Rapid Limestone Calcination Using Microwave Assist Technology

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ABSTRACT

Ceralink Inc. is applying Microwave Assist Technology™ (MAT™) to the calcination of limestone to demonstrate the potential for significant energy reduction in the manufacturing of lime. MAT™ is a method to simultaneously apply traditional radiant heat and microwave energy in the same kiln, leading to fast volumetric product heating. Microwave thermal activation targets and directly heats limestone, eliminating the reliance on thermal conduction as a means of energy transfer. In addition, less energy is wasted in heating non-product, such as the atmosphere and kiln lining. This paper includes studies of microwave materials interactions through dielectric property measurements, and lab-scale microwave hybrid calcination tests. This technology shows potential to increase the speed of lime production by enhancing the reaction rate, which will significantly reduced energy consumption. Production scale implementation of MAT™ calcining is projected to save trillions of BTU/yr in the lime and cement industries. This work is supported through a Department of Energy Industrial Grand Challenge grant.

Introduction

This paper discusses the initial results from the DOE Stage 2 project for demonstrating decreased energy consumption for calcining of limestone. Ceralink has applied MAT™ to this process to demonstrate through sophisticated modeling and laboratory-scale experiments that lime can be produced with equivalent properties, lower energy consumption and shorter cycle time. The overall goal is to develop a MAT™ rotary calciner system for lime and cement production, with immediate Stage 2 goals of demonstrating the feasibility and benefits of MAT™, while developing the tools required for building an industrial-scale MAT™ calciner. The experimental portion of this DOE project is presented below, along with the projected large scale MAT™ benefits.

Background

Background on Limestone and Reactions

Over 300 million years ago, an inland sea covered most of the Midwestern United States. This sea teemed with billions of microscopic creatures, shell fish, and other denizens of the deep, who when they died, created the calcium rich limestone deposits that are mined today. The discovery and use of limestone dates back as far as 2500 BC, when ancient Egyptians burned limestone and mixed it with water for use in the construction of the pyramids [1].

Lime (the calcined product of limestone) is an important raw material, and is used extensively in many different industries today, including steel, environmental, chemical, construction, and pharmaceutical. Even now, the general concept of preparing lime is not much different from the early days of the Egyptians, where it was burned or calcined to remove carbon dioxide.

The concept of applying radiant heat to limestone, whether in the form of a wood fire, coal burner or gas flame, employs the same slow, inherently energy intensive process of thermal conduction to transfer heat. In addition, the dissociation reaction from $CaCO_3$ to CaO, is highly endothermic, and begins when the temperature is between 780 ºC to 1340 ºC[2]. The elevated temperature must be maintained to support the reaction.

The endothermic nature of the $CaCO_3$ to CaO calcination indicates that heat transfer is a significant issue, as Moffat determined [2], in the calcination of lime. The endotherm means that as the reaction progresses, the material is actively cooling itself, preventing the diffusion of heat deeper into the unreacted limestone. Heat transfer is effectively stopped at the reaction front. This is a significant problem in other ceramic systems as well. In conventional heating, an extremely slow heating rate and long dwell times are required through these endothermic regions, which are bottlenecks in the heating process.

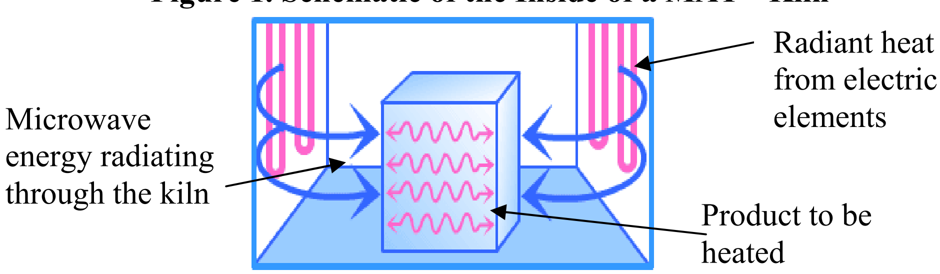
In a typical calcination reaction, dissociation of the calcium carbonate starts at the outer surface of the particle and moves inward, leaving a porous layer of CaO on the surface[2]. For MAT™ processing, radiant heat combined with direct microwave activation means that the dissociation of $CaCO_3$ to CaO should simultaneously take place at the center and the surface of the particle, thus increasing the rate and uniformity of calcination.

Background on Microwave Processing

Direct internal microwave heating overcomes the inherently slow thermal conduction in minerals such as limestone, metal ore, and ceramic powders. This enables reactions and diffusion to occur in shorter times and at lower temperatures[3]. MAT™ is the simultaneous application of microwave energy with radiant heat, in the same kiln, as shown in Figure 1. Figure 1 is an example where a traditional electric kiln (electric elements) has been adapted to apply microwave energy in the kiln cavity.

