REACTION MECHANISMS OF MAGNESIUM SILICATES WITH CARBON DIOXIDE IN MICROWAVE FIELDS

William B. White
Michael R. Silsbee
B Joe Kearns

Materials Research Institute
The Pennsylvania State University
University Park, PA 16802

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ABSTRACT

The objective of the investigation was to determine whether microwave fields would enhance the reactions of CO_2 with silicates that are relevant to the sequestration of carbon dioxide. Three sets of experiments were conducted. (1) Serpentine and CO_2 were reacted directly at one atmosphere pressure in a microwave furnace. Little reaction was observed. (2) Serpentine was dehydroxylated in a microwave furnace. The reaction was rapid, reaching completion in less than 30 minutes. A detailed investigation of this reaction produced an S-shaped kinetics curve, similar to the kinetics from dehydroxylating serpentine in a resistance furnace, but offset to 100 ˚C lower temperature. This set of experiments clearly demonstrates the effect of microwaves for enhancing reaction kinetics. (3) Reactions of serpentine with alkaline carbonates and in acid solution were carried out in a microwave hydrothermal apparatus. There was a greatly enhanced decomposition of the serpentine in acid solution but, at the temperature and pressure of the reaction chamber (15 bars; 200 ˚C) the carbonates did not react. Overall, microwave fields, as expected, enhance silicate reaction kinetics, but higher CO_2 pressures are needed to accomplish the desired sequestration reactions.

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1.0 INTRODUCTION

1.1 Objectives

The proposed research concerns the sequestration of CO_2 by reactions with the magnesium silicates to produce environmentally benign $MgCO_3$.

$$Mg_2SiO_4 + 2\,CO_2 \rightarrow 2\,MgCO_3 + SiO_2$$

$$Mg_3Si_2O_5(OH)_4 + 3\,CO_2 \rightarrow 3\,MgCO_3 + 2\,SiO_2 + 2\,H_2O$$
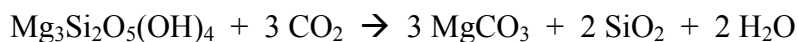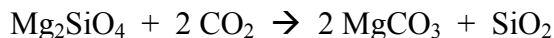
These reactions are thermodynamically favorable but suffer from exceeding slow reaction rates. Research by others has shown that reaction rates can be accelerated by use of aqueous carbonate solutions and high CO_2 pressures. The proposed research offers an alternative rate enhancement mechanism through the use of microwave fields.

1.2 Scope of Work and Task List

The Scope of Work and list of tasks are taken directly from the original proposal. Progress and accomplishments on the tasks are then summarized in the sections that follow.

Two series of experiments were proposed. In series (1) a gas stream of CO_2 containing variable amounts of water vapor would be reacted directly with the magnesium silicates at modest temperatures in a microwave cavity. The objective would be to determine the rate of reaction as a function of temperature, water vapor partial pressure, magnesium silicate particle size, and microwave power. In series (2) experiments, aqueous solutions would be reacted with CO_2 under pressures up to 80 bars and temperatures up to 200 C in a Teflon high pressure reactor in a microwave field. One objective of this portion of the research would be to compare the efficacy of microwave processing with similar compositions, temperatures and pressures without microwaves.

Task 1. Adapt existing microwave equipment for continuous gas stream reaction.

Task 2. React magnesium silicates with wet CO_2 at a sequence of water contents, temperatures, and microwave power levels.

Task 3. Characterize products from Task 2 experiments and determine rates of reaction.

Task 4. Construct equipment for microwave hydrothermal experiments.

Task 5. React silicates in aqueous alkali carbonate solutions at autogeneous steam pressures in the microwave field.

Task 6. React silicates in aqueous alkali carbonate solutions at high CO_2 pressures in the microwave field.

Task 7. React silicates under similar conditions to Tasks 5 and 6 but in absence of microwave field

Task 8. Characterize results of experiments in Tasks 5, 6 and 7 and compare rates and reaction mechanisms.

2.0 EXPERIMENTAL

2.1 Construction of Microwave Furnace

The project was able to take advantage of the Center for Microwave Processing already in existence in the Materials Research Institute. The project was assigned use of an Amana Radrange commercial microwave furnace producing 2.0 kW of microwave energy at a frequency of 2.45 GHz. All that was required was to modify the furnace for use in the magnesium silicate/gas phase reactions.

