ABSTRACT

The inventory and characterization of limestone and dolomite resources are essential for promoting increased utilization of high-sulfur Illinois coal. To achieve this goal, the Illinois State Geological Survey began an ICCI-funded project for the September 03-August 04 funding cycle to locate and characterize limestone resources near utility sites in the southern half of the state. Phase II of the project completed during the September 04-August 05 funding period concentrated on the inventory and characterization of limestone and dolomite resources in the northern half of the state. The proposed project had four major tasks. In tasks 1 and 2, we characterized the availability and properties of limestone and dolomite resources in the northern half of the state and nearby counties of Indiana, Iowa, and Wisconsin. The results include a) chemical, mineralogical and physical data for 100 representative samples; and b) a GIS-based digital database and map showing the location of active limestone and dolomite quarries, the transportation network, and the location of existing coal-fired power plants. In task 3 and 4 we measured the reactivity of selected limestone/dolomite layers with respect to sulfur oxide capture under FGD and FBC conditions. The results indicate that limestone primarily occurs in quarries located in the southern half of the study area. Some limestone layers are high-purity, containing greater than 90 percent CaCO₃. Dolomite is the dominant carbonates extracted in the northern half of the study area and nearby regions of Indiana, Iowa and Wisconsin. Reactivity data calculated from a pH-stat auto-titration experiment indicate that limestones are the most reactive sorbents under FGD systems. Reactivity among the limestone tested is, however, variable and may be more dependent on limestone constituents (fossil fragments, microcrystalline calcite matrix, sparry calcite cement, non-skeletal grains, etc.) than limestone purity alone. The FBC tests indicate that dolomites are the most reactive sorbents for this system. However, the reactivity of dolomite is also highly variable and appears to be in part dependent on physical properties such as crystal size and absorption. Results from this study compliment those from Phase I and provide a database and maps on the quality and distribution of scrubber stone resources needed for Illinois coal-fired power plants. The information from these studies 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 existing or planned coal-fired power plants.
EXECUTIVE SUMMARY

In 2004, the Illinois State Geological Survey, with support from the Illinois Clean Coal Institute, prepared a comprehensive database that identified and characterized appropriate limestone and dolomite resources in the southern half of the state that lie within economic transportation distances from existing and planned coal-fired power plants. Phase II of the project, completed during September 04-August 05 funding cycle, concentrated on an inventory and characterization of limestone and dolomite resources in the northern half of the state and nearby regions.

The main objectives of this project were 1) to characterize and map the availability and quality of limestone and dolomite in northern Illinois and immediately adjacent counties of Indiana, Iowa, and Wisconsin suitable for wet flue-gas desulfurization (FGD) and fluidized bed combustion (FBC) units; 2) to prepare a digital map and database showing the distribution of scrubber stone resources and locations of active limestone and dolomite quarries in northern Illinois; 3) to measure limestone and dolomite reactivity with respect to sulfur capture under FGD conditions; and 4) to test scrubber stone performance in lab-scale FGD experiments and under FBC conditions.

Task 1 - Northern Illinois scrubber limestone resources: Limestone and dolomite quality and areal distribution were determined in detail for the northern half of the state and immediately adjacent counties of Indiana, Iowa, and Wisconsin. Representative quarries in northern Illinois and nearby regions were visited and geological descriptions including, observations on the general quality, were made for selected quarries. Selected samples (about 104) were characterized chemically, mineralogically, and petrographically. Other physical properties such as grindability, bulk specific gravity, and water absorption also were determined. The results are summarized in Table 1, Appendix A at the end of this report. Petrographically, limestone and dolomite studied are quite varied and include microcrystalline limestone and dolomite, fossiliferous limestone, and coarsely crystalline dolomite. Mineralogical and chemical data show that some limestones in the northern part of the state are high purity with greater than 90 percent CaCO₃ content. Insoluble residue ranges from 0.24 percent to 64.30 percent. Samples with the highest insoluble residue are related to high chert content. However, the majority of the samples contain less than 10 percent insoluble residue. Specific gravity ranged from 2.2 to 3.1 and absorption percentages ranged from 1.0% to 8.0%. The highest absorption values were found mainly in microcrystalline dolomites. Microcrystalline limestones and many of the coarsely crystalline dolomite 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 7.78 to 29.28. Microcrystalline dolomites 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.

