In three previous research projects, funded by the CIC and ICDB through the CRSC, a proprietary hydration process to produce high surface area (HSA) hydrated lime was developed at the ISGS. The objective of the current study was to produce pound-size quantities of HSA hydrates from one commercial lime and two specially prepared limes and to evaluate the SO$_2$ removal performances of the hydrates under Coolside, boiler economizer and spray drier conditions.

Specially-prepared limes were produced at Manufacturing Technology Conversion International (MTCI) in an indirectly heated fluidized-bed reactor and at the ISGS in a rotary kiln (RTK). Optimum operation conditions for manufacture of HSA hydrates from a commercial lime and the two specially-prepared limes were determined. More than 110 bench-scale hydration runs were made to produce 200 pounds each of the three hydrates. The surface area of hydrates made from the commercial, RTK and MTCI limes were 34, 45, and 60 m$^2$/g, respectively.

Pilot-scale Coolside tests at CONSOL showed that the ISGS HSA hydrates had higher SO$_2$ removals and higher calcium utilizations than the best performing commercial hydrated lime at similar Ca/S ratios. At Ca/S = 2, 1500 ppm SO$_2$, and 25°F approach to adiabatic saturation temperature, the system removals were 50, 65, 67 and 81% for the sorbents with surface areas of 20 (commercial), 34, 45, and 60 m$^2$/g, respectively. Boiler economizer tests at RC-EST showed 57% SO$_2$ removal for a 40 m$^2$/g HSA hydrate and 50% removal for a 22 m$^2$/g commercial hydrate at 1000°F. Similar tests at U.S. EPA revealed that higher SO$_2$ removal is possible when HSA hydrate is injected at a temperature of about 914°F. Under spray drier conditions the SO$_2$ removal efficiency increased from 30% to 52% (no fabric filter) with an increase in hydrate surface area from 40 to 60 m$^2$/g.
EXECUTIVE SUMMARY

Impending environmentally motivated federal acid rain legislation that has passed the U.S. Senate and House will require utilities in Illinois to reduce SO$_2$ emissions from targeted plants to about 2.5 lb SO$_2$/MMBtu by 1995 and to 1.2 lb SO$_2$/MMBtu by 2000. Since, with no SO$_2$ control, Illinois high-sulfur coal emissions, on the average, 5 lb SO$_2$/MMBtu, an increasing number of utilities using Illinois coal will switch to burning low-sulfur western coals to meet these environmental regulations if alternative cost-effective technologies for SO$_2$ control are not developed soon. Wet scrubbers using a lime-water slurry to adsorb SO$_2$ from stack gases can be cost effective for large plants provided there is adequate space, but are not generally cost effective for smaller power plants. Dry sorbent injection technologies which inject limestone, lime or hydrated lime powder to adsorb SO$_2$ from stack gases are better for smaller power plants because these technologies cost less to install, require less space than wet scrubbers, and have low projected capital cost. The Electric Power Research Institute (EPRI) estimates that 450 power plants east of Colorado, 150 MW or less in size, and accounting for 35,000 MW total capacity could benefit by installing dry sorbent injection systems (Toole-O'Neil, 1990).

Dry Sorbent Injection Technologies

The processes that have been researched considerably by U.S. EPA, EPRI, and U.S. DOE, and are considered to be emerging technologies for SO$_2$ emissions control for power stations, include furnace sorbent injection (FSI), boiler economizer injection, and post furnace duct-injection/humidification (Coolside) and spray driers. In these three dry sorbent injection technologies, a calcium-based sorbent, such as hydrated lime, is injected into different locations within a pulverized coal boiler unit. The SO$_2$-removal performance of the sorbents has the greatest impact on the operating cost of these technologies.

Typical SO$_2$ capture efficiencies in dry sorbent injection technologies are about 40 to 50% for commercial hydrated limes (Beittel et al., 1985; Snow et al., 1986; Bortz et al., 1986; Withum et al., 1989). These SO$_2$ removal levels correspond to less than 30% of the theoretical SO$_2$ saturation capacity for the sorbents. It is unlikely that large additional gains in utilization will be obtained by simply optimizing process parameters. Further increase in sorbent utilization for dry sorbent injection technologies, thereby improving the economics, will be by use of a new generation of super-active hydrated lime which is more reactive than current commercial products.

