ABSTRACT

The use of Illinois coal may rise significantly if plans to develop several new coal-fired power plants at mine-mouth sites are implemented. This is expected to increase demand both for Illinois coal and for the high-purity limestone and dolomite needed for flue-gas desulfurization (FGD) and fluidized-bed combustion (FBC) units. The main objective of this project was to create a database on the quality and quantity of limestone and dolomite near existing and potential Illinois utility sites that will potentially use this material. The proposed project had four major tasks. In tasks 1 and 2, we characterized the availability and quality of limestone and dolomite resources suitable for wet FGD units in southern Illinois and nearby counties of Indiana, Kentucky, and Missouri. The results include a) chemical, mineralogical and physical data for 125 representative samples; b) reactivity data for selected samples with respect to sulfur oxide capture under FGD and FBC conditions; and c) generalized geologic descriptions of limestone layers in active quarries. In task 3, we prepared a GIS-based digital database and statewide map showing the location of active limestone and dolomite quarries, the transportation network, and the location of existing coal-fired power plants. The results indicate that limestone primarily occurs in the southern half of the state and the nearby regions of Indiana, Kentucky, and Missouri. Dolomite is rare and generally limited to thin beds in a few limestone quarries. Only one quarry in central Illinois (Douglas County) extracts dolomite. Substantial amounts of dolomite, however, occur near the Illinois border in the southeastern part of Missouri. Reactivity data calculated for FGD systems indicate that limestones are the most reactive sorbents. Reactivity among the limestone tested is, however, variable and may be dependent on limestone constituents (fossil fragments, microcrystalline calcite matrix, sparry calcite cement, non-skeletal grains, etc.). The FBC tests indicate that dolomites are the most reactive sorbents for this system. However, reactivity of dolomite appears to be highly dependent on crystal size and absorption. Dolomites with the smallest crystal size and high absorption rates are the most reactive under FBC conditions. The information from this study will be useful to the utility industry, limestone producers, and government agencies to facilitate acquisition of the best scrubbing agent for the FGD or FBC systems to be used at the existing or planned coal-fired power plants.
EXECUTIVE SUMMARY

In Illinois, development of new coal-fired power plants may be accelerated, in part, by new incentives offered by state government. Construction of new coal-fired power plants and the more stringent pollution control requirements facing the existing utility sites are expected to increase demand for high-quality limestone and dolomite raw materials for flue-gas desulfurization (FGD) and fluidized-bed combustion (FBC) units.

This ICCI-funded project produced a comprehensive database and maps that identify and characterize appropriate limestone and dolomite resources near existing and planned coal-fired power plants. The database and maps produced in this project will be useful for locating the most effective sorbents locally and at a relatively low cost. The main objectives of the project were: 1) to characterize and map the availability and quality of limestone suitable for wet FGD units in southern Illinois and nearby regions; 2) to characterize and map the areal distribution and quality of dolomite and/or dolomitic limestone suitable for FBC units; and 3) to prepare a digital statewide map and database showing the locations of active limestone and dolomite quarries.

Task 1 - Southern Illinois scrubber stone resources: Limestone and dolomite quality and areal distribution were determined for southern Illinois and nearby counties of Indiana, Kentucky and Missouri. The sources of information for this phase of the project included 1) extensive ISGS files of field notes, existing GIS and analytical databases, maps and cross-sections, reports and journal articles, and archived samples and cores; 2) samples collected at active quarries in the area; and 3) extensive ISGS well records including oil, coal and mineral tests. The results obtained under this task are as follows:

A – Description of available limestone resources: Most quarries in the southern Illinois area were visited and detailed geological descriptions including the general quality were made for representative quarries. Units within each rock formation that are suitable sources of scrubber stone were delineated. A stratigraphic column with lithologic descriptions was prepared for selected quarries. Samples were collected from selected quarries and from well cuttings and cores for this study. More than 125 samples were processed and analyzed for chemical, mineralogical, and physical properties.

B – Limestone/dolomite distribution and quality: The information from task 1A along with available published and unpublished information at the ISGS was utilized to prepare a generalized, GIS-based geologic map showing the distribution of limestone in southern Illinois and nearby regions. See discussion under task 3 below for details.

C – Chemical and physical properties: Representative samples (about 125) collected under (A) were characterized chemically and petrographically. Physical properties such as grindability, bulk specific gravity, and water absorption were also measured. Specific gravity ranged from 1.9 to 2.8 and absorption percentages ranged from 0.6% to 16.6%. The highest absorption values were found mainly in microcrystalline dolomites and clay-rich limestones. Microcrystalline limestones have the lowest absorption values. Grindability is a measure of a limestone’s hardness. Hard stones have lower values than softer, more easily ground stones. Grindability values range from 7.67 to 38.62. Microcrystalline dolomites, clay-rich limestones, oolitic and coarsely fossiliferous limestones have higher grindability values, whereas microcrystalline limestones, cherty
limestones, and coarsely crystalline dolomites are generally harder and have lower grindability values. Petrographically, limestone and dolomite are quite varied and include oolitic limestone, microcrystalline limestone and dolomite, fossiliferous limestone and coarsely crystalline dolomite. Mineralogical and chemical data show that the majority of the limestones in the southern part of the state are high purity limestones.

D – Reactivity measurements for FGD systems: In this part of the study, an acid titration technique was employed to investigate the dissolution performance of limestone and dolomite rocks as an indicator of their reactivity in wet FGD systems. Thirty six samples were tested. The results indicate a general trend of higher reactivity with higher calcite content (or CaO content). A similar correlation trend was also found for acid neutralization capacities of absorbent. The reactivity of dolomite-dominated carbonate rocks was two to three times lower than that of a calcite-dominant rock. Reactivity of limestone also appears to be in part dependent on limestone constituents as revealed in thin section. The most reactive limestones are either oolitic or fossil-fragment (especially bryozoan) rocks. Small amounts of micrite or microcrystalline calcite matrix in coarse-grained limestone appears to enhance reactivity.

Task 2 – Evaluation of reactivity under FBC condition: Calcination and sulfation performances of 36 limestones and dolomites were examined using an atmospheric thermogravimetric analyzer (TGA) technique. Sulfation capacities were measured under a simulated flue gas atmosphere at 850°C for samples calcined under a 15%CO2-85%N2 atmosphere. Calcium utilization for calcites ranged from 11.6% to 64.8% for the 16x20 mesh particles. Sulfation reactivity generally increased with increasing MgO content of samples. SO2 capture capacities of samples tested ranged from 0.07 to 0.22 g SO2/g limestone or dolomite. Sulfation reactivity was the highest in highly absorbent, microcrystalline dolomite. These results indicate that for FBC applications, selection of the proper limestone or dolomite could reduce sorbent consumption and the amount of ash to be disposed of by a factor of about four.

Task 3 – Digital statewide map of limestone quarries: In this part of the project, a statewide map was produced showing the areal distribution of limestone and dolomite, the locations of active limestone and dolomite quarries and coal mines, existing coal-fired power plants, and road, rail and waterway systems. Only one quarry in central Illinois (Douglas County) extracts dolomite in substantial quantities. Dolomite is also extracted from a number of quarries near the Illinois border in the southeastern part of Missouri. The major dolomite-producing part of the state is, however, confined to the northern half of the state. Limestone occurs abundantly in the southern half of the state. It primarily includes thick formations of Mississippian age in the western and southern parts and relatively thin limestones of Pennsylvanian age in the central part. Mississippian limestones are also quarried near the borders of Indiana, Kentucky, and Missouri. High-calcium limestone, which has proven to be one of the best scrubber stones in FGD systems, is particularly abundant within the Mississippian units and is being mined from a number of quarries. In Ste. Genevieve, Missouri, two major lime plants use one of the Mississippian high-calcium limestones (Salem Limestone) for the manufacture of lime, another important raw material for scrubber systems. Ordovician limestones, some high-calcium, are quarried along the Mississippi River on the Missouri side.
OBJECTIVES

The main objectives of the project during the contract period were as follows:

1) Create a comprehensive digital database characterizing the limestone and dolomite resources primarily in southern Illinois and nearby counties of Indiana, Kentucky, and Missouri and identifying resources that are especially suited for use in FGD and FBC systems.

2) Prepare a digital statewide map and database showing the locations of active limestone and dolomite quarries, all coal-fired power plants, lime manufacturing plants, and major relevant infrastructure including roads, railways, waterways, barge loading facilities, and major towns.