Task 2 - Digital map of the northern Illinois limestone and dolomite resources: In this part of the project, a GIS database and maps were produced showing the distribution of limestone/dolomite and location of quarries in the northern part of the state, physical
and chemical properties of limestone and dolomite samples collected, and information on areal distribution of scrubber stone resources. Limestone primarily occurs in the southern half of the study area and mainly includes units in the Pennsylvanian and Mississippian rock formations. High-calcium limestone, which has proven to be one of the best scrubber stones in FGD systems, is found only in some layers within the Mississippian Burlington Limestone. Pennsylvanian limestones are variable in purity but may contain up to 90 percent CaCO₃. A few Silurian and Ordovician quarries contain dolomitic limestones in the northern part of the state. However, northern Illinois is dominated by dolomite deposits most of which are used for construction purposes. Some of these dolomites, especially those that are soft and have high absorption values and/or small crystal sizes, appear to be most suitable for use in scrubber systems equipped with FBC units.

**Task 3 – Reactivity measurement under FGD conditions:** In this task, the dissolution performance of limestones at a controlled pH value was investigated for 24 samples. The dissolution performances of limestones varied significantly. The dissolution rates ranged from 3.5% to 30% in 60 minutes, and their neutralizing capacities varied from 0.7 to 4.5 mol H⁺/ kg limestone. A weak correlation between the dissolution rate of limestone and the dolomite content was observed. Limestones with higher dolomite contents were dissolved more slowly in the acid, and thus exhibited lower reactivities. The neutralizing capacity also showed a weak dependence on the dolomite, calcite and CaO contents, and increased with decreasing dolomite content and increasing calcite and CaO content. Reactivity of limestone also appears to be in part dependent on limestone constituents as revealed in thin section.

**Task 4A – Lab-scale FGD experiments:** In this task, a lab-scale continuous stirred tank reactor (CSTR) was used to measure SO₂ absorption capacities of three limestone and one dolomite samples using a simulated flue gas. The results showed that the three limestone samples had comparable, but higher absorption reactivity than the dolomite. The dissolution rate of the dolomite and limestones measured by titration method was highly correlated to the enhancement in SO₂ absorption capacity (enhancement factor) calculated based on the lab-scale SO₂ absorption test.

**Task 4B – Reactivity measurements under FBC conditions:** The objective of this task was to measure the reactivity of Illinois limestone and dolomites for removal of SO₂ generated in fluidized-bed combustors using a Thermo-Gravimetric Analysis (TGA) technique. Correlations of the calcium utilization with the mineralogy and chemical composition indicate that the calcium utilization was slightly dependent on the dolomite content and CaO content. Limestone samples with more dolomite content tended to be more reactive than the calcite limestones.

The results from this project along with those produced in Phase I will provide a comprehensive, statewide database and maps useful for locating the most effective sorbents locally and at a relatively low cost. This should encourage investment in new coal-fired power plants, lead to increased utilization of Illinois coal, and help to create a cleaner environment by increasing efficiency in removing sulfur oxides and other emissions from flue gases.
OBJECTIVES

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

1) To create a digital database characterizing the limestone and dolomite resources in northern Illinois and immediate counties of Indiana, Iowa, and Wisconsin for use in FGD and FBC systems.

2) To prepare digital maps showing the distribution of limestone and dolomite resources, locations of active limestone and dolomite quarries, all coal-fired power plants, lime manufacturing facilities, and major infrastructure including roads, railways, waterways, barge loading facilities, and major towns.

3) To measure limestone and dolomite reactivity with respect to sulfur capture under FGD and FBC conditions and to correlate reactivities with physical, mineralogical, and chemical properties.

4) To conduct lab-scale experiments to test limestone and dolomite performances under simulated FGD conditions and correlate the results with those produced by titration procedure.

The overall objective of the proposed project was to create a comprehensive database identifying and characterizing appropriate limestone and dolomite resources primarily for the northern Illinois region within economic transportation distances from existing and planned coal-fired power plants. The focus of this phase of the study was the northern Illinois region and the nearby counties of Indiana, Iowa, and Wisconsin. 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. The complete database containing the location of active quarries and chemical, mineralogical, and physical properties of selected samples, lithologic descriptions and other useful information are given in Appendices at the end of this report. A full-size map showing bedrock geology (Illinois only), the location of active quarries, power plants and major infrastructures is also included in the appendices. The appendices are available from the ICCI and ISGS by request.

INTRODUCTION AND BACKGROUND

Introduction

U.S. environmental regulations make it imperative that any new coal-fired power plants be equipped with scrubber 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. In Illinois, development of new coal-fired power plants may be accelerated, in part because of new incentives offered by state government. Construction of new coal-fired power plants and the more stringent pollution control requirements facing 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. Because of the importance of limestone and dolomite as scrubbing agents and the prospects for development of new coal-fired power plants, it is essential that 1) the location of active quarries and the areal distribution of limestone and dolomite raw materials most suitable for FGD and FBC be known; 2) the characteristics of the rock formations that contain the most suitable limestone or dolomite be determined; and 3) the units within each rock formation that are most reactive with respect to sulfur oxides be identified.