ISGS Hydration Process

Since 1986, the ISGS has been developing a process to produce high-surface-area (HSA) hydrated lime with far more activity for adsorbing SO$_2$ than commercially available hydrated limes (Rostam-Abadi et al., 1986, 1988, 1989, 1990). A patent application covering the ISGS hydration process was filed with the U.S. Patent office on July 24, 1990. The research has cost a total of approximately $740K of which $460K has been
sponsored by the CRSC and $280K has been contributed by the ISGS. To date more than 1,500 pounds of HSA hydrated lime with surface areas ranging from 35 to 85 m²/g have been produced using a bench-scale hydrator located at the ISGS. These surface areas are among the highest ever reported in the literature and are 2 to 6 times higher than the surface areas of currently available commercial hydrates.

In the ISGS hydration process lime is hydrated at atmospheric pressure with an aqueous solution of a proprietary reagent (one-step process) followed by an optional post-hydration wash step (two-step process). The one-step process is capable of producing a hydrate with surface area ranging between 40 and 50 m²/g using commercial quick limes as feed materials. Higher surface area hydrates, above 50 m²/g, can be made using the two-step process. With either the one-step or the two-step hydration methods, hydrates with even higher surface areas (up to 85 m²/g) can be made using specially-prepared limes.

During the past four years more than 250 experiments have been conducted to optimize the ISGS hydration process and identify key parameters influencing hydrate properties (Rostam-Abadi et al., 1986, 1988, 1989, 1990). These tests were conducted both at gram quantities in a laboratory-scale unit and in a bench-scale batch hydrator capable of producing 5 to 7 pounds of hydrated lime per batch. The dependence of the hydrate properties important for SO₂ capture (surface area, porosity, particle size and crystallite size) on operating conditions including hydration temperature, contact time, type and quality of lime, quantity of water and solvent, and the amount of solvent used in the post-hydration wash step have been investigated. Based on the results of these tests, the optimum conditions for producing HSA hydrates from different limes have been determined. HSA hydrate prepared by the ISGS method has considerably higher surface area and porosity, and smaller mean particle diameter and crystallite size than commercial hydrated lime.

SO₂ Removal Performance of ISGS Hydrate

During the 1988-89 contract period, pilot-scale dry sorbent injection tests were performed using several ISGS HSA hydrates to evaluate the SO₂ removal efficiencies under typical conditions of burning high-sulfur Illinois coals. These data indicate that the ISGS hydrate removed, depending on the test system, up to 100% more SO₂ than commercial hydrated limes tested under similar conditions. Pilot-scale tests were performed in Consolidation Coal Company’s 100 kW Coolside pilot unit (Library, PA), in Research-Cottrell’s 146 kW boiler economizer furnace (Irvine, CA), and in U. S. EPA’s 14 kW Innovative Furnace Reactor unit under FSI conditions (Research Triangle Park, NC). The FSI tests at U. S. EPA were performed with a 40 m²/g ISGS hydrate and five other commercial and specially-prepared hydrates while burning four high-sulfur Illinois coals from the Illinois Basin Coal Sample Program. At a Ca/S ratio of 2:1, except for a high pyritic sulfur coal for which the ISGS hydrate showed 60% removal, SO₂ removal obtained with the ISGS hydrate ranged from 72 to 77% for the coals tested compared to 45 to 65% for the commercial hydrates tested (Gullett et al., 1989).
Under boiler economizer conditions, the SO₂ reduction achieved with a 40 m²/g ISGS hydrate was 58% compared to only 32% with a 20 m²/g commercial hydrate (Rostam-Abadi et al., 1989). Under Coolside conditions, the maximum SO₂ removal obtained with a 20 m²/g commercial hydrate was 49% compared to 56% with a 40 m²/g HSA hydrated lime. The superior performance of the ISGS hydrates observed in these pilot-scale tests is attributed to their high surface area and small particle size.

Economic Evaluation of the ISGS Hydration Process

In 1989, a technical and economic evaluation of the ISGS hydration process was conducted by Arthur L. Conn and Associates, Ltd. to determine the probable cost and the suitability of the ISGS hydrate for manufacture on a commercial scale (Conn et al., 1989). The project was sponsored by the Illinois Coal Development Board through the CRSC. The design basis was a plant large enough to handle the demand of a 1000 MW coal-fired power plant site using a 12,000 Btu/lb Illinois coal containing 3.5% sulfur. The study concluded that the process to manufacture HSA hydrates by the ISGS method is technically feasible and that conventional commercial equipment should be applicable. The capital required for the one-step process was estimated at $13.8M and the operating cost was expected to be $63.7 per ton of product. The high-performance HSA hydrate will have a similar price to commercial hydrates which currently sell for approximately $61 per ton.

Results of 1989-90 Contract Period

The objective of the 1989-90 research project was to produce a minimum of 150 pounds of HSA hydrates each from two specially prepared limes and a commercial lime and to evaluate the SO₂ removal performances of the hydrates under Coolside, boiler economizer and spray drier conditions.