The overall objective of the proposed project was to create, for the first time, a comprehensive database identifying and characterizing appropriate limestone and dolomite resources primarily for the southern Illinois region within economic transportation distances from existing and planned coal-fired power plants. The focus of this phase of the study was the southern Illinois region and the nearby counties of Indiana, Kentucky and Missouri. A pilot investigation involving the northern part of the state was also undertaken because of the abundant occurrences of dolomite in that region that may be well suited for use in FBC boilers. The project focused on the identification, description, characterization, and inventory of limestone and dolomite resources found to be especially suitable for the removal of sulfur oxides from flue gases of coal-fired power plants. Additionally, selected limestone and dolomite samples were tested under FBC and wet FGD conditions to evaluate carbonate reactivities in relationship to mineralogical, physical, and chemical properties. Using new data collected in the field and existing data already available at the ISGS, a map was prepared to show the regional distribution and general quality of limestone suitable for FGD and FBC units, and the locations of active limestone and dolomite quarries, lime manufacturing plants, all coal-fired power plants and major infrastructure. Active quarries were visited, rock units at selected quarries were described, and representative samples were taken from representative units. Lithologic sections were prepared for selected quarries and regional cross sections were constructed to show the lateral and vertical variability in limestone properties. The study also involved examination of outcrop sections and well cutting sand core samples archived at the ISGS to obtain information for areas where access to quarries was not possible or exposures at the quarries may not be accessible.
INTRODUCTION AND BACKGROUND

Introduction

U.S. environmental regulations make it imperative that any new coal-fired power plant be equipped with systems to reduce sulfur oxide emissions. This is because the Clean Air Act not only limits emissions at the plant level but also caps the total national sulfur emissions for the unlimited future. Limestone- and lime-based desulfurization technologies in coal-fired power plants are proven means of meeting the clean air standards. Illinois has abundant limestone resources (e.g., Krey and Lamar, 1925; Goodwin, 1983; Lasemi et al., 1999; Lasemi and Norby, 2002). However, the suitability of those limestones for flue-gas desulfurization (FGD) applications varies, and the most suitable high-purity limestone resources are probably not widely available (Goodwin and Baxter, 1981; Lasemi and Norby, 2001).

Recent studies have suggested that dolomite and dolomitic limestone are the most suitable for sulfur capture in FBC units, especially in pressurized fluidized-bed combustion (PFBC) (Rostam-Abadi et al., 1989). Dolomite and dolomitic limestone are abundant in Illinois but are near the surface mostly in the northern third of the state where they are generally quarried for construction aggregate. These dolomitic limestones and dolomites, like limestones, are variable in quality and physical properties. Because of expanding use of FBC technologies, demand for dolomite and dolomitic limestone may increase in the future. These dolomites need to be characterized with respect to their mineralogical and physical properties and their efficiency in capturing sulfur oxides. In addition, the location of minable resources with respect to coal-fired power plants needs to be determined.

The cost of transporting limestone by truck is so high that at 30 to 50 miles from the mine the price of the FGD-suitable limestone nearly doubles (Bhagwat, 2000). For Illinois coal to sustain its current market position it is necessary to ensure that the total cost to obtain electricity from Illinois coal is minimized. An essential part of the strategy to ensure that Illinois coal will remain in demand is, among other measures, to minimize the delivered cost of limestone. Geologic studies to find, analyze, and calculate the quantity of FGD- and FBC-suitable limestone and dolomite available near current and likely future utility sites are, therefore, integral to this strategy.

About one third of the nation’s coal-burning power plants that use flue-gas desulfurization units to remove SO\textsubscript{2} emissions are located in the six-state region of Illinois, Indiana, Kentucky, Ohio, Pennsylvania, and West Virginia (Foose and Barsotti, 1999). In 1989, only 29 of the more than 160 coal-fired electric power plants within this region used FGD units. By 1994, the number of FGD units had increased to 40. This trend toward increasing numbers of FGD units is expected to continue far into the future, especially with the implementation of Phase II of the Federal Clean Air Act, which began in 2000. The result has been an increased demand for high-purity limestone for removing gaseous sulfur oxides. Wet FGD systems also are capable of removing up to 60% of flue-gas mercury (Bhagwat and Ipe, 1998), which further highlights the importance of
characterizing the availability and chemical and physical properties of limestone.

Generally, for every 199 truckloads of coal (sulfur content of 3.5%) combusted, 10 truckloads of limestone are required to neutralize the emitted SO₂ (Foose and Barsotti, 1999). According to recent estimates, worldwide consumption of lime and limestone for FGD is forecast to exceed 40 million tons per year by 2010 (McIlvaine, 2002). In Illinois, government incentives for the use of Illinois coal have also accelerated plans for the development of new coal-fired power plants (Lasemi et al., 2003), which must be equipped with FGD units. Thus, the issues associated with limestone availability, transport, and suitability for use in FGD power plants need to be addressed. Nearby sources of suitable limestone raw material must be found to feed existing and new scrubber installations and to aid the selection of proper resources for desulfurization systems in the future.

**Background**

Previous studies carried out at the ISGS and elsewhere have shown that numerous factors affect the reactivity of limestone and dolomite during desulfurization (e.g., Borgwardt and Harvey, 1972; Harvey et al., 1974). These studies demonstrated that limestones with certain physical properties, such as softness, low abrasion resistance, high water absorption capacity, and low specific gravity generally had relatively high reactivity toward sulfur oxides. The softest, finest-grained limestones had significantly higher reactivity indices for SO₂ than hard but relatively fine crystalline limestone, even though the latter had the highest purity. Also, fine-grained, dense limestones appeared to be generally more reactive than coarse-grained, highly crystalline limestones.

Recent microscopic analyses (thin section petrography) of high-calcium limestones have revealed significant petrographic differences that affect the quality of lime produced from the stone (Lasemi, 1998, 1999, 2003). The results indicate that differences in the type and size of grains in the rocks and the amount and size of intergranular calcite cement or microcrystalline calcite matrix may also cause significant variations in the ability of a limestone to capture sulfur oxides from coal-burning power plants, as demonstrated by experimental studies (Borgwardt and Harvey, 1972; Harvey et al., 1974). Because of its demonstrated capability to identify significant differences between limestones, petrographic analysis was a principal technological tool for this project.

Certain compounds, such as magnesium carbonates, iron oxides, and other trace and major elements may increase or decrease the ability of limestone to capture sulfur oxides and remove other pollutants during the desulfurization process (Boynton, 1980, p. 122). Even small amounts of dolomite, clay minerals, and quartz diminish a stone’s usefulness for FGD scrubbing (Shaffer and Sadowski, 1999). In wet FGD systems, limestones with just 5-10% MgCO₃ appear to be significantly less reactive than purer limestones, and reactivity further suffers as the MgCO₃ content increases to the level of a dolomite at 35-42% MgCO₃. In addition, the use of limestone with high MgCO₃ content creates a disposal problem for magnesium sulfate, which is 150 times more soluble than calcium sulfate (Boynton, 1980, p. 123). Therefore, it was essential that the chemical and physical properties of limestones and dolomite be determined and their effects on desulfurization
efficiency be evaluated. Limestone and dolomite reactivity, which is primarily controlled by physical and chemical properties, also was determined for selected samples. Electric utilities depend on computer models for predicting FGD system efficiency, and geological data, such as reactivity values, are needed to determine which geologic units can provide stone suitable for the most efficient sulfur removal (Shaffer and Sadowski, 1999).

Dolomite and dolomitic limestone, on the other hand, appear to be more efficient in capturing sulfur oxides in FBC units, especially under pressurized FBC (PFBC) conditions (e.g., Rostam-Abadi et al., 1989), a conclusion also supported by the results of this study. Limestone is not usually considered as a sorbent for SO₂ capture for most PFBC systems because it does not calcine at partial pressures of CO₂ above 0.5 atmospheres at 850℃. Dolomite is preferred because it undergoes half-calcination readily at temperatures as low as 570℃ even at 10 atmospheres of CO₂ partial pressure via:

\[
\text{CaCO}_3\cdot\text{MgCO}_3 \rightarrow \text{CaCO}_3\cdot\text{MgO} + \text{CO}_2
\]

However, MgO does not react significantly with SO₂ and, depending on the FBC operating conditions, only small quantities of Mg₂Ca(SO₄)₄ or CaSO₄•3MgSO₄ are formed. The calcination of MgCO₃ generates extensive porosity in the dolomite particles and the CaCO₃ in them is able to react more efficiently with SO₂ (Lee and Georgakis, 1981).

**Limestone Resources**

Illinois is a major producer of crushed stone. In 2001, the latest year for which data are available, Illinois produced 86 million short tons of limestone and dolomite from 151 quarries (Lasemi et al., 2003). However, limestone resources are not distributed evenly around the state and transportation of stone is an important and costly issue for coal-fired power generating plants. Higher-quality (higher CaCO₃ content) limestone is even less available than lower-quality material. There is also a competition factor that influences limestone availability. Highly durable limestones are required for asphalt and concrete pavements and are thus relatively higher-valued commodities with high demand for state- and federally-funded road projects. However, these durable raw materials are commonly not reactive enough to be effective as scrubbing agents. The same quarries that produce high-quality road material also have layers composed of high-purity limestone that is too soft to be suitable for construction use. These softer raw materials must be mined but are discarded or are sold at a much lower price for use in agriculture or on low-duty roads. Because of their high reactivity, these soft raw materials can serve as excellent scrubbing agents in FGD units. These soft carbonates also have the advantage of being much less costly to pulverize than highly durable rocks. Thus, knowing the availability and distribution of limestones with the right characteristics for use in FGD systems makes economic sense.
ANALYTICAL AND EXPERIMENTAL PROCEDURES

Physical Properties

Data for specific gravity (weight of rock relative to an equal volume of water) and absorption (rough measure of pore space) were determined by immersing samples in water and comparing dry and wet weights. The ASTM method C127 – 88 for coarse aggregate was followed for these analyses.