Illinois has abundant limestone and dolomite resources (e.g., Krey and Lamar, 1925; Goodwin, 1983; Lasemi et al., 1999; Lasemi and Norby, 2004). However, limestone and dolomite are not readily available throughout the state. In general, dolomites are mainly found in the northern part of the state whereas limestones primarily occur in the central, western and southern parts of the state. The suitability of limestone and dolomite for FGD and FBC applications also varies, and the most suitable high-purity limestone and dolomite resources are probably not widely available (Goodwin and Baxter, 1981; Lasemi and Norby, 2001).

Recent studies by ISGS scientists have suggested that dolomite and dolomitic limestone are most suitable for sulfur capture in FBC units, especially in pressurized fluidized-bed combustion (PFBC) (Rosatm-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 their 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 proximity of minable stone resources with respect to coal-fired power plants needs to be determined.

The cost of transporting limestone by truck is so great that at 30 to 50 miles from the mine the price of the scrubber-suitable limestone nearly doubles (Bhagwat, 2000). For Illinois coal to sustain its current market position it is necessary to ensure that the total cost of generating 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.

**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 SO$_2$ 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).

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% MgCO$_3$ appear to be significantly less reactive than purer limestones, and reactivity further suffers as the MgCO$_3$ content increases to the level of a dolomite at 35-42% MgCO$_3$. In addition, the use of limestone with high MgCO$_3$ content creates a disposal problem for magnesium sulfate, which is 150 times more soluble than calcium sulfate (Boynton, 1980, p. 123). Therefore, it is 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 needs to be determined. 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). Limestone is not usually considered as a sorbent for SO$_2$ capture for most PFBC systems because it does not calcine at partial pressures of CO$_2$ above 0.5 atmospheres at 850°C. Dolomite is preferred because it undergoes half-calcination readily at temperatures as low as 570°C even at 10 atmospheres of CO$_2$ 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 SO$_2$ and, depending on the FBC operating conditions, only small quantities of Mg$_2$Ca(SO$_4$)$_4$ or CaSO$_4$$\cdot$3MgSO$_4$ are formed. The calcination of MgCO$_3$ generates extensive porosity in the dolomite particles and the CaCO$_3$ in them is able to react more efficiently with SO$_2$ (Lee and Georgakis, 1981).
EXPERIMENTAL PROCEDURES

Database and Maps
Using new data collected in the field and existing data already available at the ISGS, maps were prepared to show the regional distribution of limestone and dolomite, 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 each unit. Lithologic sections were prepared for selected quarries to show the lateral and vertical variability in limestone properties. Additionally, selected limestone and dolomite samples were tested under wet FGD and FBC conditions to evaluate carbonate reactivities in relationship to mineralogical, physical, and chemical properties.

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. Fifty petrographic thin sections were prepared at a commercial laboratory for samples subjected to FGD and FBC tests. The thin sections were examined in detail under transmitted light microscope and crystal/grain diameters were measured.

Methods for measuring grindability and other relevant procedures are given in Appendix C at the end of this report.

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 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). For detailed experimental procedures and theoretical background see the Final

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.

Assessment of SO₂ absorption into limestone slurries in a CSTR reactor — A lab-scale continuous stirred tank (CSTR) system was designed and fabricated to measure SO₂ absorption capacities of selected limestones using a simulated flue gas. The schematic diagram of the system is shown in Figure 1. The system allows for continuous flows of both the gas and liquid phases.

![Diagram of the experimental CSTR system](image)

**Figure 1.** Diagram of the experimental CSTR system

The CSTR reactor, made of plastic glass, is 3.5 inch in ID and 8 inch in height. Four vertical baffles, each 0.5 inch width, are evenly attached inside the inner wall of the reactor to maintain a good mixing of the slurry in the reactor. An axial 4-blade stirrer (BDC-2002, Caframo) with adjustable spinning speed, 0-3000 rpm, is used to stir the slurry. The reactor is placed inside a thermostatic water bath. The pH of the slurry inside the reactor is measured online using a pH meter (Model 420, Thermo Orion).

The simulated flue gas is metered by a rotameter, enters the bottom of reactor where a gas diffuser is installed to generate small bubbles uniformly, and exits through a tube located above the liquid surface. A portion of the exhaust gas is extracted for SO₂ concentration analysis using an online fluorescent SO₂ analyzer with a detection range of 0-5000 ppm (Model 40, ThermoElectric).