With MAT™, the microwave energy couples with and heats the center of the product, independent of the cooling endothermic reaction occurring closer to the surface during the dissociation. The amount of heat that can be generated in the material by microwave energy is gauged by the dielectric properties, which is measured as a function of temperature, because the properties vary with temperature.

Figure 1. Schematic of the Inside of a MAT™ Kiln



The microwave energy volumetrically heats the product, while the radiant heat prevents losses from the surface. This creates a uniform temperature profile through the product, enabling faster, more uniform heating compared to conventional heating.

Microwave heating occurs through dielectric loss mechanisms, which can be measured at high temperatures using the cavity perturbation method[4]. The dielectric property which is most useful for predicting microwave heating behavior is the loss tangent (Tanδ). Tanδ is the dielectric loss (e”) divided by the permittivity (e’). Interpretation of the Tanδ provides a general guide to microwave heating behavior and aids in the development of a microwave process.

As a rule of thumb, when Tanδ is less than 0.01, the material is fairly microwave transparent (weakly absorbing of microwaves)[4]. Weak microwave absorption causes the material to remain cool, or to heat very slowly in a microwave field. Above Tanδ of 0.01, the material begins to absorb more strongly. A Tanδ greater than 0.1 indicates good microwave absorption, which indicates faster dielectric heating.

Results and Discussion

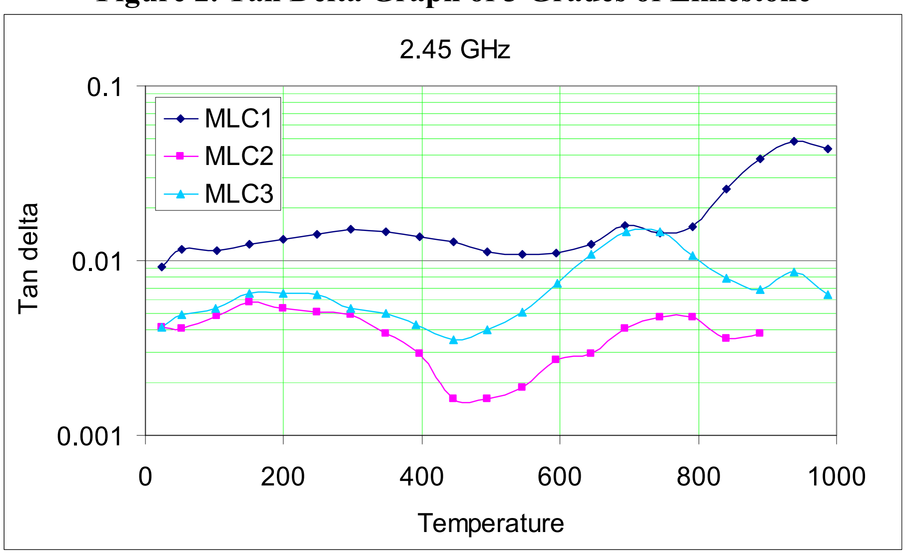
Dielectric Property Results

The dielectric properties of three different grades of limestone (varying impurity levels) were measured at 2.45 GHz and 915 MHz from room temperature to 1000 ºC using the cavity perturbation method[4]. The dielectric property measurements were performed in 50°C increments to ~1000°C, where the measurement was repeated, and then in 200 ºC steps back down to room temperature.

Figure 2 is a graph of Tanδ as a function of temperature, which shows the results of these measurements. This data indicates that MLC1 would heat the strongest by microwave energy, followed by MCL3, with MLC2 heating the least. As far as impurity levels, MLC1 has the highest level, followed by MCL3 and then MLC2, which demonstrates that increased impurity level corresponds with the higher dielectric heating.

The dielectric behavior is also temperature dependent. For example, the data for MLC1 indicates it should absorb microwave energy from room temperature up through 1000 ºC, as the value of Tanδ is above 0.01 through the entire temperature range. For MLC3, the Tanδ indicates the material is only absorbing microwave energy from 625 to 800 ºC. In the case of MLC2, the values show it to be transparent throughout the whole temperature range, indicating a poor microwave absorber.