Samples collected in the field were examined for petrographic analysis. More than 125 petrographic thin sections were prepared at a commercial laboratory. Thirty five of the 125 thin sections, which were subjected to reactivity measurement under FGD and FBC conditions, were examined in details under transmitted light microscope. The thin sections were point-counted for various skeletal (fossils) and non-skeletal grains, microcrystalline calcite and dolomite matrix, and intergranular cement. Approximately 300 grains, matrix, and cement were point-counted for each slide and the results were converted to weight percentages.

Chemical and Mineralogical Analysis

The non-carbonate portion of stone is not useful in removing SO₂. The acid insoluble residue was determined by dissolving approximately 25g of powdered sample in a 10% HCl solution. The sample was then washed twice with 500ml of de-ionized water, filtered, dried, and weighed. The final weight of the residue was then calculated and reported as a percentage of the original sample.

An automated X-ray diffractometer was used for mineralogical analysis. Samples were prepared using standard operating procedures (SOPs). 60-100g of sample were ground into a powder of <250µm with a Shatterbox. 4g of the sample were then milled down to <2µm with a McCrone Micronizing Mill. A SCINTAG x-ray diffractometer with a germanium detector and copper x-ray source was used to analyze the <2µm powder. Mineral concentrations were determined using methods developed by Hughes, et al. (1987).

Wavelength-dispersive X-ray fluorescence spectrometry (XRF) was used to determine the concentrations of major and minor elements in the samples. Elements that were determined include silicon (Si), aluminum (Al), iron (Fe), potassium (K), calcium (Ca), magnesium (Mg), sodium (Na), titanium (Ti), phosphorus (P), and manganese (Mn) and trace elements barium (Ba), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), rubidium (Rb), strontium (Sr), vanadium (V), zinc (Zn), and zirconium (Zr). This is a whole-rock analysis and the results will reflect the purity of limestone samples being examined.

Chemical analyses for trace elements in the carbonate fraction were performed using a Thermo Jarrell-Ash Model ICAP 61e inductively coupled plasma spectrometer (ICP) at the Illinois State Water Survey. The standard operating procedures followed by the ISGS Geochemistry Section were used to digest samples for this analysis. Over 30 cations are analyzed simultaneously. The elements determined include Al, As, B, Ba, Be, Ca, Cd,
Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sc, Se, Si, Sr, Te, Ti, Tl, V, and Zn. Instrument operation, inter-element interference correction, background correction, and data collection are controlled using ThermoSPEC/AE 6.20 software. Blanks, calibration check standards, and reference standards are run with each analysis set.

Limestone samples were analyzed for total mercury content by Cold Vapor Atomic Absorption Spectrometry (CVAAS) using a Perkin-Elmer FIMS-100 Flow-Injection Mercury Analyzer. Samples were prepared according to US EPA Method 245.5, “Determination of Mercury in Sediments by Cold Vapor Atomic Absorption Spectrometry”. In summary, the limestone sample is digested with aqua regia followed by potassium permanganate. The mercury in the digested sample is then reduced with stannous chloride and the mercury vapor is measured by cold vapor atomic absorption. Blanks, reference standards, and sample replicates (10%) were run with each analysis set.

Experimental Procedures

Measuring the reactivity of carbonates in wet FGD system — Limestone reactivity is generally determined by the speed at which the limestone dissolves in a solution. Factors such as the pH of the solution can affect reactivity (Radian International LLC, 1996). Sulfuric acid or hydrochloric acid can be used to measure the reactivity of the limestone instead of gaseous SO₂, as the reaction mechanism is comparable to that in a wet FGD systems equipped with air oxidation of sulfite (Shih et al., 2000; Ahlbeck et al., 1993, 1995). Recently, ASTM developed a standard test method for determination of total neutralizing capability and dissolved calcium and magnesium oxides in lime for flue-gas desulfurization (ASTM C:1318-95). This method also recommends an acid titration procedure.

Thirty six samples were analyzed in a lab-scale reactor to determine their dissolution rates or reactivities. For each limestone or dolomite sample, about 0.5kg of the sample (particle size of about 10 mm) was ground and sieved using a three-step procedure (Fig. 1). The sample from the step 3 was dried at 120°C in a vacuum oven for 24 hours sieved to sizes of >200, 200x250, 250x275, 275x325, <325 meshes. The 200x250 mesh size fraction was for reactivity tests. Several tests were also performed to determine the impact of particle size on the reactivity.

The reactivity of stones for wet FGD was determined by measuring the dissolution rate and the neutralizing capacity of the samples at acid conditions (ASTM, Designation: C 1318-95). The reactivity was measured in a batch reactor at constant pH using a pH-stat apparatus. As shown in Figure 2, the apparatus consists of an auto-titrator (Mettler DL21) for pH-stat titration, a pH electrode (Thermo Orion), a variable speed stirrer (Lightnin series 30), a water bath and a data logging system.
Figure 1. Procedure of absorbent sampling and grinding

Figure 2. Schematic of auto-titration experimental system

(1) Autotitrator, (2) HCl bottle, (3) pH probe wire, (4) HCl titrant line, (5) temperature compensation electrode wire, (6) stirrer, (7) reactor, (8) water bath
In a typical experiment, 2.5 g of a sample was first dissolved in 200 ml of de-ionized water. The slurry was then titrated with a solution of 1 M HCl. The pH value was automatically controlled at 6 (simulating the wet FGD operating acidity) by adding HCl solution as needed. The experimental temperature was kept at 50° C during the titration. The stirrer was controlled at 200 rpm. Little changes in dissolution rate occurred at higher rpms. Duration of each experimental was 60 minutes. The cumulative dissolution was determined directly from the total volume of HCl volume added during a reactivity test.

Reactivity of carbonates in Fluidized bed Combustion system — A thermogravimetric analyzer (TGA, RG 2000 Cahn) was used for atmospheric calcinations and sulfation tests (Fig. 3). In a typical test, about 40 mg of a sample (16x20) mesh was heated to 850° C at a heating rate of 20° C/min in 14 % CO₂ and balance N₂ (250 mL/min (STP)). The sample was maintained at 850° C for 80 minutes and then a simulated coal combustion flue gas containing 3000 ppm SO₂, 14 % CO₂, 5 % O₂, and balance N₂ (250 mL/min (STP) was admitted into the TGA 850° C for 90 minutes. At the end of this period the reaction was terminated by replacing the flue gas with pure nitrogen and cooling the sample to room temperature under the nitrogen purge.

Figure 3. Schematic of TGA Experimental System

The results from screening experiments revealed that the sample size and the gas flow rate employed in these experiments assured that sulfation experiments were performed under chemical reaction controlled conditions (as opposed to mass transfer limitations).

Limestone and dolomite samples were also calcined in 15% CO₂, balanced N₂ at 850° C using a LECO Proximate Analyzer (MAC-400). N₂-BET surface areas of these samples were measured using a Quantachrom (Monosorb) surface area analyzer. In addition, selected calcined and sulfated samples were examined by scanning electron microscopy (Hitachi S-4700) coupled with energy dispersive x-ray analyses, SEM-EDX (Oxford Instruments) at the University of Illinois’s Materials Research Laboratory.
RESULTS AND DISCUSSION

Task 1 — Southern Illinois Scrubber Limestone Resources

The Phase I of the project focused on limestone quality and availability in southern Illinois and the nearby counties of Indiana, Kentucky, and Missouri. The source of information for this phase of the project included 1) extensive ISGS files of field notes, GIS and analytical databases, maps and cross-sections, reports and journal articles, and archived samples and cores; 2) active limestone quarries in the area; and 3) extensive ISGS well records, particularly those for oil, coal, and mineral tests.

This study has compiled the first comprehensive database identifying and characterizing limestone and dolomite resources suited for use in FGD and FBC systems that are within economic transportation distances of existing and planned coal-fired power plants. The database contains relevant chemical, mineralogical and physical property data, and experimental results on reactivity measurements under FGD and FBC conditions. A GIS-based digital map atlas was created to show the distribution of limestone and dolomite resources, regional stratigraphic correlations, and all existing limestone and dolomite quarry locations. Representative geologic sections from representative quarries identify units that are the most suitable raw material for sulfur capture in scrubber systems. The information from this study is useful to the utility industry, limestone producers, and government agencies to facilitate acquisition of the best scrubbing agent for the FGD or FBC systems to be used at existing or planned coal-fired power plants.