The limestone slurry was prepared by mixing the limestone sample and de-ionized water
to maintain the solid concentration at 1 g/L. The prepared slurry was continuously stirred on a magnetic stirrer and kept at 50°C during feeding. A peristaltic pump with adjustable liquid flow rate (MasterFlex, Cole Parmer Instrument, Co.) was used to feed the slurry to the reactor at 60 ml/min. Another peristaltic pump (Mini Pump, Fisher Scientific) was used to remove the liquid from the reactor at the same flow rate. The liquid volume in the reactor was kept at 400 ml for all runs. The temperatures of the water bath and the feed slurry were kept at 50°C. The reaction temperature inside the reactor was, however, 40.3-40.6°C at a gas flow rate of 6 L/min, and 40.9-41.3°C at a flow rate of 3 L/min. The simulated flue gas used contained 3155 ppm SO₂, 14.87% CO₂, 4.99% O₂, and balanced N₂.

A number of experiments, the SO₂ adsorption performances were investigated in a KOH solution and a pure water solution to examine the impact of mass transfer in the gas and liquid phases in the CSTR reactor. A 0.1 M KOH solution was used to determine the gas phase mass transfer coefficient. The SO₂ absorption test in the pure water solution was used to determine the combined effects of both the gas and liquid phase mass transfer.

**Reactivity of carbonates in fluidized bed combustion system** — A thermogravimetric analyzer (TGA, RG 2000 Cahn) was used for atmospheric calcinations and sulfation tests. For detailed experimental procedures see Appendix F at the end of this report and the Final Technical Report for Phase I submitted to the ICCI in August 2004.

**RESULTS AND DISCUSSION**

**Task 1 — Northern Illinois Scrubber Limestone Resources**

Phase II of the project focused on limestone and dolomite availability in the northern half of the state and the nearby counties of Indiana, Iowa, and Wisconsin. 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 a database for the northern half of the state 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 results from this study compliments those produced in Phase I for the southern half of the state and provide a valuable resource for 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.
**Task 1A – Available limestone and dolomite resources:** Limestone quarries in the northern half of the state and the nearby counties of Indiana, Iowa, and Wisconsin were visited and detailed geological descriptions, including assessment of the general limestone quality for FGD and FBC applications, were made for representative quarries (Fig. 2; Appendix A, Table 1). More than 100 representative samples were analyzed for chemical, mineralogical, and physical properties and reactivities under FGD and FBC conditions were measured for 51 selected samples.

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 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.

**Task 1B – 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, 104 samples collected under task 1A were characterized chemically (major, minor and trace element constituents); mineralogically (calcite, dolomite, clay minerals, quartz, etc.); and petrographically (e.g., grain size, crystal size, interparticle cement). Physical properties such as grindability, bulk specific gravity, and water absorption were also determined.
Figure 2. Limestone and dolomite extraction sites, sampled locations, and other mines and industrial plants
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 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 given below.

Specific gravity ranged from 2.2 to 3.1 and absorption percentages ranged from 1.0% to 8.0%. As expected, there is a strong negative correlation between specific gravity and absorption. The highest absorption values were found mainly in microcrystalline dolomites. Microcrystalline limestones and many of the coarse crystalline dolomites 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 7.78 to 29.28. Microcrystalline dolomites 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 microcrystalline limestone and dolomite, fossiliferous limestone, and coarsely crystalline dolomite. Mineralogical and chemical data show that the some limestones in the northern part of the state are high purity limestones with greater than 90 percent CaCO₃ content. Some layers in the Mississippian Burlington Limestone contain up to 98% CaCO₃.

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 in northern part of the state.

Acid insoluble residue ranges from less than 0.24% to 64.30%, mostly less than 10%. Very high values come from quartz-bearing samples. Quartz occurs as detrital silica grains or more commonly as chert. The Mississippian Burlington Limestone is especially very cherty in part but contains units of high-purity limestone as well.

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 northern half of the state is dolomite. Calcite is the dominant mineral in samples from several quarries in the southern half of the study area. Dolomitic limestones contain mixtures of calcite and dolomite and were found in samples from the Silurian carbonates in Iroquois County and some Ordovician carbonates in northern Illinois and Iowa. Other major minerals include quartz and in some samples clays. Quartz primarily occurs as chert. Other minor non-carbonate minerals include pyrite and
feldspars. Calcium carbonate content ranges from 0.11% to 93%. The majority of the samples with low CaCO₃ values are dolomitic or dolomite. A few of the low-calcium limestones are rich in silica 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 3, there is a strong negative correlation between the amount of MgO and dolomite and between the percentages of dolomite and calcite, suggesting the source of Mg is primarily from dolomite in the samples.