A horizontal mullite tube was installed through the middle of the furnace (Fig. 1). The tube was insulated with Fiberfrax in the hot zone in the middle of the furnace. Samples were placed in alumina boats in the hot zone. Temperatures were measured with an infrared pyrometer which observed the sample through a window placed on the end of the mullite tube on the outside of the furnace. Fittings placed on the end of the mullite tube allowed selected gas mixtures to be passed through the furnace so that the
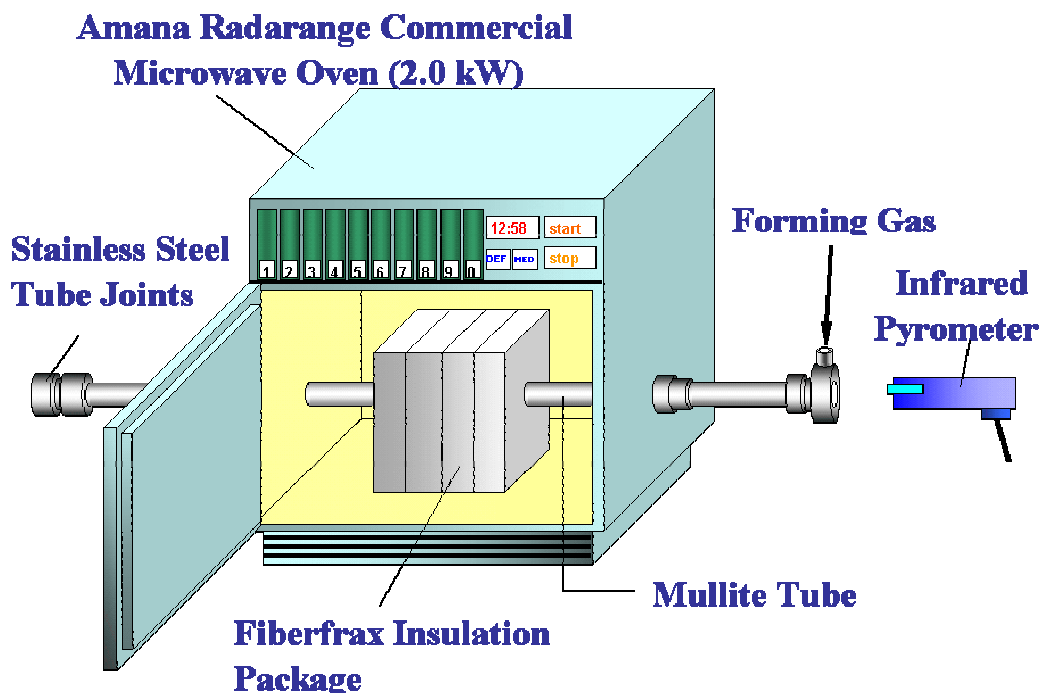

Figure 1. Drawing of microwave furnace.

samples were continuously bathed in a gas atmosphere of known composition. This arrangement proved to be very effective and all of the solid/gas microwave experiments were performed with this equipment.

2.2 Microwave Hydrothermal Apparatus

The objective of this task was to devise an apparatus that would allow hydrothermal reactions in a microwave field. For this purpose we used a microwave digester such as used by analytical chemists for taking incalcitrant samples into solution. The pressure vessel is composed of Teflon. It will tolerate pressures to around 15 bars and temperatures to 200 ˚C. The apparatus is shown in Figure 2.

Figure 2. Microwave reaction chamber for hydrothermal experiments.