Available limestone resources: Limestone quarries in the southern Illinois area and the nearby counties of Indiana, Kentucky, and Missouri were visited and detailed geological descriptions, including assessment of the general limestone quality for FGD and FBC applications, were made for representative quarries (Fig. 4; Appendix A, Table 1). Within each rock formation, units that are especially suitable as sources of scrubber stone were delineated. The ISGS’s sample and core library were also used for this study. More than 125 representative samples were analyzed for chemical, mineralogical, and physical properties, and for 36 selected samples, reactivities under FGD and FBC conditions were measured. The samples were collected on the basis of proximity to coal-fired electrical generating plants.

The samples utilized for this study were primarily collected from stock piles at each individual quarry or mine. The stock piles at quarries may represent specific benches, multiple benches, specific units or the entire quarry section. In a few cases, samples were collected from the quarry wall or from cores to provide more precise lithologic unit information. The standard procedure that was used to sample the individual stockpiles generally followed the Illinois DOT procedure that we refer to as the “three bucket sampling pad”. A quarry loader would obtain three buckets of crushed stone from three different areas of the stock pile and place them into one pile and then spread the pile out into a flat pad. A small shovel was used to randomly sample several different areas of the pad to obtain approximately a 20-pound sample. This would be our stock sample for all subsequent tests. In most cases CA-11 (1" to 1/8") was the preferred material size.
Figure 4. Limestone and dolomite extraction sites, sampled locations, and other mines and industrial plants.
although CA10 (1" to 0"), CA7 (1.5" to 1/8"), Ag lime and other sizes were occasional collected. In a few cases, where it was not feasible to lay out a standard sampling pad, a steel tube (3 inches in diameter x 40 inches long) was driven into the pile at several intervals and heights to obtain a random sample of about 20 pounds. In other cases, samples were hand collected from the quarry walls from specific intervals or benches. Each sample would be labeled with a field number and data as to size, when sampled, etc. The samples were split in the lab for various analysis following standard operation procedures and ASTM methods. The flowchart in Appendix B illustrates the laboratory approach to splitting samples for various analyses.

B – Limestone distribution and quality: The information from task 1A along with available published and unpublished information at the ISGS was utilized to prepare a generalized, GIS-based geologic map showing the distribution of limestone in southern Illinois and nearby regions (See discussion under task 3 for details). Limestone and dolomite resources of various ages are primarily concentrated in the northern, western, and southern parts of the state (e.g., Krey and Lamar, 1925; Goodwin, 1983; Goodwin and Baxter, 1981; Mikulic, 1990). Limited amounts of limestone occur in the central part of the state, where they are sporadically present near the surface and mined at several locations (Fig. 5). Units of the Ordovician and Silurian systems are the sources of carbonates in northern Illinois, especially the Chicago area, where dolomites are quarried. Much of this hard, dense material is used as construction aggregate, and these deposits are probably not suitable as scrubbing agents in wet FGD systems due to their high content of magnesium carbonate and the much lower reactivity of dolomite (Boyton, 1980, p. 123; Shaffer and Sadowski, 1999, and this study). In the western and southern parts of the state and in nearby counties of Indiana, Kentucky and Missouri, limestones in the Mississippian System are actively exploited for construction aggregates, lime manufacture, and other chemical purposes (e.g., Baxter, 1965; Lamar, 1959; Lasemi and Norby, 2001, 2002; Lasemi et al., 1999). Ordovician carbonates, both limestone and dolomite, commonly occur in Missouri within 50 miles from the Illinois Border. Some of these carbonates, especially the Kimmswick Limestone, are high-calcium limestones that are quarried in several areas in Missouri near the Illinois border. The Kimmswick Limestone also was mined in Monroe County, Illinois, near the village of Valmeyer until the mine closed in the 1980s.

C – Chemical, mineralogical, and physical properties: Previous research by ISGS scientists and others have demonstrated the strong correlation between various chemical, mineralogical, and physical properties and efficiency of limestone in wet FGD systems. Coal-fired power plants rely on computer models for selecting the parameters that determine the quantity and efficiency of the scrubbing agent added. To be effective, these models require geological data such as chemical and physical properties and reactivity indices. Because of the importance of these data, 125 samples collected under task 1A and task 2 were characterized chemically (major, minor and trace element constituents); mineralogically (calcite, dolomite, clay minerals, quartz, etc.); and petrographically (e.g., grain size, crystal size, porosity, interparticle cement). Physical properties such as grindability, bulk specific gravity, and water absorption were also determined.
Mostly Ordovician Dolomite with some Silurian Dolomite.

Mostly Silurian Dolomite with some Ordovician Dolomite.

Mostly Upper Mississippian Limestone.

Mostly Devonian cherty limestone.

Mostly thin Pennsylvanian Limestone.

Mostly thicker Pennsylvanian Limestone.

Figure 5. Limestone and dolomite resource map.
Analytical results are given in Appendix A, Tables 2-6. Previous studies have shown that several properties of limestone, such as its chemical composition, surface area, mineral matrix characteristics, and particle size distribution, may influence its reactivity (e.g., Borgwardt and Harvey, 1972; Harvey et al., 1974). Therefore, the physical and mineralogical data given in Appendix A, Tables 2-6 will be useful for the power plant industry in selecting the best stone for a particular scrubber system. A summary of the results of physical, mineralogical, and chemical properties are give below.

Specific gravity ranges from 1.9 to 2.8 and absorption percentages ranges from 0.6% to 16.6%. As expected, there is a strong negative correlation between specific gravity and absorption. Samples with the highest absorption are mainly microcrystalline dolomites and clay-rich limestones. Coarse grained fossiliferous and oolitic limestones also have relatively high absorption values. Microcrystalline limestones (very finely crystalline limestone) have the lowest absorption values.

Grindability is a measure of the limestone hardness. Hard stones have lower values than softer, more easily ground stones. Grindability is a measure of energy needed to reduce stone to particle sizes useful in wet FGD system. The method for measuring grindability is outlined in Appendix C. Very hard stone requires excessive energy to grind. Grindability values ranges from 7.67 to 38.62. Microcrystalline dolomites, clay-rich limestones, oolitic and coarsely fossiliferous limestones have higher grindability values, whereas microcrystalline limestones, cherty limestones, and coarsely crystalline dolomites have lower grindability values. There is a slight positive correlation between grindability and absorption.

Carbonate rocks are quite varied petrographically and this variation can have a significant influence on their reactivity with respect to sulfur capture. Petrographically, limestones examined during this study range from coarse-grained limestone to microcrystalline calcite or micrites. Coarse-grained limestones are typically rich in sparry calcite cement that binds the grains together. Some limestones are composed of a mixture of coarse-grained material and microcrystalline calcite matrix. The proportion of grains and matrix in these limestones varies from grain dominated to matrix dominated. The grains typically consist of remains of calcareous organisms such as bryozoans and echinoderms. Some limestones are oolitic that consist of rounded grains with concentric bandings, whereas others may be peloidal consisting of rounded grains composed of microcrystalline calcite.

Dolomites or dolostone predominantly consist of the mineral dolomite. The majority of dolomites formed from an originally limestone precursor. Most of the grains in the original limestone have been destroyed beyond recognition. Dolomites can be grouped in three major categories: 1) coarsely crystalline dolomite, 2) microcrystalline dolomite, and 3) dolomitic limestones, a mixture of calcite and dolomite. All three types of dolomite occur in variable quantities. They are rare in the southern half of the state but abundant in the northern half. For the areas studied under this project, dolomite and dolomitic limestone are found in large quantities only in southeastern Missouri.
Acid insoluble residue ranges from less than 0.4% to 58%, mostly between 0.4% and 22.35%. Very high values (up to 58%) come from clay-or quartz-bearing samples. Quartz occurs as detrital silica grains or commonly as chert. Some Pennsylvanian limestones (e.g., Omega Limestone) are rich in clay and silt-size quartz grains. The Mississippian Burlington Limestone, Fort Payne Formation, lower part of the Ullin Limestone and parts of the St. Louis Limestone are cherty. Residues in pure limestones and dolomites ranged between less than 1% and 3%.

In addition to visual examination samples were also analyzed by X-ray diffraction to determine mineralogy (Appendix A, Table 2). The dominant mineral in the samples analyzed from the southern half of the state is calcite. Dolomite is the dominant mineralogy in samples from several quarries in northeastern Illinois and from a quarry in Douglas County and an abandoned quarry in Jersey County. Dolomitic limestones contain mixtures of calcite and dolomite and were found in samples from the Silurian carbonates in Iroquois County and Ordovician carbonates in Missouri north of St. Louis. Other major minerals include quartz and in some samples clays. Quartz primarily occurs as chert and in some sample as detrital silt and sand-sized quartz grains. Other minor non-carbonate minerals include pyrite and feldspars. Calcium carbonate content ranges from 33% to 97%, mostly better than 80%. The majority of the samples with low CaCO₃ values are dolomitic or dolomite. A few of the low calcium limestones are clay or quartz rich as indicated by the acid insoluble content.