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, mostly ranging from less than 5 to 10 parts per billion.

Figure 3. Relationship between calcite & dolomite (top left), Dolomite & MgO (top right) and insoluble residue and SiO₂ (bottom left).
Task 2 – Digital Map of the Northern Illinois Limestone and Dolomite Resources

The information from this study along with available published and unpublished information at the ISGS was utilized to prepare generalized, GIS-based geologic maps showing the distribution of limestone and dolomite resources (Figs. 2 and 4). In the northern half of the state, limestone primarily occurs in the southern half of the study area and mainly includes units in the Pennsylvanian and Mississippian rock formations. High-calcium limestone, which has proven to be one of the best scrubber stones in FGD systems, is found only in some layers within the Mississippian Burlington Limestone. Pennsylvanian limestones are variable in purity but may contain up to 90 percent CaCO₃. A few Silurian and Ordovician quarries contain dolomitic limestones in the northern part of the state. However, northern Illinois is a major dolomite-producing area of the state. Most of the dolomites mined are used for construction purposes in the region. Some of these dolomites, especially those that are soft and have high absorption values and/or small crystal sizes, appear to be most suitable for use in scrubber systems equipped with FBC units.

Task 3 – Reactivity of Limestone and Dolomite in Wet FGD Systems

In this task, a pH-stat auto-titration technique was employed to investigate the dissolution performance of limestones at a controlled pH value. The reactivity measured by this method can be used to compare the relative performance of a limestone for removal of SO₂ in wet flue gas desulfurization processes. In Phase I of this study, completed in August 2004, 36 limestone samples were tested. In the current study, an additional 24 limestone samples were assessed. For a more detail discussion of experimental procedures and results see Appendix D.

For the 24 samples tested, the dissolution rates of Ca and Mg ranged from 3.5% to 30% in 60 minutes. The neutralizing capacities ranged from 0.7 to 4.5 mol H⁺/kg limestone. These two indexes are proportional to each other if the purities of the total Ca and Mg are comparable between different limestones. However, if the purities of Ca and Mg in the sample are low, the neutralizing capacity could be low even when the dissolution percentage is high.

Correlation with sample properties — The main minerals in the limestone include calcite, dolomite and quartz, and dominant chemical components are CaO and MgO. The dissolution rate of the carbonate samples was correlated as a function of the dolomite content and the MgO content (Fig. 5a). The correlation coefficients R² for the linear regressions were 0.47 and 0.46 for the dolomite and the MgO, respectively. Limestones with higher dolomite contents are dissolved more slowly in the acid, and thus are less reactive for SO₂ absorption.

Only a very weak dependence existed between the dissolution rate of the limestone and the calcite content (Fig. 5b). The dissolution rate slightly increased with the increasing calcite content. No correlation was found between the dissolution rate and the CaO content. This may indicate that calcium is distributed both in the calcite and the dolomite, and its reactivity in different mineral forms differs significantly.
Figure 4. Statewide limestone and dolomite resource map and active quarries and mines
The acid neutralizing capacity of the limestone also showed a slight dependence on the dolomite or the MgO content (Fig. 6a). While increasing dolomite content in the sample adversely impacted the dissolution rate of the limestone, it also resulted in a decrease in the acid neutralizing capacity.

A weak correlation between the neutralizing capacity with either the calcite content or the CaO content was observed (Fig. 6b). An increase in calcite content in the limestone tended to increase both the dissolution rate and the total calcium content. Therefore, the observed neutralizing capacity could increase with the increase in the calcite content of the limestone. An increase in CaO content could also have a positive impact on the total capacity. Although the CaO contents showed no impact on the dissolution rate of the
limestones, an increase in the CaO content could provide more alkaline carbonate and thus increase the neutralizing capacity of limestone.

![Graphs showing correlations between acid neutralizing capacity and sample properties](image)

(a) Correlation with dolomite and MgO contents

(b) Correlation with calcite and CaO contents

Figure 6. Correlations between acid neutralizing capacity and selected sample properties

**Task 4A – Assessment of SO₂ Absorption into Limestone Slurries in a Lab-Scale CSTR Reactor**

In task 3 of this study, the dissolution rates of 24 dolomite and calcite limestone samples were measured using a pH-stat titration technique. In this task, a lab-scale continuous stirred tank reactor (CSTR) system was used to measure SO₂ absorption capacities of selected limestones using a simulated flue gas. It was expected that, while the results of the titration tests could provide an assessment of the relative reactivities of different
limestones, the reactivities measured in the gas absorption tests would be more realistic and better represent the performances of the samples in the wet FGD processes. See Appendix E for detailed discussion of experimental procedures and results.

