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Overview of High-Calcium Limestone Resources in Illinois for Flue-Gas Desulfurization Systems

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ABSTRACT
Stringent pollution control requirements imposed by regulatory agencies have accelerated the installation of limestone-based flue-gas desulfurization (FGD) systems in coal-fired power plants. This trend toward increasing numbers of FGD units is expected to continue into the future as long as coal remains a viable source of fuel for generating electricity. Because of the importance of high-calcium limestone as a scrubbing agent in FGD systems, it is essential that issues associated with the transport, availability, and suitability of high-calcium limestone resources be addressed. Nearby sources of suitable limestone raw material must be found to feed existing and new scrubber installations and to aid in the selection of proper resources for desulfurization systems in the future. Illinois has abundant limestone and dolomite resources; however, high-calcium limestone is not readily available throughout the state. The suitability of high-calcium limestone for FGD applications also varies, and the most suitable limestone resources are not widely available. The Illinois State Geological Survey conducted a statewide study through a grant from the Illinois Clean Coal Institute to inventory and characterize high-calcium limestone resources. This paper provides a brief overview of the distribution and properties of existing and potential high-calcium limestone resources in Illinois. A more detailed report on the location and characteristics of these high-calcium limestone resources will appear in a subsequent publication.

INTRODUCTION
The demand for high-calcium limestone has increased in recent years. This upsurge occurred in response to environmental regulations set by state and federal governments that have made it necessary for coal-fired power plants to be equipped with limestone-based scrubber systems to reduce emissions of sulfur dioxide (SO\textsubscript{2}) and other pollutants. Stringent SO\textsubscript{2} control requirements have accelerated plans for installation of limestone-based flue-gas desulfurization (FGD) systems. With partial funding from the Illinois Department of Commerce and Economic Opportunity through the Office of Coal Development and the Illinois Clean Coal Institute (ICCI), the Illinois State Geological Survey conducted several statewide studies characterizing limestone and dolomite resources mined from Illinois quarries to identify the best sorbent for desulfurization (Lasemi et al. 2004, 2005, 2008). The samples for these studies were primarily collected from quarry stockpiles. Because of the large scope of the projects, bed-by-bed examination and delineation of zones containing the highest quality limestone [95% or better calcium carbonate (CaCO\textsubscript{3})] were not within the project time frames or budgets. Nevertheless, the results of these studies were well received by the utilities industry and other industries using limestone for desulfurization.

Limestone-based desulfurization technologies in coal-fired power plants are a proven means of meeting the clean air standards. Illinois has abundant limestone and dolomite resources (e.g., Krey and Lamar 1925; Goodwin and Harvey 1980; Goodwin and Baxter 1981; Goodwin 1983; Mikulic 1990; Lasemi et al. 1999, 2004; Lasemi and Norby 2001). Most limestone quarries in Illinois produce construction-quality aggregates primarily for asphalt and concrete pavements. For such uses, hardness, ease of abrasion, and high absorption are generally more of a concern than high purity with respect to the CaCO\textsubscript{3} needed for desulfurization. Limestone purity needs to be even higher for manufactured products such as lime (CaO) or when used for other chemical and pharmaceutical applications, such as raw material for heartburn medicine and dietary supplement pills.

For this study, maps, primarily ones from previous studies showing locations of potential high-calcium limestones, were digitized and updated when possible (Lasemi et al. 2011 and manuscript in preparation). A number of 7.5-minute bedrock geologic maps of southern and southwestern Illinois that show the surficial distribution of bedrock are also available from the Illinois State Geological Survey. These maps are a valuable source of information for delineating the distribution of bedrock units containing high-calcium limestone resources (e.g., Nelson and Devera 1995; Nelson et al. 1995a,b, 1999; Denny 2004; Denny and Devera 2008; Denny et al. 2009; Devera 2010; Denny and Seid 2014). Other publications dealing directly or indirectly with high-calcium limestone resources in Illinois include Stith et al. (1997), Cloos and Baxter (1981), Goodwin and Baxter (1981), Lamar (1957, 1959), Lamar and Harvey (1966), and Lamar and Willman (1931).