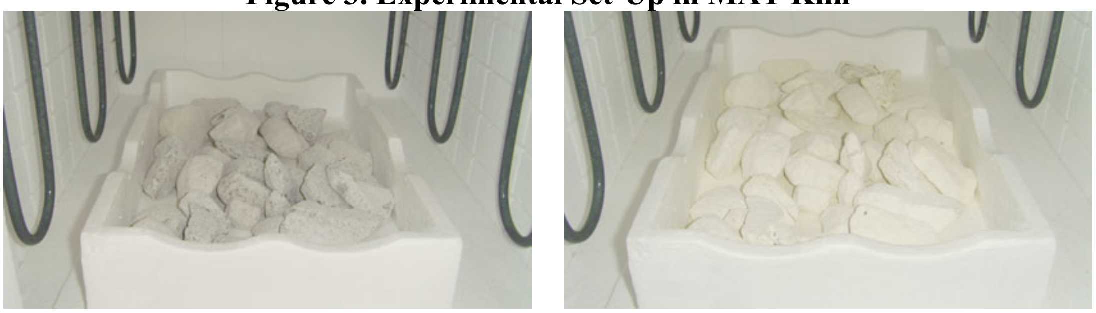
Figure 2. Tan Delta Graph of 3 Grades of Limestone



Experimental Results

Procedure. The laboratory experiments were performed in two lab-scale Microwave Assist Technology™ kilns located at Ceralink Inc. One kiln is a CM Rapid Temp model, with 3 kW of microwave power and an overall temperature rating of 1700 ºC. The second kiln is a Carbolite C-MAT model MRF 16/22, with 1.8 kW of microwave power and an overall temperature rating of 1600 ºC. Limestone was calcined in each of these kilns in mullite coated mullite Ultralite saggers from Sencer (Penn Yan, NY). The mass change (Ohaus AR1530, 3 decimal balance) and visual observations were made for each run. A series of calcining runs using 1 kg samples (Figure 3) from each of the 3 different grades of limestone (MLC 1, 2 &3) were calcined varying the processing parameters, such as temperature, dwell time, ramp rate and microwave power level.

Figure 3. Experimental Set-Up in MAT Kiln

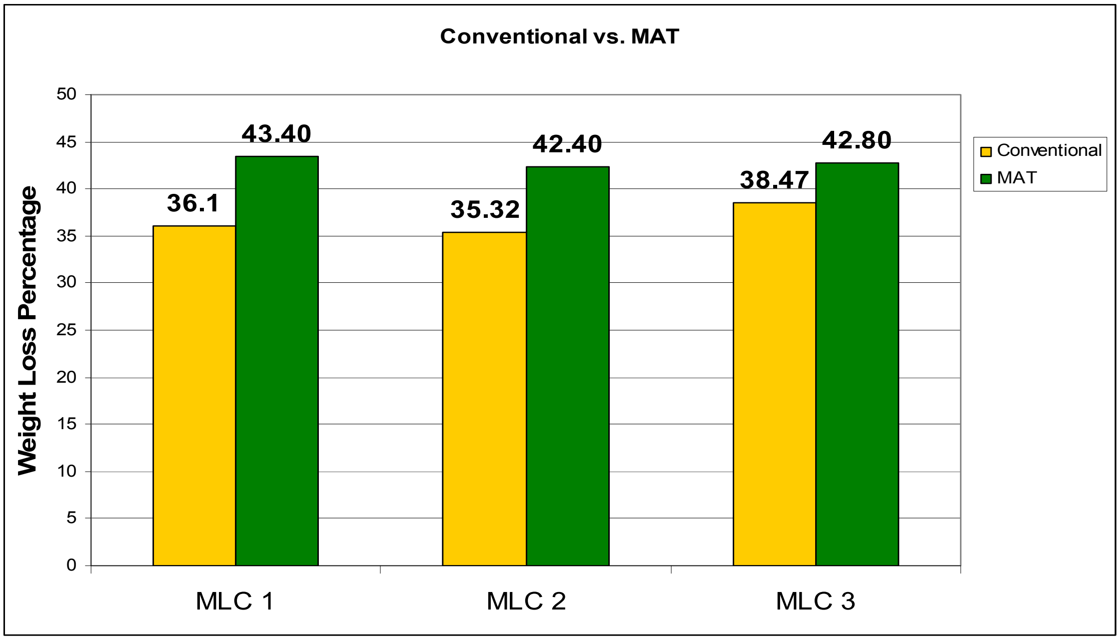


A) B)

One kilogram of limestone in the mullite sagger in the MAT kiln A) pre-calcining and B) post calcining. Note the white color in B) indicating the product has been calcined.