Chemical analyses are reported in Appendix A, Tables 3 and 4. Major and minor elements were determined by X-ray fluorescence spectrometry and reported as oxides. This is a whole rock analysis and includes trace and major elements derived from both acid soluble and insoluble fractions. As shown in Figure 6, there is a strong negative correlation between the amount of MgO and CaO and between the percentages of dolomite and calcite, suggesting the source of Mg is primarily from dolomite in the samples. This is supported by a strong positive correlation between dolomite Mg values derived from the acid soluble fraction. The data also show that the majority of the samples in the southern part of the state are of high purity limestones. A few samples are rich in silica primarily derived from cherts in some rock formations. Only two samples from a quarry in Shelby County are highly impure with CaCO₃ only in 33% to 38% range. This limestone is quite argillaceous and contains abundant silt-sized quartz grains.

All samples were analyzed for trace and major elements in the acid soluble fraction. More than 30 elements were analyzed and reported in Appendix A, Table 4. The influence of these elements except for Mg on limestone reactivity is not clear at this time. More reactivity data is needed to determine whether any correlation exists between elemental concentrations and reactivity. Mercury concentration was also measured in 36 samples. The concentration of mercury in most of the samples analyzed is quite low, ranging between 2 to 8 parts per billion.
Figure 6. Relationship between calcite & dolomite (top left), CaO & MgO (top right) and Dolomite and Mg (bottom left).

D – Reactivity of limestone and dolomite for use in wet FGD systems: Reactivity of 36 limestone and dolomite samples collected under task 1A and 2 were tested in a lab-scale reactor (Fig. 2). For this test, an acid titration technique was employed to investigate the dissolution performance of limestone and dolomite rocks as an indicator of reactivity for the wet FGD systems. The goal of this study was to measure and compare the dissolution characteristics for Illinois limestone and dolomite samples with different geological origins and properties.

In a water medium, limestone and dolomite dissolve very slowly according to:
\[
\text{CaCO}_3 \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-} \quad (1)
\]
\[
\text{MgCO}_3 \leftrightarrow \text{Mg}^{2+} + \text{CO}_3^{2-} \quad (2)
\]

However, if a strong acid such as HCl is added, the acid completely dissociates to form hydrogen ions. Hydrogen ions react with carbonate ions generated in reactions (1) an (2), and thus more absorbent dissolves. The reactions involved in this procedure are listed as follows,
\[
\text{CO}_3^{2-} + \text{H}^+ \leftrightarrow \text{HCO}_3^- \quad (3)
\]
\[
\text{HCO}_3^- + \text{H}^+ \leftrightarrow \text{CO}_2(\text{aq}) + \text{H}_2\text{O} \quad (4)
\]
\[
\text{CO}_2(\text{aq}) \leftrightarrow \text{CO}_2(\text{g}) \quad (5)
\]

These reactions involve the diffusions of ions H\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), OH\(^-\), CO\(_3\)\(^{2-}\), HCO\(_3\)\(^-\), CO\(_2\)\(^{\text{aq}}\) within a liquid film surrounding a particle. The film theory can be used to describe the complete mass transfer reactions.
The overall reactions of limestone and dolomite are:

\[ \text{CaCO}_3 + 2\text{HCl} \leftrightarrow \text{CaCl}_2 + \text{CO}_2 + \text{H}_2\text{O} \quad (6) \]
\[ \text{MgCO}_3 + 2\text{HCl} \leftrightarrow \text{MgCl}_2 + \text{CO}_2 + \text{H}_2\text{O} \quad (7) \]

Using the film theory, it can be shown that an average molar conversion rate of the carbonate, i.e., the fraction of dissolution over the titration period can be expressed as follows:

\[
\text{Conversion rate} = \frac{C_{\text{HCl}} \Delta V}{2 \Delta t} \frac{1}{W_0 \left( X_{\text{CaO}} / 56 + X_{\text{MgO}} / 40 \right)}
\]

where \( W_0 \) is the initial weight of absorbent in slurry; \( X_{\text{CaO}} \) and \( X_{\text{MgO}} \) are the CaO and MgO contents of absorbent, \( V \) is volume of HCl, and \( t \) is time, respectively.

A typical titration data curve is displayed in Figure 7. Initially, the addition of HCl acid dramatically decreased the pH of the starting slurry (pH=10-12). With addition of controlled amount of HCl, the pH stabilized at about 6 during the remaining test period. The titration curves show a parabolic shape for both samples shown in Figure 7. The curve gradually leveled off for the sample TRQ-3, but not for sample CVDLQ-1 because the ion strength was less accumulated for this sample.

Figure 7. Typical titration curve of limestone slurry

Figure 8 shows the effects of pH on the dissolution fraction for two limestone samples. As shown in reactions (3) and (4), \( \text{H}^+ \) ion plays an important role in the dissolution of limestone. \( \text{H}^+ \) concentration increases by 10 times when pH increase changes from 6 to 5. However, due to mass transfer limitations, the increase of dissolution rate was only 2-3.
The size of particles directly determines the area of external surface, which impacts the mass transfer flux of ions and the availability of reaction surfaces for non-porous particles. As expected, the dissolution rate increased with decreasing particle size as shown in Figure 9.

The particle size commonly used in most wet FGD plants is reported about 90 %w through the 200 mesh. Accordingly, a particle size of 200x250 mesh was employed for
all reactivity measurement tests.

Table 1 summarizes the data for the samples tested. The dissolution fraction, a measure of reactivity, is defined as the molar conversion rate of calcium and magnesium carbonates as an indicator for the absorbent reactivity for the wet FGD. Meanwhile, the acid neutralization capacity, defined as the molar H\(^+\) adsorption per mass of absorbent, was also estimated for each sample.

The dissolution fractions for 36 tested samples ranged from 6% to 30%, while the acid neutralization capacity of absorbent ranged from 1 to about 6 mol H\(^+\)/kg absorbent.

The dissolution fraction generally increased with increasing CaO and calcite contents and decreasing MgO and dolomite contents (Fig. 10). The reactivity of a dolomite-dominant carbonate rocks were two to three times lower than that of a calcite-dominant rock. The chemical property data were also correlated with the acid neutralization capacity of absorbents. The trends observed were similar to those in Figure 10. The morphologies of select samples were examined with SEM and the results are shown in Appendix D.