We also examined a number of quarries that had the highest potential for containing high-calcium limestone resources. We visited the key quarries and made detailed descriptions of the potential high-purity limestone zones. In most cases, detailed descriptions were made from available cores drilled at or near the quarry properties. Quarry and core samples were characterized.

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chimically [X-ray fluorescence (XRF)], minerallogically [X-ray diffraction (XRD)], and petrographically (polarized light microscopy) to better constrain the high-purity limestone zones within those quarries (Lasemi et al. 2011 and manuscript in preparation).

This paper provides a brief overview of the research project conducted as part of the grant from the Illinois Office of Coal Development through ICCI regarding the distribution of high-calcium limestone resources in Illinois (Lasemi et al. 2011). A more comprehensive treatment of the results from this project, along with maps of potential high-calcium resources, will be the subject of a subsequent publication.

**RESULTS AND DISCUSSION**

About one third of the nation’s coal-burning power plants that use desulfurization units to remove SO₂ 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 has continued to date, following implementation of the U.S. Clean Air Interstate Rule. The result has been an increased demand for high-purity limestone to remove gaseous sulfur oxides.

High-purity limestone resources (≥95% CaCO₃), now considered the most suitable for FGD applications, are not widely available throughout the state. They are mostly confined to rocks of the Mississippian System and the Ordovician Kimmswick Limestone (Figure 1), which are at or close to the surface in the western and southern parts of the state, especially near the Mississippi and Ohio Rivers. Very little high-purity limestone is found in the northern part of the state, where dolomite of the Ordovician and Silurian Systems predominates (Figure 2). Often, high-calcium limestone beds are interlayered with low-purity intervals. It is quite rare for high-calcium limestone to constitute the bulk of a rock formation. Therefore, selective mining is necessary to be able to extract the high-calcium limestone zones. A few quarries already do selective mining; others will be amenable to such practices if demand arises.

**Distribution of the High-Calcium Limestone Resources in Illinois**

Rock units from which high-calcium limestone is currently produced or that have potential for future production mainly include (1) the Ordovician Kimmswick Limestone; (2) the Lower and Middle Devonian Backbone, Grand Tower, and Wapsipinicon Limestones; and (3) the Middle Mississippian Burlington, Ullin, Salem, and Ste. Genevieve Limestones, and the Upper Mississippian Glen Dean and Haney Limestones (Figure 1).

The Ordovician Kimmswick is at or near the surface at Thebes, Illinois. Various companies that are prospecting for high-calcium limestone have conducted extensive studies in the area, which is in close proximity to the Mississippi River. In Calhoun County, the Kimmswick Limestone is exposed along the Mississippi River bluffs in Sections 32 and 31, T 11 S, R 2 W (Rubey 1952; Devera 2010). Proximity to the Mississippi River provides a relatively inexpensive mode of transportation. About 75 ft (22.9 m) of Kimmswick is exposed here, with the upper 55 ft (16.8 m) being of the highest purity. The Kimmswick was also mined underground near Valmeyer, Illinois, before the mine closed in the early 1990s. The Kimmswick Limestone consists primarily of light gray, relatively coarse-grained, fossiliferous (crinoidal-bryozoan), high-calcium limestone. The upper part of the Kimmswick (Morelock Member) is exceptionally pure in western Illinois, northeastern Missouri, and southern Illinois near Thebes. Calcium carbonate content of the upper Kimmswick ranges between 94% and 98% (Baxter 1970; this study), making this formation an excellent source of high-calcium limestone for various applications. Because of its high purity, the Kimmswick is an excellent source of limestone for FGD in coal-burning power plants. The Kimmswick is presently being mined near Cape Girardeau and Clarksville, Missouri. The Kimmswick is at the Huntington Quarry, northeastern Missouri, contains a 55-ft (16.8-m) high-purity limestone interval in the upper part underlain by a 65-ft (19.8-m) interval that is less pure, with a high magnesium carbonate (MgCO₃) content. The upper high-purity interval presently supplies the scrubber stone for the wet FGD system of a major coal-fired power plant in west-central Illinois.