The specially prepared limes were produced at the ISGS in a rotary kiln from an Illinois limestone (limestone A) and at Manufacturing Technology Conversion International, Santa Fe Springs, California, California from a California limestone (limestone B). The surface area of limes made from limestones A and B were 3.0 and 6.9 m²/g respectively and the surface area of the commercial lime was 1.8 m²/g.

More than fifty optimization tests were conducted to evaluate the hydration conditions for producing hydrates with high surface area and small mean particle diameter (MPD) from each lime. Based on the results of the optimization study more than 110 production runs were made in a 5-7 pounds/batch hydrator to produce 200 pounds each of the hydrates. The surface areas (m²/g) and MPD (micrometers) of hydrates made from lime A (HSA1), lime B (HSA2) and commercial lime (HSA3) were 44 and 0.7, 61 and 0.8, and 34 and 1.1 respectively. The baseline commercial hydrate tested for comparison had a 20 m²/g surface area and a MPD of 1.7 micrometers.

The Coolside test program involved testing the HSA and commercial hydrates at Ca/S ratios of 0.5, 1.0, and 2.0 and approaches to adiabatic saturation temperature of 25 and 35°F. A simulated flue gas containing 1500 ppm SO₂
was used. The three HSA samples showed higher SO₂ removals and higher calcium utilizations than the best-performing commercial hydrated lime at similar Ca/S ratios. The highest SO₂ removal was observed using HSA2. The average system removals were 33, 53° and 81% at 0.5, 1.0 and 2.0 Ca/S, respectively, using HSA2 at 25°F approach to adiabatic saturation temperature. This represents 154, 71 and 62% (relative) higher SO₂ removal than a 22 m²/g commercial hydrated lime. Sorbents HSA1 and HSA3 showed lower SO₂ removal than HSA2, but higher removal than commercial hydrated lime at similar Ca/S ratios. At 0.5, 1.0 and 2.0 Ca/S and 25°F approach, SO₂ removals using HSA1 were 28, 47 and 67%, respectively (representing 115, 52 and 34% relative improvement over commercial hydrate), and 30, 44 and 65%, respectively, using HSA3 (representing 131, 42 and 30% relative improvement over commercial hydrate). Using commercial hydrated lime at 25°F approach, the SO₂ removals were 13, 31 and 50% at 0.5, 1.0 and 2.0 Ca/S, respectively.

At 35°F approach to adiabatic saturation and 1.0 Ca/S, the ISGS samples again showed substantially higher removal than the commercial hydrated lime. The SO₂ removals were 45, 41 and 37% for HSA1, HSA2, and HSA3, respectively, compared to 22% using the commercial hydrated lime. These represent improvements of 101, 84 and 66% (relative) over the commercial hydrated lime.

The boiler economizer tests were conducted at RC-EST and U.S EPA. These tests were performed in an isothermal reactor using a simulated flue gas containing 3000 ppm SO₂. The results obtained at RC-EST at 1000°F showed 25% SO₂ reduction at Ca/S=1 and 50% SO₂ reduction at Ca/S=2 for the commercial hydrate and 36% and 57% SO₂ reductions at Ca/S=1 and 2 for a 40 m²/g HSA hydrate. In these tests the highest surface area hydrate (60 m²/g) did not perform as well as the 40 m²/g hydrate. This was attributed to the agglomeration tendency of the 60 m²/g hydrate particles when injected into the flue gas stream.

The boiler economizer tests at U.S. EPA showed that the optimum injection temperature for the HSA hydrate was lower than those for the commercial hydrates tested (Gullett, 1990). For a 50 m²/g HSA hydrate, 60% calcium utilization was observed at 914°F. The maximum calcium utilization for two commercial hydrates (50%) occurred at 1000°F.

The spray dryer tests were conducted in a lab-scale reactor at the University of Illinois, Urbana-Champaign. In these tests a flue gas containing 1500 ppm SO₂ was used. An increase in specific surface area of hydrate from 34 to 60 m²/g resulted in an increase in SO₂ collection efficiency from 30% to 52%. A numerical model describing the SO₂ removal efficiency indicated that HSA hydrates are most effective at SO₂ concentrations typically observed in flue gases generated from burning high-sulfur coal (3500 ppm).

Based on the results obtained at the ISGS during the past four years, it is recommended that a 10 to 50 lb/hr continuous process optimization unit be constructed to obtain scale-up and design data for rapid transfer of the ISGS HSA hydrated lime process to industry.