The Teflon pressure vessels are chemically resistant so that strongly basic or strongly acidic solutions can be reacted. The temperature is measured directly within the chamber but the pressure must be calculated from the known thermodynamic properties of water. Pressure can be varied by varying the volume of solution placed in the reaction vessel. The pressure vessel is shown in Fig. 3
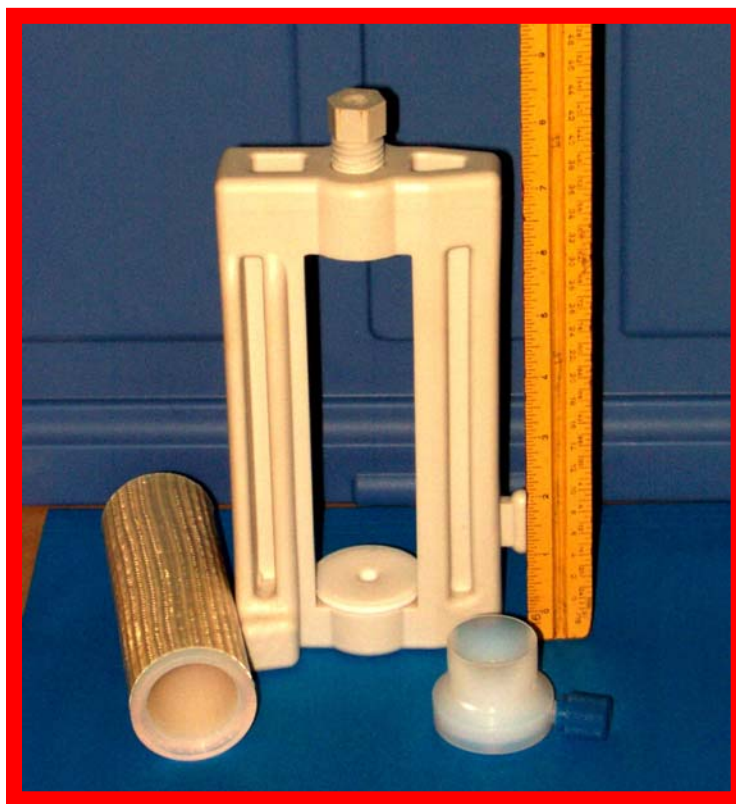
Figure 3. Teflon microwave hydrothermal pressure vessel is disassembled form.

3.0 RESULTS AND DISCUSSION

3.1 Direct Reaction of Serpentine and CO_2

The main thrust of the investigation was the direct reaction of serpentine with CO_2 in the microwave furnace. Three different serpentines were available referred to by their sources as Welch, Wards, and Cedar Hill. Their mineralogy is listed in Table 1.The Welch serpentine was mostly used in the direct carbonation experiments.

The carbonation reaction

$$Mg_3Si_2O_5(OH)_4 \; + \; 3\,CO_2 \; \rightarrow \; 3\,MgCO_3 \; + \; 2\,SiO_2 \; + \; 2\,H_2O$$
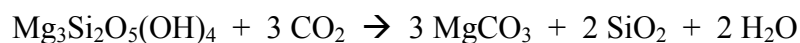
Depends on both the CO_2 partial pressure and water vapor pressure as well as the temperature. The equilibrium constant for the reaction is

$$\frac{P_{H_2O}^2}{P_{CO_2}^3} = K_{serp}$$

Table 1. Properties of Serpentine Starting Materials

Sample	Mineralogy
Welsh	Lizardite + minor dolomite
Wards	Chrysotile + minor antigorite
Cedar Hill	Lizardite + minor antigorite

It is also necessary to consider the stability of magnesite because at high temperatures magnesite will decompose into periclase (MgO) and release the CO_2. The reaction is

$$MgCO_3 \rightarrow MgO + CO_2$$

This reaction also depends on both temperature and CO_2 pressure.

$$P_{CO_2} = K_{mag}$$

Equilibrium constants for both reactions were calculated from available thermodynamic data (R.A. Robie and B.S. Hemingway, 1995). These allowed the plotting of univariant reaction curves for both reactions (Fig. 4).

The univariant reaction curve for the carbonation reaction was calculated using a fixed partial pressure of water of 0.029 bars, the saturation vapor pressure of water at ambient temperatures. These curve define a minimum CO_2 pressure and a maximum temperature at which the carbonation reaction can take place.