Four limestone samples were selected: a dolomite (DGCC-1), and three calcites (FRMTQ-2, TRQ-3 and TRQ-4). The particle size of samples was 200-250 US ASTM mesh. The major physical and chemical properties of the samples are listed in Table 1. The mineralogy and chemical composition data were obtained from the XRD and the XRF analysis, respectively.

<table>
<thead>
<tr>
<th>Mineralogy, %</th>
<th>LOI, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Specific Gravity</td>
<td>Non-LOI, %</td>
</tr>
<tr>
<td>Quartz</td>
<td>Calcite</td>
</tr>
<tr>
<td>DGCC-1</td>
<td>2.24</td>
</tr>
<tr>
<td>FRMTQ-2</td>
<td>2.61</td>
</tr>
<tr>
<td>TRQ-3</td>
<td>2.50</td>
</tr>
<tr>
<td>TRQ-4</td>
<td>2.49</td>
</tr>
</tbody>
</table>

**SO₂ Absorption in the Limestone Slurry** — The experimental results are plotted to show the changes in the SO₂ concentration at the reactor outlet from the beginning of an experiment to the time when the steady state conditions were reached. In a typical run, the inlet gas flow rate was first kept at 6 L/min for about 30 minutes and then the flow rate was adjusted to 3 L/min for another 20-30 minutes. For each gas flow rate, all of the tests showed a similar SO₂ concentration-time profile. A good mixing condition was achieved in the CSTR system. Increasing the stirring speed from 300 rpm to 450 rpm only slightly increased the SO₂ absorption rates. A stirring speed of 300 rpm was used in this study.

The rates observed for the three limestone were comparable and were higher than the absorption rate of the dolomite by 40-50% at G=6 L/min, and by about 15% at G=3 L/min. The pH values for the different limestone slurries ranged from 3-3.5 at G=6 L/min, and 3-3.8 at G=3 L/min. It was observed that an increase in the pH value resulted in an increase in the SO₂ absorption rate.

The absorption enhancement factor was defined by the ratio of the rate of SO₂ adsorption in the limestone slurry to that in water alone, and only represents the impact of the limestone dissolution. As shown in Figure 7, the enhancement factor E increased with decreasing the gas flow rate for each limestone. This is expected because the driving force for SO₂ absorption was smaller at a lower gas flow rate. Since the E was based on the SO₂ absorption test, it can be a good indication of the limestone reactivity in an actual wet FGD process.
Comparison of SO$_2$ absorption data with the acid titration test — Titration tests were performed to measure the dissolution rates of the samples tested in the CSTR. The tests were conducted in the pH-stat auto-titration system. These tests were performed with slurries with solid concentrations of 1 g/L. The slurries were prepared using the 200-250 mesh size fractions of the sorbents. A 0.08 M HCl solution was used as the titration solution. The titration tests were conducted both at pH=3 and pH=6. The temperature and stirring speed were kept at 50°C and 300 rpm during the tests, respectively.

The results of the titration tests are plotted in Appendix E, Figure 7. The dolomite sample showed the lowest dissolution rate compared to the three calcites. At pH =3, which was a similar acidity observed in the SO$_2$ absorption tests, the three calcites were dissolved completely after 20 minutes reaction time. They also exhibited comparable neutralizing capacities. A comparison of the dissolution rates in the first 400 seconds, the residence time of the slurry in the CSTR absorption tests, indicated that the order of acid consumption was TRQ-4 =TRQ-3 > FRMTQ-2 > DGCC-1. The same trend was observed in the titration tests at pH=6.

Based on the results of the titration experiments, the Ca+Mg utilization and the dissolution rates for the four samples are summarized in Table 3. It should be noted that the contribution of the neutralizing capacity of the water from pH=8 to pH =3 or pH = 6 was excluded from the reported dissolution rates of the samples.
Table 3. Summary of the results from the titration test