Results and discussion. Overall, the MAT™ runs showed that the addition of microwave energy enhanced the calcining reaction rates compared to conventional heating for all 3 grades of limestone. Evidence of this is shown in Figure 4. In order to compare the affect of microwave energy, the conventional heating portion of both runs was kept the same, e.g. 10 ºC/min to 1200 ºC with a 10 minute dwell. The MAT™ runs had the addition of 1.8 kW microwave energy from the start of the run through the end of the dwell. In Figure 4, the first two columns in the graph are for MLC1. The conventional run showed a weight loss of 36.1%, while the MAT run was 43.4%, which is an increase of 7.3%. Similar increases were also observed for MLC2 and MLC3. This data shows that the microwave power helps to drive the dissociation reactions for all 3 grades of limestone.

Figure 4. Weight Loss Comparison of MAT vs. Conventional



Conventional and MAT runs had a 10 min dwell at 1200°C using 1Kg of limestone. In the MAT runs, microwave energy was applied at 1.8 kW through the duration of the heating and dwell times, which demonstrated an enhanced reaction rate, through higher weight loss.

The difference in weight loss was also observed visually by breaking open the individual limestone samples after calcining to see the core. Unreacted limestone appears gray, where as fully reacted limestone is white. Figure 5 shows images of 1) un-calcined limestone, 2) the un-reacted core of a conventionally processed sample and 3) a MAT™ sample of similar size, where the gray core in the MAT™ sample is significantly smaller than observed in conventionally heated limestone. This is a visual means of corroborating the enhanced reaction in the MAT™ sample.

As discussed above, similar processing conditions were used to compare reaction rates. In order to compared energy consumption, MAT and conventional runs were performed to determine processing parameters which yielded fully calcined material (e.g. weight loss of >43%). Figure 6 shows a conventional run vs. a MAT™ run where both runs had a similar weight loss of 43.5%. The conventional run required a longer dwel (45 min) to achieve the same weight loss as the MAT™ run, which only required a 10 min dwell. This resulted in a 16% energy savings for the MAT™ process. It should be noted that the energy consumption from the microwave portion of the MAT run is small compared to the total energy consumed.

As scale-up studies ensue, it is expected that MAT™ will show even higher energy efficient compared to conventional heating. The reasoning is that the larger the load, the slower it needs to be heated in a conventional kiln due to the limitation of thermal conduction to move the heat through a large mass. The MAT processing is not limited by thermal conduction, and the microwave energy will more efficiently heat a large load.

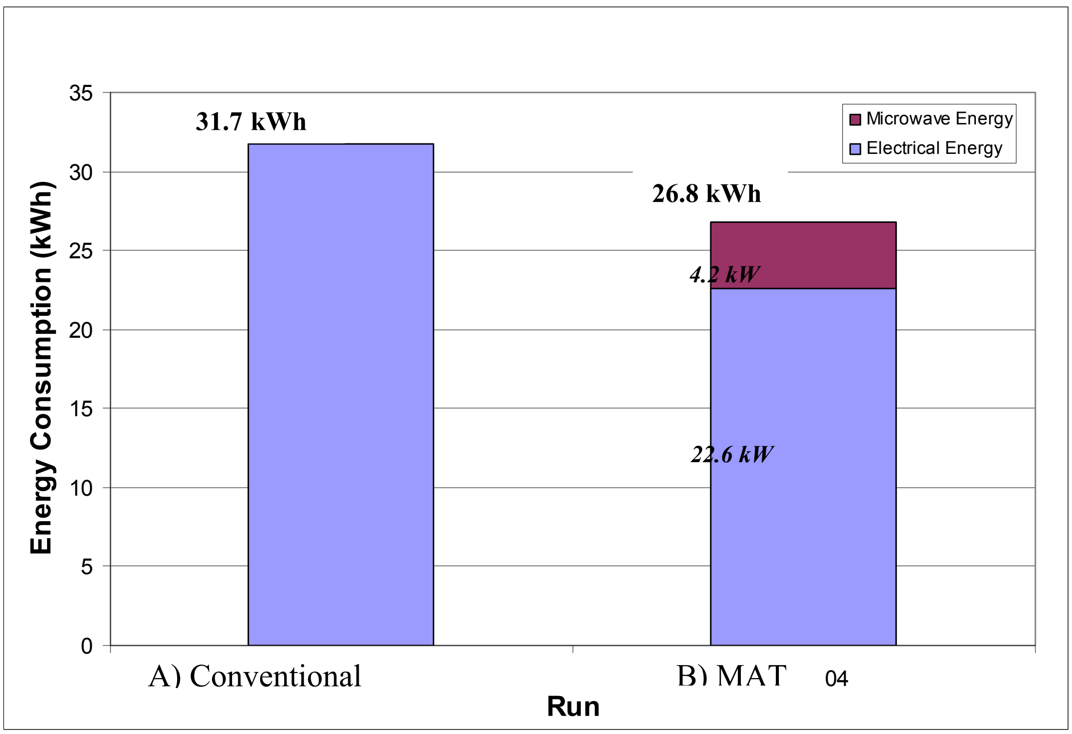
Figure 5. Images of Conventional vs. MAT™ Calcined Limestone for the Same Heating Cycle

A B C

A) Uncalcined limestone B) Conventionally calcined limestone C) MAT calcined limestone

Shows evidence of enhanced calcining rate with MAT™ processing through smaller unreacted (gray) area.