Half gram quantities of serpentine were reacted in the microwave furnace in an atmosphere of CO_2 gas that has been saturated with water vapor at various temperatures over the range of 375 to 650 ˚C. Reaction products were characterized by x-ray diffraction and by infrared spectroscopy. Although traces of carbonate minerals were discernable in the x-ray diffraction patterns, it was entirely possible that these represented traces of carbonate minerals present in the original serpentine samples.
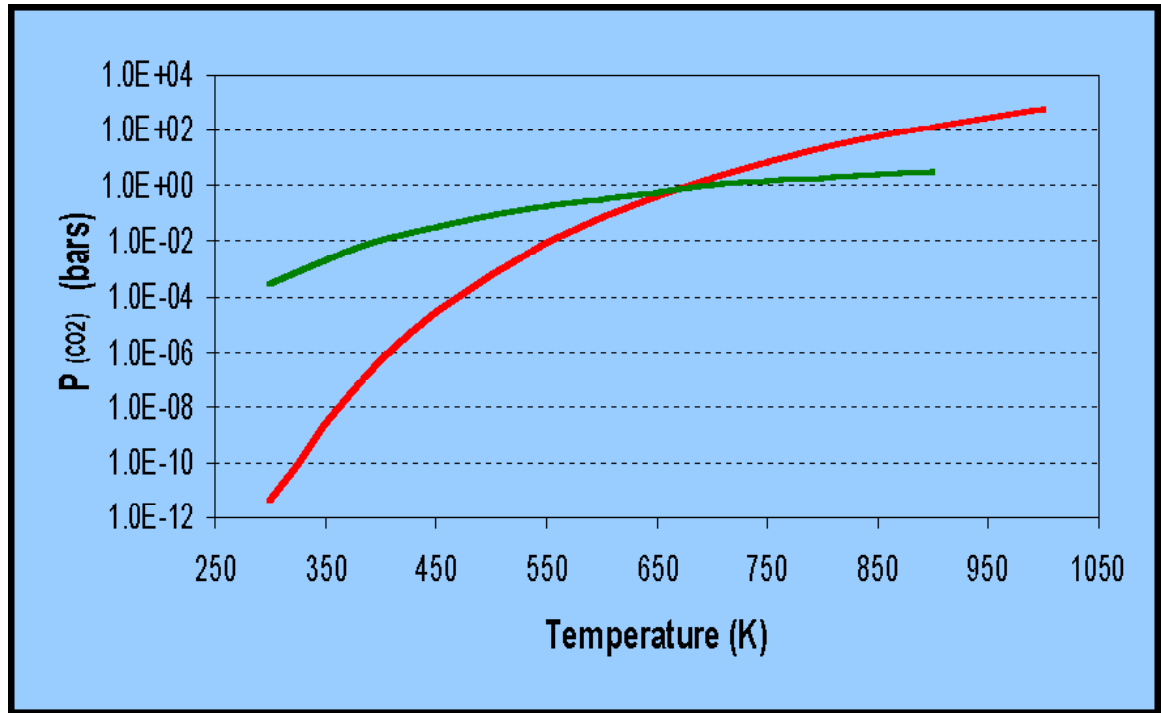
Figure 4. Univariant reaction curves for the carbonation of serpentine (green curve) and the decomposition of magnesite (red curve).

The furnace design allowed only atmospheric pressure for the gases. Given the limitations set by the thermodynamics, it was not possible to raise the temperature high enough to drive the carbonation reaction. It would be necessary to conduct microwave enhanced reactions at higher pressures.

3.2 Dehydroxylation of Serpentine

The influence of the microwave field was most pronounced in the dehydroxylation of serpentine. At somewhat higher temperatures than those involved in the carbonation reactions, serpentine breaks down into forsterite, Mg_2SiO_4 and silica. The reaction is