In Jackson and Union Counties in extreme southern Illinois, the Lower Devonian Backbone Limestone is a relatively pure limestone (95 to 98 wt% CaCO₃) up to 43 ft (13.1 m) thick (Lamar 1959). The Backbone Limestone outcrops in the Shawnee National Forest, but the chance for mining at this location is minimal because of the thick overburden and environmental considerations involved with surface mining. The Middle Devonian Wapsipinicon Limestone (Grand Tower equivalent; Figure 1) is mined in Rock Island County and in a nearby underground mine (Linwood Mine) across the Mississippi River east of Buffalo in Scott County, Iowa. The high-calcium limestone is mined selectively from the Otis Member of the Wapsipinicon Limestone. Available data indicate that the CaCO₃ content of the Otis generally exceeds 94.5%. The Middle Devonian Lingle Limestone (St. Laurent Formation of Nelson et al. 1995b) is also mined in central Illinois near Tuscola in Douglas County, northwestern Illinois, but its CaCO₃ content rarely exceeds 95%.

An area rich in high-calcium limestone resources includes the St. Louis Metro East region in southwestern Illinois (Baxter 1960, 1965; Lasemi et al. 1999; Lasemi and Norby 2001; Denny 2004; Denny and Devera 2008; Denny et al. 2009). The St. Louis Metro East region as defined in this study extends from Alton (Madison County, Illinois) to Prairie du Rocher (Randolph County, Illinois) and Ste. Genevieve (Ste. Genevieve County, Missouri). Mississippian limestones...
Figure 1 Stratigraphic column for the Illinois Basin. Intervals shown in blue indicate rock formations that contain high-calcium limestone. From Lasemi et al. (2003).
Figure 2  Statewide limestone and dolomite resource map showing active quarries and mines, and locations of the quarries or underground mines studied. Resource map compiled and modified from an unpublished map by J.E. Lamar, Illinois State Geological Survey.
are the most widely exposed bedrock formations in the St. Louis Metro East region. In general, bedrock in the region dips toward the Illinois Basin to the east-southeast from the north (i.e., Alton area) and to the east-northeast from the south (i.e., Prairie du Rocher area). As a result, thick Mississippian limestone units (Valmeyeran and lower Chesterian strata) are progressively more deeply buried beneath the predominantly siliciclastic rocks of the upper Mississippian and Pennsylvanian System. Substantial erosion during the Pennsylvanian Period resulted in thinning or complete removal of Chesterian strata (Weller and Weller 1939), exposing the thick Mississippian limestone intervals in many areas, especially in the bluffs of the Mississippi River. Overburden, which includes the Quaternary deposits and upper Mississippian (Chesterian) and Pennsylvanian siliciclastics, thickens to the east away from the bluffs to more than 200 ft (61 m) within 3 to 10 miles (4.8 to 16.1 km). In areas of thick overburden, underground mining is economically more feasible than an open pit quarry operation, which would require the removal of a substantial amount of overburden material.

**Chemical, Mineralogical, and Petrographic Characterization**

To identify potential high-calcium limestone zones for future extraction, limestone units from selected quarries were characterized chemically, mineralogically, and petrographically. The results showed that high-purity limestone zones could be clearly identified in active quarries by using chemical and mineralogical data (Figures 3–5). These data can be used as a guide for selecting the most suitable limestone for scrubber systems. This information also provides the quarry operators with a means for selectively extracting the high-purity limestone when needed. Two charts showing the distribution of XRD (mineralogical) and XRF (chemical) data are shown as examples in Figures 6 and 7. The data clearly allow for identification of zones that have the highest potential as a source of high-calcium limestone (Figure 8). Quick identification of high-purity zones can be made by using bulk pack, semiquantitative XRD analysis methods. Once potential high-calcium limestone zones are identified, they can be further analyzed by chemical analysis techniques such as XRF spectroscopy or other methods to obtain a more accurate picture of the purity of the limestone. Because of the proprietary nature of the data, specific details regarding the analytical results are not included in this section but will appear in a subsequent publication.