Figure 10. Correlation of dissolution fraction with sorbent properties
<table>
<thead>
<tr>
<th>Sample</th>
<th>Added volume of acid (ml)</th>
<th>Initial pH value of slurry</th>
<th>Dissolution fraction (%)</th>
<th>Acid neutralization capacity (mol H⁺/kg absorbent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANNQ-2</td>
<td>4.825</td>
<td>11.356</td>
<td>10.27%</td>
<td>1.93</td>
</tr>
<tr>
<td>ASHQ-1</td>
<td>9.1347</td>
<td>9.442</td>
<td>21.67%</td>
<td>3.65</td>
</tr>
<tr>
<td>BCM-1</td>
<td>5.6099</td>
<td>10.812</td>
<td>11.82%</td>
<td>2.24</td>
</tr>
<tr>
<td>BRCR-1</td>
<td>3.46</td>
<td>10.682</td>
<td>15.21%</td>
<td>1.38</td>
</tr>
<tr>
<td>BRQ-1</td>
<td>14.44</td>
<td>10.296</td>
<td>29.91%</td>
<td>5.78</td>
</tr>
<tr>
<td>CASEY-1</td>
<td>10.13</td>
<td>10.973</td>
<td>21.49%</td>
<td>4.05</td>
</tr>
<tr>
<td>CHAR-1</td>
<td>9.3747</td>
<td>11.744</td>
<td>19.69%</td>
<td>3.75</td>
</tr>
<tr>
<td>CIRQ-2</td>
<td>6.5449</td>
<td>11.28</td>
<td>14.04%</td>
<td>2.62</td>
</tr>
<tr>
<td>CIRQ-5</td>
<td>8.3998</td>
<td>10.527</td>
<td>19.78%</td>
<td>3.36</td>
</tr>
<tr>
<td>CRC-2</td>
<td>5.1299</td>
<td>11.135</td>
<td>10.84%</td>
<td>2.05</td>
</tr>
<tr>
<td>CSQ-1</td>
<td>7.7898</td>
<td>10.536</td>
<td>16.65%</td>
<td>3.12</td>
</tr>
<tr>
<td>CSQ-4</td>
<td>6.6299</td>
<td>11.563</td>
<td>13.93%</td>
<td>2.65</td>
</tr>
<tr>
<td>CVDLQ-1</td>
<td>6.2899</td>
<td>10.912</td>
<td>13.08%</td>
<td>2.52</td>
</tr>
<tr>
<td>CYQ-2</td>
<td>11.615</td>
<td>10.87</td>
<td>24.05%</td>
<td>4.65</td>
</tr>
<tr>
<td>DGCC-1</td>
<td>2.885</td>
<td>12.089</td>
<td>6.21%</td>
<td>1.15</td>
</tr>
<tr>
<td>DGCC-2</td>
<td>5.8149</td>
<td>10.959</td>
<td>11.72%</td>
<td>2.33</td>
</tr>
<tr>
<td>FRMTQ-2</td>
<td>5.9199</td>
<td>11.02</td>
<td>12.39%</td>
<td>2.37</td>
</tr>
<tr>
<td>GSPTQ-2</td>
<td>5.0899</td>
<td>10.816</td>
<td>10.58%</td>
<td>2.04</td>
</tr>
<tr>
<td>HASM-4</td>
<td>5.9949</td>
<td>11.775</td>
<td>12.98%</td>
<td>2.40</td>
</tr>
<tr>
<td>HTN-1</td>
<td>4.21</td>
<td>9.671</td>
<td>8.63%</td>
<td>1.68</td>
</tr>
<tr>
<td>JQ-2</td>
<td>10.115</td>
<td>10.883</td>
<td>20.91%</td>
<td>4.05</td>
</tr>
<tr>
<td>KASM-2</td>
<td>5.2149</td>
<td>11.043</td>
<td>10.86%</td>
<td>2.09</td>
</tr>
<tr>
<td>KIM-1</td>
<td>11.585</td>
<td>10.291</td>
<td>24.01%</td>
<td>4.63</td>
</tr>
<tr>
<td>KLRQ-1</td>
<td>3.54</td>
<td>10.71</td>
<td>7.58%</td>
<td>1.42</td>
</tr>
<tr>
<td>KNQ-2</td>
<td>4.5299</td>
<td>10.773</td>
<td>10.30%</td>
<td>1.81</td>
</tr>
<tr>
<td>NKMS-2</td>
<td>4.77</td>
<td>11.159</td>
<td>10.07%</td>
<td>1.91</td>
</tr>
<tr>
<td>ONLQ-1</td>
<td>7.3348</td>
<td>10.744</td>
<td>15.62%</td>
<td>2.93</td>
</tr>
<tr>
<td>PTNMQ-2</td>
<td>6.6649</td>
<td>11.599</td>
<td>13.84%</td>
<td>2.67</td>
</tr>
<tr>
<td>QNC-2</td>
<td>4.9149</td>
<td>10.827</td>
<td>10.13%</td>
<td>1.97</td>
</tr>
<tr>
<td>RDQ-1</td>
<td>7.9748</td>
<td>11.001</td>
<td>16.61%</td>
<td>3.19</td>
</tr>
<tr>
<td>SYCQ-1</td>
<td>3.975</td>
<td>10.748</td>
<td>7.84%</td>
<td>1.59</td>
</tr>
<tr>
<td>TRQ-3</td>
<td>15.445</td>
<td>10.56</td>
<td>31.80%</td>
<td>6.18</td>
</tr>
<tr>
<td>TRQ-4</td>
<td>9.6697</td>
<td>10.974</td>
<td>19.90%</td>
<td>3.87</td>
</tr>
<tr>
<td>TUSQ-1</td>
<td>7.0699</td>
<td>11.807</td>
<td>13.41%</td>
<td>2.83</td>
</tr>
<tr>
<td>TUSQ-5</td>
<td>6.5049</td>
<td>11.515</td>
<td>13.59%</td>
<td>2.60</td>
</tr>
<tr>
<td>UQ-1</td>
<td>11.08</td>
<td>11.538</td>
<td>23.14%</td>
<td>4.43</td>
</tr>
</tbody>
</table>

Reactivity of limestones is quite variable even among those that are high purity materials. Among limestones with low MgO content, reactivity appears to correlate with petrographic characteristics. Microcrystalline limestone or micritic limestones have much lower reactivity. This is because these limestones contain tightly cemented, interlocking calcite crystals with very little porosity. The most reactive limestones are oolitic limestone, limestone with abundant bryozoans, and coarse-grained limestones with some
microcrystalline matrix. High reactivity in bryozoan-rich samples is due to the abundance of small pores in the skeletal structure. The reason for the high reactivity in oolitic limestones and samples with a mixture of grains (oooid or fossil fragments) and matrix is not clear at this time. More research, especially at the electron microscope level is needed.

Many limestone units in the study area can provide excellent raw material for wet FGD systems. These include the oolitic and fossiliferous limestone of the Salem Limestone, oolitic units within the Ste. Genevieve Limestone, and bryozoan-rich units within the Ullin Limestone. Some of the Pennsylvanian limestones in central Illinois that contain a mixture of coarse material (fossil fragments) and micritic limestone matrix are also excellent raw material for FGD systems. This study shows that petrographic properties appear to have a strong influence on limestone reactivity. More work is needed to better constrain the exact nature of the relationship between petrography and reactivity.

**Task 2 – Inventory and Characterization of Dolomite and Dolomitic Limestone Resources for FBC Units**

The source of information for this task is similar to that described under task 1. In task 2, the regional distribution of dolomite and dolomitic limestone resources in the southern part of the state and nearby regions were mapped (Fig. 5); locations of active quarries with substantial resources of dolomite or dolomitic limestone were identified; and the chemical, mineralogical, and physical properties of selected dolomite and dolomitic limestones were determined (Appendix A). The northern half of the state was not studied in detail and the results presented here for that part of the state is preliminary.

Major dolomite and dolomitic limestone units occur in three areas. In Douglas County, central Illinois, one quarry extracts dolomite of variable quality from the Silurian and Devonian rocks (Fig. 4). Silurian dolomite also occurs in parts of Jersey and Calhoun Counties in western Illinois (Fig. 5). There is, however, very little potential for quarry operation in this region in the near future, although the possibility of potentially mining these resources underground is being explored. Southeastern Missouri is the only major dolomite-bearing region in the vicinity of the study area. This area contains a significant quantity of Ordovician-age dolomite that is being currently mined in a number of quarries. Many of these quarries are within 50 miles from the Illinois border and thus lie within a reasonable transportation distance (Fig. 4). Dolomite is also the major rock unit that is quarried or mined in the northern half of the state. Only a limited number of quarries were sampled from this area. Characterization of these dolomites will be the focus of the next phase of the project to be funded by ICCI and will begin September 1, 2004.

Evaluation of desulfurization reactivity of Illinois carbonate rocks for use in Fluidized-Bed Combustion: In task 2, thirty six representative limestone, dolomite, and dolomitic limestone samples that were collected under task 1 and task 2 were subjected to calcination and sulfation experiments. The purpose of this task was to evaluate calcination and sulfation reactivities under simulated FBC conditions. The starting
samples for this experiment were the same as those used for reactivity measurements under FGD conditions described above.

A thermogravimetric analyzer (TGA, RG 2000 Cahn, Fig. 3) was used for atmospheric calcinations and sulfation tests. A typical TGA data is shown in Figure 11. During the calcinations stage, the sample decomposed according to the following reactions:

Limestone: \( \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \)
Dolomite: \( \text{CaCO}_3 \cdot \text{MgCO}_3 \rightarrow \text{CaO} \cdot \text{MgO} + 2\text{CO}_2 \)

![Figure 11. Typical TGA data curve (sample: ASHQ-1)](image)

During the sulfation stage, SO\(_2\) reacted with the calcined sorbent to form calcium sulfate:

\( \text{CaO} + \frac{1}{2} \text{O}_2 + \text{SO}_2 \rightarrow \text{CaSO}_4 \)
\( \text{CaO-MgO} + \frac{1}{2} \text{O}_2 + \text{SO}_2 \rightarrow \text{CaSO}_4 \cdot \text{MgO} \)

Magnesium does not react with SO\(_2\) under the experimental conditions employed. For both the limestone and dolomite, the calcium utilization for SO\(_2\) removal was calculated as follows:

\[
\text{Calcium utilization (\%) = } \left( \frac{W_f - W_0}{80 \text{ g/mol} \times 56 \text{ g/mol}} \right) \times 100
\]
Where, \( W_t \) = Weight of sample after 90 minutes sulfation; \( W_0 \) = Weight of sample after 80 minutes calcination; \( W_i \) = Initial weight of sample for the TGA test; \( 56 \) = molecular weight of \( \text{CaO} \); \( 80 \) = molecular weight of \( \text{SO}_3 \); \( C_{\text{CaO}} \) = \( \text{CaO} \) content in the raw limestone or dolomite.

The theoretical weight loss during the calcinations of pure limestone and dolomite are 44 wt % and 47.8 wt %, respectively. The theoretical weight loss based on the chemical analysis data and the actual weight loss measured during the calcination experiments in the TGA are presented in Table 2. For all samples, the theoretical and actual weight loss generally agreed within 5 wt %.

The surface areas of calcined samples ranged from 0.2 to 2 m\(^2\)/g and generally increased with increasing MgO content. The presence of MgO in carbonate rocks is known to increase the porosity in the calcined sample.