Figure 6. Energy Comparison of Conventional Vs. MAT™ for samples with similar weight loss



This figure shows the energy consumption required to achieve fully calcined 1 kg batch of limestone using A) conventional heating and B) MAT heating . The processing parameters were A) were 1200 ºC for a 45 min dwell and B) 1200 ºC for a 10 min dwell with 1.8 kW microwave energy.

Energy Impact and Market Benefits

Based on the initial results of this study and previous experience with large-scale MAT™ sintering trials (other ceramic materials), a conservative estimate of 50% reduction in energy using MAT™ calcining[5, 6] was applied in the calculations shown in Table I. This project is focused on calcining of limestone for lime, but this same process will also be readily applicable to calcining in cement production.

The estimated energy and environmental benefits are shown in Table I for the year 2020, assuming that 10% of the lime/cement industry implements MAT™ calcining in manufacturing. A ten percent uptake is equivalent to implementation of 16 production size MAT™ calciners, which would be designed in a follow-on, scale-up project.

Table I. Projected Annual Energy and CO_2 Savings for MAT Implementation for Lime and Cement Production for the Year 2020

Year	Energy Savings (Tril BTU/yr)	Environmental Benefit CO_2 (Mlb)	Economic Benefit ($/yr)
2020	24	9.0×10^6	18.7 Mil

Calculations for the total energy used in US cement and lime production for 2008 is based on cement production in tons (88 mil tons[7]), multiplied by the energy required to calcine limestone (4.5 mil BTU/ton). This yielded a total of 396 Tril BTU/year. The same calculation was performed for lime production, based on a production rate of 19.8 mil tons[8], yielding 89 Tril BTU/yr. Therefore, the total energy used in the calcining process for lime and cement industries is 485 Tril BTU/yr.

Ceralink projects that 10% of the market will implement MAT™ processing by 2020, therefore 10% of the total energy consumed in calcining per year (485 Tril BTU/yr x 0.1) is equal to 48.5 Tril BTU/yr. Applying a projected 50% energy savings using MAT™ provides an energy savings of 24.3 Tril BTU/yr for these two industries.

Reduction of CO_2 emissions was calculated based on the reduced energy consumption for calcining. CO_2 reduction will be realized through the decreased amount of coal required for heat generation, since direct microwave heating is more efficient. The reduced coal consumption was calculated by dividing the energy savings (24.3 Tril BTU/yr calculated above) by the amount of energy released from burning 1 short ton of coal (17.6 Mil BTU). The tons of coal saved per year (1.38 Mil) were multiplied by the amount of CO_2 released per ton coal (650 lbs/ton coal[9], to yield total CO_2 saved per year (896 M lbs).

The current cost of coal (8,800 BTU/lb) is $13.60/short ton[10]. The amount of coal saved per year (1.38 M tons) multiplied by the price provides a savings of $18.7Mil/yr.

Market Benefit (US Economy)

The impact of demonstration and commercialization of MAT™ for the lime and cement industries will serve as an important demonstration for many other energy intensive industries. For example, rotary calciners are used in processing metal ores, structural and electroceramic powders, and catalysts. MAT™ kilns can be used to save energy in the high temperature processing of thousands of products, such as refractories, insulators, metal casting molds, and filters. The technology will provide significant benefits for commercial application, but industry needs a large-scale demonstration at a manufacturing site. The successful implementation of a MAT™ rotary lime calciner will lead to MAT™ uptake, decreasing energy and green house gas emissions by 50% for a wide range of high temperature processes.

Conclusions

Ceralink has demonstrated that the concept for using MAT™ as a means to efficiently calcine limestone has merit, due to the fact that MAT™ was shown to enhance the rate of calcining compared to conventional processing. Based on these findings, estimates for large scale MAT™ calcining benefits were calculated, assuming a 10% uptake of MAT™ in manufacturing by the year 2020. This estimate showed that over 24 Tril BTU/yr could be saved, with additional reduction in CO_2 emissions, and significant economic savings. The remainder of this DOE Stage 2 project will lay the groundwork for building a prototype MAT™ calciner in a follow-on project, for large scale MAT™ demonstration.

Acknowledgments

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