<table>
<thead>
<tr>
<th></th>
<th>PH=3</th>
<th>PH=6</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In the first 400 s</td>
<td>In 60 min</td>
</tr>
<tr>
<td>Volume of 0.08 M HCl solution added, ml</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DGCC-1</td>
<td>10.91</td>
<td>38.64</td>
</tr>
<tr>
<td>FRMTQ-2</td>
<td>25.02</td>
<td>47.47</td>
</tr>
<tr>
<td>TRQ-3</td>
<td>30.08</td>
<td>50.59</td>
</tr>
<tr>
<td>TRQ-4</td>
<td>32.75</td>
<td>47.09</td>
</tr>
<tr>
<td>Ca+Mg utilization, %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DGCC-1</td>
<td>18.12%</td>
<td>77.84%</td>
</tr>
<tr>
<td>FRMTQ-2</td>
<td>47.02%</td>
<td>93.92%</td>
</tr>
<tr>
<td>TRQ-3</td>
<td>56.90%</td>
<td>99.20%</td>
</tr>
<tr>
<td>TRQ-4</td>
<td>62.62%</td>
<td>92.31%</td>
</tr>
<tr>
<td>Dissolution rate, mol HCl/kg limestone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DGCC-1</td>
<td>3.36</td>
<td>14.46</td>
</tr>
<tr>
<td>FRMTQ-2</td>
<td>9.01</td>
<td>17.99</td>
</tr>
<tr>
<td>TRQ-3</td>
<td>11.03</td>
<td>19.24</td>
</tr>
<tr>
<td>TRQ-4</td>
<td>12.10</td>
<td>17.84</td>
</tr>
</tbody>
</table>

A correlation of the limestone SO\textsubscript{2} reactivities measured in the from the CSTR tests (enhancement factor E) with those the acid dissolution rates measured in the titration tests (dissolution rate up to 400 s) are shown Figure 8a. A similar correlation using the dissolution rates at 60-minute reaction time is presented in Figure 8b. The dissolution rates from the titration tests at pH =3 and pH=6 were examined. The results showed that for all of the experimental conditions examined, the enhancement factor E obtained from the CSTR SO\textsubscript{2} absorption tests was highly correlated with the dissolution rate obtained from the titration test ($R^2 \geq 0.9$). This indicated that a similar trend in the limestone reactivity was obtained in both the CSTR and the titration tests.

In summary, the results show that the three calcites had comparable, but higher absorption reactivity than the dolomite. The enhancement in SO\textsubscript{2} absorption capacity (enhancement factor) due to the dissolution of particles in the solution ranged from 3-4 for the calcites, and 1-2 for the dolomite, depending on the gas flow rate used in the experiment. The dissolution rate of the dolomite and limestones measured by a titration method was highly correlated to the enhancement factor E calculated based on the SO\textsubscript{2} absorption test. Both experimental approaches can be used for assessing and comparing the reactivity of the limestone for use in wet FGD processes.
Figure 8. Correlation of the results from the absorption and the titration test

Task 4B – Reactivity Measurements under FBC Conditions

The objective of this task was to measure the reactivity of Illinois calcites and dolomites for removal of SO₂ from combustion flue gases generated from burning high-sulfur Illinois coals in fluidized-bed combustors (FBC). During Phase I of this study, completed in August 2004, SO₂ removal reactivities of 33 Illinois calcite and dolomite stones were measured using a Thermo-Gravimetric Analysis (TGA) technique. In the present study, the reactivities of an additional 23 calcite and dolomite samples were measured. See Appendix F for detailed discussion of the experimental setup, results and discussion.
Limestone/dolomite calcination — the decomposition of the samples during the calcination tests initiated at about 600-800 °C (Figure 1). However, for most samples, calcination initiated at about 700 °C was not completed when the gas temperature reached 850 °C. For almost all of the samples tested, an additional 10 minutes reaction time was required to achieve complete calcinations.

The total carbonate sample weight loss was measured during the calcination tests and estimated for each sample tested based on the XRF analysis of CaO and MgO contents in the raw materials. The weight loss data obtained in the TGA tests and the theoretical estimations are generally in agreement within 5 wt%.

Calcium reactivity with SO2 — TGA sulfation data were used to a plot calcium conversion vs. reaction time (reactivity) for calcined samples (Appendix F, Figure 2). The SO2 capacities at 90-minute sulfation reaction time are summarized in three ways: molar percent of CaO conversion to CaSO4 (calcium utilization); mass of SO2 captured per mass of raw limestone; and mass of SO2 captured per mass of calcined sample. A wide range of reactivity was observed for the limestones. The calcium utilization varied from about 16% to 69%. In terms of the SO2 capacity, it varied from 0.06 to 0.20 g SO2/g limestone. These two types of capacities, one based on the amount of calcium in the sample and the other on the mass of the raw material, are not proportional because of the differences in the calcium purity in the limestones.

Correlation between reactivity and limestone properties — Efforts were made to correlate the reactivity with some of the properties of the limestone samples. The properties which potentially impact the reactivity include the mineral structure and the chemical composition. XRD and XRF analysis data showed that quartz, calcite and dolomite were the dominating mineral contents, and CaO and MgO were the major chemical components in most samples.