$$2\ Mg_3Si_2O_5(OH)_4\ \rightarrow\ 3\ Mg_2SiO_4\ +\ SiO_2\ +\ 4\ H_2O$$

There was a certain temperature required for the onset of the reaction. As the temperature increased, the reaction proceeded rapidly to completion. At a fixed time of 30 minutes, the fraction of serpentine (or olivine formed) was described by a characteristic S-shaped (or Avrami) type kinetics curve (Fig. 5). The kinetics curve for the reaction in the microwave furnace was compared with the dehydroxylation reaction for serpentine in a conventional resistance-heated furnace. The reaction curves were
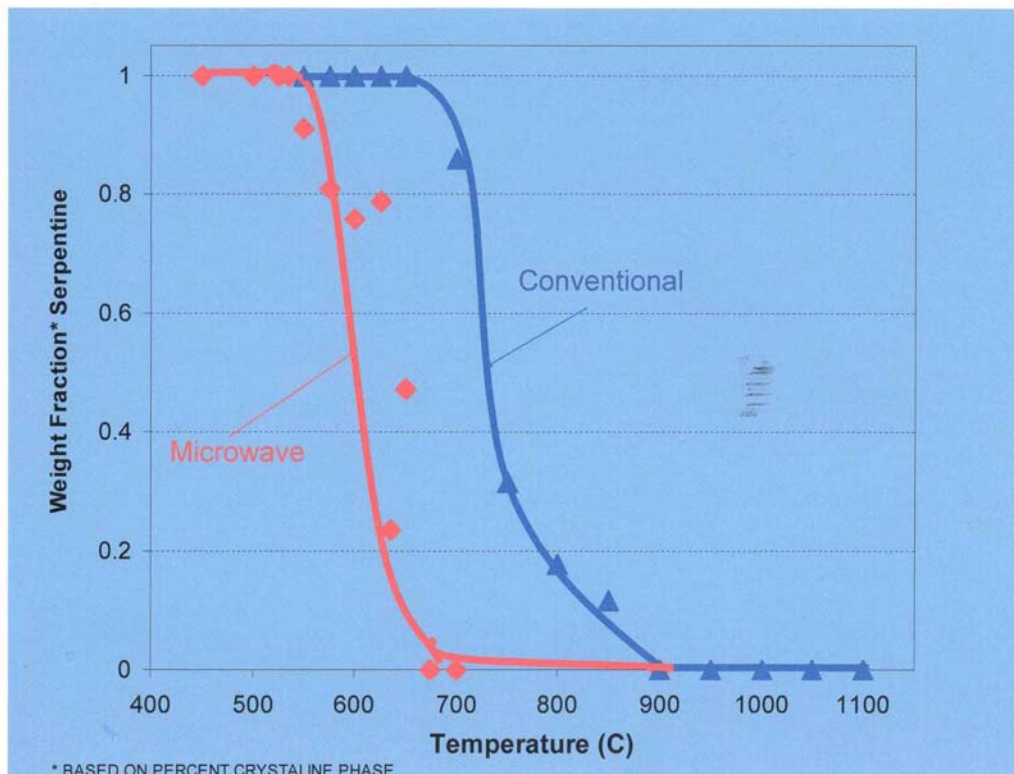
Figure 5. Rate curves for the dehydroxylation of serpentine comparing microwave-
       assisted reaction with reaction in conventional resistance-heated furnace

similar but the microwave-assisted kinetics curve was offset about 100 ˚C to lower
temperature. As found in many other experiments, microwave assisted reactions tend to
be faster and/or require less thermal activation that the same reaction by thermal
activation alone.

        This set of experiments was followed up in considerable detail and the results
prepared for publication. The manuscript is attached as an appendix to this report.
Completed references comparing these experiments with previous research is also given
in the appendix.

3.3 Microwave Hydrothermal Experiments

        The microwave digester described above was used in two series of experiments to
investigate the reaction of serpentine with a variety of fluids. The Teflon reaction vessel
allows a great range of solutions but limits pressure and temperature to about 15
atmospheres and 200 ˚C

In the first series of experiments Cedar Hill serpentine was reacted with alkali carbonates:

Serpentine + 1 M Na_2CO_3
Serpentine + 1 M $NaHCO_3$
Serpentine + 1 M NaOH + 0.64 M $NaHCO_3$
Serpentine + 1 M NaCl + 0.64 $NaHCO_3$

These mixtures were reacted for various periods of time and the products examined for the formation of carbonate minerals. In these alkaline solutions no reaction products were found.