The results of the sulfation tests are also presented in Table 2 and Figure 12. SEM images and EDX data on reacted and original sample are given in Appendix E. The \( \text{SO}_2 \) saturation capacities (sulfation capacities) are presented in three ways: molar percent conversion of \( \text{CaO} \) to \( \text{CaSO}_4 \) (calcium utilization); mass of \( \text{SO}_2 \) reacted per mass of raw limestone/dolomite; and mass of \( \text{SO}_2 \) reacted per mass of calcined sample. The calcium utilization indicates the chemical reactivity of the limestone and dolomite, while the latter two are indicators of the relative sorbent utilization based on the chemical and physical properties of the sample. The calcium utilizations varied from 11.6% to 64.8%. However, on a mass basis, \( \text{SO}_2 \) capture capacities varied only by a factor of three (from 0.07 to 0.22 g \( \text{SO}_2 \)/g raw sorbent).

A general trend of increasing calcium utilization with increasing MgO content (\( R = \) correlation coefficient = 0.52) and decreasing \( \text{CaO} \) content (\( R = 0.63 \)) in the raw sorbents was observed (Figs. 12a and b). The presence of Mg in the sample resulted in a more porous structure in the calcined stone, thus enhancing the sulfation capacity. Figure 13c shows that calcium utilizations of dolomite samples (based on the XRD analysis) were two to three times higher than those of the limestone samples. Correlations of the sulfation capacity data with MgO and \( \text{CaO} \) contents of stones showed similar trends observed for calcium utilization data (Figs.15a and b). However, the dependence of the \( \text{SO}_2 \) capacity on \( \text{CaO} \) and MgO content were weaker than those observed for calcium utilization data.

Efforts were made to correlate calcium utilization data with other chemical and physical properties. A weak correlation between calcium utilization and the grindability index of sorbent was observed (Fig. 14). Attempts to correlate the data with other properties (surface area, elements in chemical analysis data) were not successful.

Although dolomites appear to be better sorbents for FBC systems, calcium utilization and \( \text{SO}_2 \) capacity are quite variable among dolomites studied. The variation in the amount of calcium utilization and \( \text{SO}_2 \) capacity appears to be inversely correlated with crystal size (measured in thin section) and water absorption. Preliminary results show that
Microcrystalline and absorbent dolomites have the highest calcium utilization and SO2 capacity than coarsely crystalline dolomites with low absorption.

Table 2. Calcination performance of limestone samples with a particle size of 16x20 mesh

<table>
<thead>
<tr>
<th>No.</th>
<th>Limestone</th>
<th>Weight loss (%)</th>
<th>Surface area of calcined stone (m²/g)</th>
<th>Ca utilization (%)</th>
<th>g SO2 reacted / g raw sorbent</th>
<th>g SO2 reacted / g calcined sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ANNQ-2</td>
<td>44.0%</td>
<td>8.412</td>
<td>20.96%</td>
<td>0.1200</td>
<td>0.2141</td>
</tr>
<tr>
<td>2</td>
<td>ASHQ-1</td>
<td>38.6%</td>
<td>5.667</td>
<td>44.39%</td>
<td>0.1760</td>
<td>0.2865</td>
</tr>
<tr>
<td>3</td>
<td>BCM-1</td>
<td>42.6%</td>
<td>7.058</td>
<td>17.10%</td>
<td>0.0942</td>
<td>0.1641</td>
</tr>
<tr>
<td>4</td>
<td>BCR-1**</td>
<td>26.6%</td>
<td>6.049</td>
<td>45.88%</td>
<td>0.1099</td>
<td>0.1497</td>
</tr>
<tr>
<td>5</td>
<td>BRQ-1</td>
<td>43.7%</td>
<td>7.255</td>
<td>20.55%</td>
<td>0.1171</td>
<td>0.2082</td>
</tr>
<tr>
<td>6</td>
<td>CASEY-1</td>
<td>42.6%</td>
<td>9.014</td>
<td>16.49%</td>
<td>0.0940</td>
<td>0.1637</td>
</tr>
<tr>
<td>7</td>
<td>CHAR-1</td>
<td>42.0%</td>
<td>5.565</td>
<td>20.87%</td>
<td>0.1241</td>
<td>0.2139</td>
</tr>
<tr>
<td>8</td>
<td>CIRQ-2</td>
<td>42.1%</td>
<td>3.750</td>
<td>20.15%</td>
<td>0.1166</td>
<td>0.2014</td>
</tr>
<tr>
<td>9</td>
<td>CIRQ-5</td>
<td>40.8%</td>
<td>3.331</td>
<td>21.96%</td>
<td>0.1050</td>
<td>0.1774</td>
</tr>
<tr>
<td>10</td>
<td>CRC-2</td>
<td>42.4%</td>
<td>6.127</td>
<td>31.49%</td>
<td>0.1842</td>
<td>0.3198</td>
</tr>
<tr>
<td>11</td>
<td>CSQ-1</td>
<td>43.5%</td>
<td>4.047</td>
<td>21.14%</td>
<td>0.1170</td>
<td>0.2071</td>
</tr>
<tr>
<td>12</td>
<td>CSQ-4</td>
<td>43.5%</td>
<td>8.217</td>
<td>16.13%</td>
<td>0.0957</td>
<td>0.1694</td>
</tr>
<tr>
<td>13</td>
<td>CUDLQ-1</td>
<td>42.4%</td>
<td>7.930</td>
<td>17.08%</td>
<td>0.0954</td>
<td>0.1655</td>
</tr>
<tr>
<td>14</td>
<td>CYQ-2</td>
<td>44.2%</td>
<td>8.370</td>
<td>19.74%</td>
<td>0.1177</td>
<td>0.2109</td>
</tr>
<tr>
<td>15</td>
<td>DGCC-1</td>
<td>41.1%</td>
<td>9.817</td>
<td>58.24%</td>
<td>0.1938</td>
<td>0.3290</td>
</tr>
<tr>
<td>16</td>
<td>DGCC-2</td>
<td>44.9%</td>
<td>10.300</td>
<td>60.42%</td>
<td>0.2204</td>
<td>0.3997</td>
</tr>
<tr>
<td>17</td>
<td>FRMTQ-2</td>
<td>43.2%</td>
<td>5.963</td>
<td>19.19%</td>
<td>0.1157</td>
<td>0.2037</td>
</tr>
<tr>
<td>18</td>
<td>GSPTQ-2</td>
<td>44.0%</td>
<td>11.020</td>
<td>32.12%</td>
<td>0.1946</td>
<td>0.3478</td>
</tr>
<tr>
<td>19</td>
<td>HASM-4</td>
<td>42.0%</td>
<td>5.858</td>
<td>25.24%</td>
<td>0.1249</td>
<td>0.2154</td>
</tr>
<tr>
<td>20</td>
<td>HTN-1</td>
<td>44.5%</td>
<td>7.110</td>
<td>24.31%</td>
<td>0.1338</td>
<td>0.2411</td>
</tr>
<tr>
<td>21</td>
<td>JQ-2*</td>
<td>NA</td>
<td>4.327</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>22</td>
<td>KASM-2</td>
<td>44.0%</td>
<td>8.938</td>
<td>13.90%</td>
<td>0.0835</td>
<td>0.1492</td>
</tr>
<tr>
<td>23</td>
<td>KIM-1*</td>
<td>NA</td>
<td>3.707</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>24</td>
<td>KLRQ-1</td>
<td>35.4%</td>
<td>10.128</td>
<td>64.80%</td>
<td>0.2089</td>
<td>0.3655</td>
</tr>
<tr>
<td>25</td>
<td>KMQ-2</td>
<td>39.0%</td>
<td>6.889</td>
<td>17.69%</td>
<td>0.0761</td>
<td>0.1178</td>
</tr>
<tr>
<td>26</td>
<td>NKMS-2</td>
<td>42.9%</td>
<td>8.557</td>
<td>12.43%</td>
<td>0.0736</td>
<td>0.1289</td>
</tr>
<tr>
<td>27</td>
<td>ONLQ-1**</td>
<td>42.4%</td>
<td>7.497</td>
<td>21.56%</td>
<td>0.1278</td>
<td>0.2217</td>
</tr>
<tr>
<td>28</td>
<td>PTNMQ-2</td>
<td>44.1%</td>
<td>7.617</td>
<td>12.95%</td>
<td>0.0786</td>
<td>0.1406</td>
</tr>
<tr>
<td>29</td>
<td>QNC-2</td>
<td>42.8%</td>
<td>4.019</td>
<td>22.23%</td>
<td>0.1363</td>
<td>0.2382</td>
</tr>
<tr>
<td>30</td>
<td>RDQ-1</td>
<td>44.6%</td>
<td>9.859</td>
<td>18.86%</td>
<td>0.1096</td>
<td>0.1977</td>
</tr>
<tr>
<td>31</td>
<td>SYCQ1</td>
<td>47.2%</td>
<td>12.055</td>
<td>28.15%</td>
<td>0.1008</td>
<td>0.1908</td>
</tr>
<tr>
<td>32</td>
<td>TRO-3</td>
<td>44.1%</td>
<td>11.027</td>
<td>11.61%</td>
<td>0.0704</td>
<td>0.1260</td>
</tr>
<tr>
<td>33</td>
<td>TRO-4</td>
<td>44.5%</td>
<td>10.376</td>
<td>17.80%</td>
<td>0.1079</td>
<td>0.1943</td>
</tr>
<tr>
<td>34</td>
<td>TUSQ-1</td>
<td>46.8%</td>
<td>13.720</td>
<td>35.70%</td>
<td>0.1178</td>
<td>0.2214</td>
</tr>
<tr>
<td>35</td>
<td>TUSQ-5</td>
<td>44.2%</td>
<td>9.400</td>
<td>24.14%</td>
<td>0.1425</td>
<td>0.2552</td>
</tr>
<tr>
<td>36</td>
<td>UQ-1</td>
<td>43.1%</td>
<td>8.006</td>
<td>23.57%</td>
<td>0.1318</td>
<td>0.2317</td>
</tr>
</tbody>
</table>