Dolomite and calcite are the two main mineral structures in limestone. Magnesium mainly exists in dolomite, but calcium could exist in both calcite and dolomite. For the samples examined, the CaO content was around 30% for dolomites, and about 45-50% for the calcite-dominated limestones (Appendix F, Figure 3).

Poor correlations were observed between the calcium utilizations and the dolomite or the MgO contents of the samples (Figure 9a). In general, samples with higher dolomite contents had slightly higher calcium utilization than the calcite limestones. An improved correlation was found with the CaO and the calcite contents (Figure 9b). Calcium utilization decreased with increasing CaO and calcite contents.

Correlations based on the SO2 adsorption capacities, amounts of SO2 adsorbed per unit weight of raw materials, showed no relations to the crystalline contents or the main chemical components of the samples. The total adsorption capacities were impacted by both the reactivity (calcium utilization rate) and the calcium content.

In summary, the TGA test showed that there were significant differences in the sulfation reactivities of the samples. The calcium utilization of the limestone samples varied from
16% to 69% after 90-minute reaction time. The SO$_2$ adsorption capacity of the raw limestone ranged from 0.06 to 0.20 g SO$_2$/g limestone.

Correlations of the calcium utilization with the main mineral structure and the chemical composition indicated that the calcium utilization was slightly dependent on the CaO content and dolomite content. Limestone samples with more dolomite contents tended to be more reactive than the calcite limestones. However, no relationships were found between the dolomite content and the amount of SO$_2$ adsorbed per unit weight of raw limestone materials.

![Graphs showing correlations](image-url)

(a) Correlation with dolomite and MgO contents

(b) Correlation with calcite and CaO contents

Figure 9. Correlation between calcium utilization and selected main properties
CONCLUSIONS AND RECOMMENDATIONS

The outcome of the project completed during this funding period and that completed in Phase I 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 Illinois and nearby regions of Indiana, Iowa, Kentucky, Missouri, and Wisconsin (Appendix A of this and 2004 reports). Additionally, data from this study and Phase I were used to create GIS-based regional maps to show the distribution and types of scrubbing stones, the locations of coal mines, all coal-fired power plants, active limestone quarries and mines, and major infrastructures such as navigable waterways, rails and major highways (Figs. 4, 10, and 11; Appendix H). The information from these studies 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.

In the northern part of the state, the focus of investigation in Phase II, limestone primarily occurs in the southern half of the study area and mainly includes units in the Pennsylvanian and Mississippian rock formations. High-calcium limestone, which has proven to be one of the best scrubber stones in FGD systems, is found only in some layers within the Mississippian Burlington Limestone. Pennsylvanian limestones are variable in purity but may contain up to 90 percent CaCO₃. A few Silurian and Ordovician quarries contain dolomitic limestones in the northern part of the state. However, northern Illinois is dominated by dolomite deposits most of which are used for construction purposes. Some of these dolomites, especially those that are soft and have high absorption values and/or small crystal sizes, appear to be most suitable for use in scrubber systems equipped with FBC units.

Statewide, limestones are primarily limited to the southern half and dolomite to the northern half of the state. In central Illinois, dolomite is quarried in Douglas County 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. Limited amounts of Pennsylvanian-age limestone occur in the central part of the state, where they are sporadically present near the surface and mined at several locations. 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. A majority of these dolomites, however, are excellent material for sulfur capture in FBC units. 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. High-calcium limestone in the upper Ordovician Kimmswick Formation is mined in eastern Missouri.
Figure 10. Active limestone and dolomite quarries and mines in Illinois and adjacent states
Figure 11. Locations of sampled limestone and dolomite quarries and mines in Illinois and adjacent states
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. Only a few quarries in the northern half of the state contain limestone that may be suitable for wet FGD scrubbers.

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. 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. The results of this study and those from Phase I show that impure, none-dolomitic limestone may also have a high reactivity under FBC test conditions.

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EQUIPMENT INVENTORY REPORT  
September 1, 2003, through August 31, 2004

Project Title: INVENTORY OF ILLINOIS LIMESTONE RESOURCES FOR FGD and FBC DESULFURIZATION UNITS

ICCI Project Number: 04-1/3.2C-1
Principal Investigator: Zakaria Lasemi, Illinois State Geological Survey (ISGS)
Project Manager: Dr. Ronald H. Carty, ICCI

List of Equipment Purchased

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PUBLICATIONS AND PRESENTATIONS
September 1, 2004, through August 31, 2005

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ICCI Project Number: 04-1/3.2C-1
Principal Investigator: Zakaria Lasemi, Illinois State Geological Survey (ISGS)
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