

FINAL TECHNICAL REPORT
November 1, 1998, through October 31, 1999

Project Title: **RAPID-SETTING CEMENT MANUFACTURE USING FGD
SLUDGE**

ICCI Project Number: 98-1/3.2A-1

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ABSTRACT

Approximately 2 million metric tons of flue gas desulfurization (FGD) sludge is produced in the U.S., only 7.5% of which is used for beneficial purposes. Sludge that has been converted to sulfate through forced oxidation has been utilized to make wall boards and portland cement. However, the sludge that is predominantly calcium sulfite is not appealing for direct utilization. Exploiting their compositional make-up, FGD residues can be utilized in manufacturing a rapid-setting cement that already has a substantial market demand. This special calcium sulfoaluminate-based cement is widely used as rapid-setting cement and shrinkage-compensating cement. In recent years, rapid-setting cements are being used in many applications, including highway pavement, and the demand is rapidly increasing.

Two FGD sludges have been investigated; one is predominantly a hydrate of calcium sulfate and the other is a hydrate of calcium sulfite. The performance of Type I portland cement prepared with the sulfate sludge was similar to or better than that prepared with standard "Terra Alba" gypsum. These results clearly indicate that sulfate sludge is a good source of gypsum in the manufacture of portland cement. Illinois cement plants can easily consume about 100,000 metric tons of sulfate sludge annually. It is also economically attractive to the cement manufacturers.

Sulfite sludge, on the other hand, is not suitable for making portland cement. However, its compositional make up is desirable in making rapid-setting cement. Rapid setting clinker was produced in a pilot-scale rotary kiln system utilizing 13% sulfite sludge, based on dry weight. The clinkering temperature was approximately 1260°C, which is 200°C lower than that required to manufacture portland cement clinker. Furthermore, as the rapid-setting clinker was much softer, substantial energy can be saved in the grinding process.

A one-to-one comparison with a commercial rapid-setting cement clearly indicates the sulfite-derived, pilot-kiln produced rapid-setting cement has superior flow properties and comparable strength development (over 15 MPa in two hours and over 30 MPa in 24 hours).

Pages 1-16 contain proprietary information.

EXECUTIVE SUMMARY

The presence of high levels of sulfate and sulfite, along with other constituents, make FGD residues not very appealing for other direct utilization purposes. In particular, the calcium sulfite content is undesirable for possible direct reuse scenarios. As a result, problems of disposal of this sludge are expected to escalate further in the future unless the market potential of these residues is realized.

The ultimate goal of this project is to utilize the FGD sludge, predominantly a hydrate of calcium sulfite produced in power plants that burn Illinois coal, to manufacture rapid-setting cement. Annually, approximately 20 million metric tons of flue gas desulfurization (FGD) sludge is produced in the U.S., of which only 7.5% is used for beneficial purposes. FGD sludge that has been converted to calcium sulfate through forced oxidation finds some use in making wall board or portland cement as synthetic gypsum, provided it contains very little of other compounds. Illinois produces about 1 million metric tons of FGD sludge per year. Because of the relatively high sulfur content of Illinois coal, utilization of sludge for commercial purposes is important to encourage continued use of Illinois coal by power plants.

A rapid-setting cement, also known as calcium sulfoaluminate cement, is substantially different from ordinary portland cement (OPC) in its setting behavior and strength development profile. This cement already has a substantial market with good prospects for further market development. As the raw materials requirement and the phase composition of these cements are different from those required for making OPC, they fall under the category of special cements. Also, production of these cements requires processing temperatures that are 200 to 300°C lower than those necessary for OPC; and, because of lower firing temperature, the pyroprocessed product is softer and substantial energy can be saved in the grinding process.

Rapid-setting cement is used in many applications such as bridge decks, airport runways, patching roadways, sidewalks, etc. where rapid strength development is necessary. Recently, sections of concrete highways have been built with this cement. In addition, it may be modified for use in shrinkage compensated concrete by mixing with portland cement and for controlled low-strength materials (CLSM) used for diggable back-filling of utility trenches. A 1996 survey indicates that 81,000 metric tons of rapid-setting cement was produced in the U.S. In recent years, the use of rapid-setting cements has increased substantially, as more and more technical data are generated in regards to their performance and durability.

Rapid-setting cement is not produced in the State of Illinois, and commercialization of this technology will have substantial commercial advantage. Two of the reasons that rapid-setting cement is not used extensively are its availability and price. Use of waste sludge makes it cheaper and will also encourage building of new plants.

Unlike the case in many other potential reuse possibilities, the form in which sulfur is present in FGD sludge is immaterial, as rapid-setting cement is produced upon pyroprocessing or heat treatment which results in the oxidation of sulfur to the sulfate state.

The following two steps are necessary to accomplish the ultimate goal of this project.

Step I: Composition formulation, process development, characterization of products, and optimization of composition to meet the primary requirements for commercial

rapid-setting cements.

Step II: Upon successful completion of Step I, "scale-up" from pilot-scale investigation to demonstration phase where rapid-setting cement will be produced in a commercial cement manufacturing plant located in Illinois. Step II was not considered in this project period.

The present program has been devised upon consideration of all relevant issues and also realizing that the likelihood of success of this route of utilization of FGD residues is high. The objective of Step I was accomplished in this project period. A cement plant in Illinois has agreed to collaborate with CTL in the demonstration phase.

Of the two FGD sludges that have been investigated, one was predominantly calcium sulfate and the other was calcium sulfite. It was immediately apparent that sulfate sludge is a good candidate for manufacturing of portland cement. Portland cement clinker is always interground with gypsum to control its setting and strength development characteristics. Also, implementation of this technology is straightforward, and may provide some incentive to both cement and power plants.

This possibility was investigated by producing portland cements using sulfate sludge and comparing the performances achieved with standard gypsum. The performance of Type I portland cement produced with sulfate sludge was equal to or superior to that of cements made with standard "Terra Alba" gypsum. This result clearly indicates that sulfated sludge is a suitable source of gypsum used in the manufacture of portland cement.

Sulfite sludge, however, is not suitable to make portland cement, and the major focus of this project has been the use of sulfite sludge to produce rapid-setting cement. Prior to making the pilot-scale production, several rapid-setting cements have been successfully produced with the sulfite sludge. The parameters that were investigated are the following: (i) compositional make up of the raw ingredients, (ii) ratio of various raw ingredients that optimizes the amount of rapid-setting phase that can be formed in the clinker, and (iii) time-temperature schedule for pyroprocessing. Based upon the information developed in this bench-scale study, pilot-scale production was performed using a rotary kiln. The final rapid setting cement was produced utilizing 13% sulfite sludge, based upon dry mass of the total raw ingredients. It is also very encouraging to note that this composition is easily clinkered at 1,260°C, which is about 200°C lower than that typically required to produce portland cement clinker.

A one-to-one comparison of flow and mortar strength development was made between this and commercial rapid-setting cements. The flow properties of this cement were much superior to those of commercial cement. For a comparable flow, the strength development of the cement made in the program was comparable to that of the commercial cement. The compressive strength was over 15 MPa at two hours and over 30 MPa at 24 hours. The setting characteristics of this cement were also comparable to those of the commercial rapid-setting cement.

The remainder of this report contains proprietary information and is not available for distribution except to the sponsor(s) of this project.