**Petrographic Analysis**

Petrography refers to a description of the constituents and texture of a limestone made by viewing a translucent thin section of the rock through a petrographic microscope. High-calcium limestones are quite variable with regard to grain composition and texture. Some limestones are composed of a mixture of fossil fragments of various sizes and shapes, whereas others may consist of microcrystalline calcite with few or no visible fossil remains. Some limestones are made up of rounded grains called ooids that may show a radial or tangential microstructure. Yet others may contain grains of variable roundness and shape that consist of very finely crystalline calcite. Some high-calcium limestones are soft, absorbent, and porous, whereas others are dense, with very little porosity. The wide variability
Figure 4  Example X-ray diffraction trace showing a more impure dolomitic limestone.

Figure 5  Example X-ray diffraction trace showing an impure limestone with significant amounts of quartz and other impurities.
Core number 14703, near Renault, Monroe Co.

Figure 6 Example of mineralogical data [based on X-ray diffraction (XRD)] obtained from a core from Monroe County. High-calcium limestone zones (indicated by the high calcite content) are clearly identified based on mineralogy. Chemical analysis shows that the actual CaCO$_3$ content may be a few percentage points higher than the amount measured by XRD.
Figure 7 Example of chemical data (based on X-ray fluorescence) obtained from a core. The high-calcium limestone zones are clearly identified based on the high CaCO$_3$ content (calculated from the percentage of CaO).
Figure 8: Geologic column from a quarry in Union County, Illinois, showing well-developed oolite beds (in yellow) in the Ste. Genevieve Limestone. These oolitic beds are often very high purity and are an excellent source of high-calcium limestone for sulfur sorbent use.
in composition and physical properties can also influence their reactivity with respect to sulfur capture regardless of their purity.

Thin-section petrography is an important tool for characterizing limestone quality. This method provides valuable information regarding the suitability of various limestones for desulfurization and other industrial applications. In selecting limestone for these uses, the major emphasis is often placed on the purity of the rock (95% CaCO₃ or better), and petrographic characteristics are generally ignored. Detailed thin-section petrography showed that high-calcium limestones can vary significantly in their petrographic characteristics and texture. These differences can affect calcination behavior during CaO production and can influence the effectiveness of the limestone in capturing SO₂ in the flue-gas scrubber systems of coal-burning power plants as well as its suitability for other industrial applications (Harvey et al. 1974; Lasemi et al. 2011).

CONCLUSIONS

High-purity limestone resources (>95% CaCO₃) in Illinois are mostly confined to rocks older than the Pennsylvanian System and are at or near the surface in the western and southern parts of the state, especially near the Mississippi and Ohio Rivers. Very little high-purity limestone is found in the northern part of the state, where dolomite of the Ordovician and Silurian Systems predominates.

The Kimmswick Limestone, the lower member of the Burlington, the Harrodsburg Member of the Ullin, and the upper Warsaw, Salem, and Ste. Genevieve are, for the most part, medium- to coarse-grained bioclastic or oolitic limestones. In some cases, these coarser limestones are somewhat porous and soft. These factors make the limestones less suitable for some construction purposes. However, these coarser-grained limestones are generally pure, with more than 95% CaCO₃ content, making them an excellent raw material for the manufacture of CaO, the capture of SO₂ in coal-burning power plants, and the production of chemical-grade calcium carbonates.

Our work documents that not all high-calcium limestones behave the same when used as sorbents for desulfurization. Variations in grain size, the amount of sparry calcite cement and cement crystal size, the relative proportion of microcrystalline matrix, the types of constituent grains, and the amounts of residual porosity all have significant influences on sulfur capture efficiency in FGD scrubbers.

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