*Data unobtainable due to severe decrepitation during calcination;
** Initial weight corrected for sample loss due to significant decrepitation during calcination.
Figure 12. Sulfation capacity of calcined samples.
Figure 13. Correlation of calcium utilization with (a) CaO, (b) MgO, and (c) dolomite content of sorbent.

Figure 14. Correlation of SO2 capture capacity with grindability of limestone

Figure 15. Correlations of SO2 capture capacity with main components of sorbent.
Task 3 - Digital statewide limestone/dolomite quarry map: This part of the proposed project employed extensive ISGS files of field notes, GIS and analytical databases, maps and cross-sections, reports and journal articles, and archived samples and cores to produce the necessary database that include all active limestone and dolomite quarries in the state. A statewide map was produced from this database showing the locations of limestone and dolomite quarries, existing coal-fired power plants, and road, rail and waterway systems (Fig. 16). This is an interactive GIS-based map that is linked to the database showing active quarry location, rock formation, and other relevant information. In addition a generalized stratigraphic column with lithologic descriptions was prepared for each quarry site visited (Appendix F). These generalized stratigraphic sections can be a useful guide for selecting the best sorbents for FGD and FBC systems.

The results show that limestone primarily occurs in the southern half the state. Except for one quarry in Douglas County, central Illinois, dolomite is rare in the southern half of the state and generally limited to thin beds in some quarries.

The limestones that are being quarried or are potential for mining in the future in the southern half of state primarily include thick Mississippian-age limestones in the western and southern parts and relatively thin Pennsylvanian-age limestones in the central part (Figs. 4 and 5). Mississippian limestones are also quarried near the borders of Indiana, Kentucky, and Missouri. Ordovician and Devonian limestone and dolomitic limestone also occur in southern Illinois and in the Missouri side of border along the Mississippi River in the southeastern Missouri and in areas north of St. Louis. High-calcium limestone, which has proven to be one of the best scrubber stones in FGD systems is particularly abundant within the Mississippian units and is being mined from a number of quarries. Near Ste. Genevieve, Missouri, two major lime plants use one of the Mississippian high-calcium limestones (Salem Limestone) for the manufacture of lime, another important raw material for scrubber systems.

CONCLUSIONS AND RECOMMENDATIONS

The outcome of the project completed during this funding period includes 1) a database containing new geological data (limestone/dolomite stratigraphy, thickness, etc.), physical property data (bulk density, water absorption, grindability, etc.), chemical data (major, minor and trace elements, reactivity indices), mineralogical data (calcite, dolomite, clay minerals, quartz, etc.), and petrographic data (grain type, grain size, interparticle cement, etc.) on limestones and dolomites from the southern part of Illinois and nearby regions of Indiana, Illinois, and Kentucky. Additionally, a GIS-based map was created to show the distribution and types of scrubbing stones, the locations of coal mines, all coal-fired power plants, limestone quarries and mines, and major infrastructures such as navigable waterways, rails and major highways.

Limestones are primarily limited to the southern half and dolomite to the northern half of the state. In the study, dolomite is quarried in Douglas County, central Illinois, and from a number of quarries in southeastern Missouri. Dolomites are also present in some areas in the western part of the state north of the St. Louis Metro East area. However, these dolomites are not available for quarrying at the present time or for the foreseeable future.
Figure 16. Limestone and dolomite resource map with active quarries and infrastructure (see Figure 5 for geologic resource legend).
Tests on limestone reactivity under FGD conditions indicate that, as expected, limestone are more reactive than dolomite. However, reactivity varies among limestones of even equal purity. The main reason appears to be related to limestone constituents revealed petrographically in thin section. Dense, microcrystalline limestones have relatively low reactivity due to a tight, interlocking crystal fabric. The types of limestone commonly quarried or mined in the southern half of the state have relatively high reactivities. These include oolitic limestone with sparry cement, oolitic limestone with microcrystalline calcite matrix, bryozoan-rich limestones, and fossiliferous limestone with sparry calcite cement or micrite matrix. The exact reason for the higher reactivities in these rocks is not clear but may be in part due to differences in surface area, grain and crystal size, and other microscopic features. More work is needed, especially at the SEM level to determine the exact causes.

Test results indicate that dolomites are much better sorbents for sulfur capture in FBC systems. Sulfation reactivity generally increased with increasing MgO content of samples. SO$_2$ capture capacities of samples tested ranged from 0.07 to 0.22 g SO$_2$/g limestone or dolomite. These results indicate that for the FBC applications, a proper selection of the limestone or dolomite could reduce sorbent consumption and the amount of ash disposed of by a factor of about four.

Impure, none-dolomitic limestone may also have a high reactivity under FBC test conditions. One such sample from the Pennsylvanian Omega Limestone in Shelby County only had 33-38% CaCO$_3$ and very little dolomite, yet it showed very high sulfation reactivity. Further investigation is needed to evaluate the behavior of low calcium and low magnesium carbonates under FBC conditions.

The results also indicate that not all dolomites behave the same under FBC conditions. There appears to be a negative correlation between dolomite crystal diameter measured in thin section and calcium utilization. A similar correlation also exists between absorption and calcium utilization. Generally, microcrystalline dolomites have a much higher reactivity and are thus better sorbents for FBC systems than coarsely crystalline dolomites. Further investigation is needed to clarify the exact nature of the relationship between various parameters and reactivity and dolomite. In addition, the high reactivity of impure limestones needs be evaluated. If true, impure limestone could well be used in place of dolomite for FBC system, especially in the southern part of state where dolomite is rare.

REFERENCES


DISCLAIMER STATEMENT

This report was prepared by Zakaria Lasemi, Principal Investigator at Illinois State Geological Survey, with support, in part by grants made possible by the Illinois Department of Commerce and Economic Opportunity through the Office of Coal Development and the Illinois Clean Coal Institute. Neither Zakaria Lasemi or ISGS nor any of its subcontractors nor the Illinois Department of Commerce and Economic Opportunity, Office of Coal Development, the Illinois Clean Coal Institute, nor any person acting on behalf of either:

(A) Makes any warranty of representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately-owned rights; or

(B) Assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method or process disclosed in this report.

Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring; nor do the views and opinions of authors expressed herein necessarily state or reflect those of the Illinois Department of Commerce and Economic Opportunity, Office of Coal Development, or the Illinois Clean Coal Institute.

Notice to Journalists and Publishers: If you borrow information from any part of this report, you must include a statement about the state of Illinois' support of the project.
EQUIPMENT INVENTORY REPORT
September 1, 2003, through August 31, 2004

Project Title: INVENTORY OF ILLINOIS LIMESTONE RESOURCES FOR FLUE-GAS DESULFURIZATION UNITS

ICCI Project Number: 03-1/1.1E-1
Principal Investigator: Zakaria Lasemi, Illinois State Geological Survey (ISGS)
Other Investigators: Subhash B. Bhagwat, Gary B. Dreher, Scott P. Koenig, Hannes E. Leetaru, Yongqi Lu, Donald G. Mikulic, Rodney D. Norby, Massoud Rostam-Abadi, John D. Steele, ISGS
Project Manager: Dr. Ronald H. Carty, ICCI

List of Equipment Purchased

None
PUBLICATIONS AND PRESENTATIONS
September 1, 2003, through August 31, 2004

Project Title: INVENTORY OF ILLINOIS LIMESTONE RESOURCES FOR FLUE-GAS DESULFURIZATION UNITS

ICCI Project Number: 03-1/1.1E-1
Principal Investigator: Zakaria Lasemi, Illinois State Geological Survey (ISGS)
Other Investigators: Subhash B. Bhagwat, Gary B. Dreher, Scott P. Koenig, Hannes E. Leetaru, Yongqi Lu, Donald G. Mikulic, Rodney D. Norby, Massoud Rostam-Abadi, John D. Steele, ISGS
Project Manager: Dr. Ronald H. Carty, ICCI

Publications and Presentations

None