. Originally intended for use in exploration of subsurface ice on Mars and other remote planets, the SIPR could also be used on Earth as an alternative to coring, drilling, and melting apparatuses heretofore used to sample Arctic and Antarctic ice sheets.

The SIPR would include an assembly of instrumentation and electronic control equipment at the surface, connected via a tether to a compact assembly of boring, sampling, and sensor equipment in the borehole (see figure). Placing as much equipment as possible at the surface would help to attain primary objectives of minimizing power consumption, sampling with high depth resolution, and unobstructed imaging of the borehole wall. To the degree to which these requirements would be satisfied, the SIPR would offer advantages over the aforementioned ice-probing systems.

The tether would include wires for power, wires or optical fibers for control and sensor data, and a narrow tube through which meltwater would be pumped to the surface. A unit containing a heater, a cam-driven agitator, and an auxiliary pump (a small peristaltic pump) would be submerged in a small pool of water at the bottom of the borehole. The heater in this unit would melt ice at the bottom of the hole. The agitator would prevent settling of any suspended sediment to the bottom of the hole. The auxiliary pump would quickly transfer the meltwater and any sediment to a small holding tank above the water surface. To minimize unwanted loss of energy through side melting and to optimize the depth resolution of meltwater samples, only a small amount of water would be left at the bottom of the hole.

The heart of the down-hole assembly would be a small well pump that would force the water and sediment from the holding tank, up through the tube, to the instrumentation assembly at the surface. The pump must provide sufficient head to lift the water from the greatest anticipated borehole depth. Alternatively, the down-hole assembly could be made smaller by placing a pump on the surface and using a two-way fluid or pneumatic loop to drive the liquid to the surface. The inevitable dissipation of electric energy in the power cables could be utilized as auxiliary heating to prevent freezing of the water in the tube. Either above or below the pump there could be an electronic camera to acquire images of the borehole wall and/or a nephelometer for acquiring data on sediment particles trapped in the wall.

The design of the tube is anticipated to demand a major part of the overall design effort. The bore of the tube must be narrow enough that the mixing length within the tube corresponds to a short column of water in the hole: this length defines the depth resolution of the system (intended to be of the order of centimeters). At the same time, the