In the second series of experiments, serpentine was reacted with low pH solutions achieved with HCl. Digestion of the serpentine was extensive with some formation of forsterite, Mg_2SiO_4, but with an amorphous mass as the bulk of the reaction product. There was extensive extraction of magnesium into solution but relatively little silica (Fig. 6)
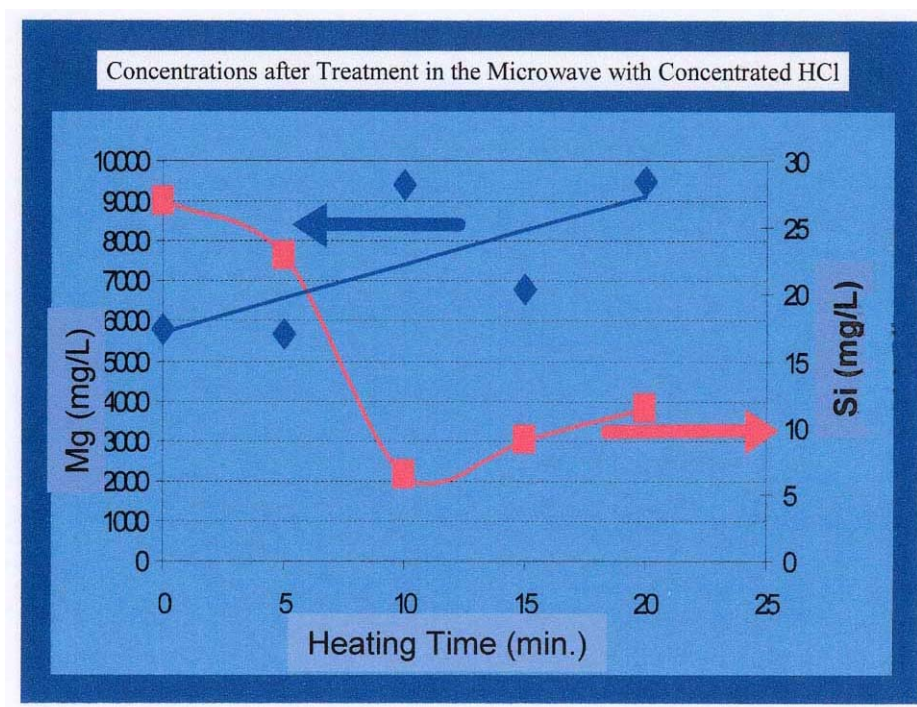

Figure 6. Uptake of magnesium and silicon following microwave hydrothermal digestion of serpentine in low pH solution.

Like the direct carbonation experiments, microwave hydrothermal experiments enhance reaction rates. However, it appears that higher CO_2 pressures will be necessary for useful carbonation reactions to proceed.

4.0 CONCLUSIONS

Overall, the exploratory study to investigate the role of microwave enhancement of silicate reaction rates reduces to two main conclusions:

(1) Reaction rates in microwave fields are substantially faster or alternatively react at lower temperatures than the same reactions driven by conventional thermal heating.. It was convenient to measure rates at variable temperature and constant time with the result that serpentine dehydroxylation occurred about 100 ˚C lower than thermally driven reactions.

(2) Given the univariant reaction curve between serpentine and CO_2 to form magnesite, it appears that future experimentation will require CO_2 pressures higher than those accessible in the present experiments. A high pressure microwave hydrothermal could be designed.

5.0 REFERENCES

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Appendix

ACCELERATION OF SERPENTINE DEHYDROXYLATION KINETICS IN MICROWAVE FIELDS

Michael R. Silsbee, B. Joe Kearns and William B. White

Acceleration of Serpentine Dehydroxylation Kinetics in Microwave Fields

Michael R. Silsbee*, B. Joe Kearns and William B. White*

Materials Research Institute, The Pennsylvania State University, University Park, PA

16802

As part of a study of the use of microwave enhancement of reaction kinetics for sequestration of CO_2 by reaction with serpentine, the kinetics of the dehydroxylation reaction of serpentine was determined. The reaction is

$$2\ Mg_3Si_2O_5(OH)_4 \ \rightarrow \ 3\ Mg_2SiO_4 \ + \ SiO_2 \ + \ 4\ H_2O$$

X-ray diffraction patterns revealed the disappearance of serpentine as the reactions proceeded and the appearance of forsterite, Mg_2SiO_4, as the only crystalline phase. However, quantitative X-ray diffraction suggests that up to 90% of the reaction product is non-crystalline. The rate curve for this reaction exhibits a characteristic S-shape or Avrami form. Comparison with the rate curve obtained by conventional thermal reaction shows that the microwave assisted reaction occurs about 100 ˚C lower.

*Member, American Ceramic Society

Author to whom correspondence should be addressed. E-mail: wbw2@psu.edu

I. Introduction

Substantial efforts are being made to devise technologies for the reduction of greenhouse gases in the atmosphere[1]. One of the more environmentally desirable technologies for the sequestration of CO_2 is the reaction of CO_2 in stack gases with serpentine, forsterite and related ultramafic minerals to immobilize the CO_2 as the benign compound magnesite[2-4]. The reaction for serpentine is

$$Mg_3Si_2O_5(OH)_4 + 3\ CO_2 \rightarrow 3\ MgCO_3 + 2\ SiO_2\ 2\ H_2O$$
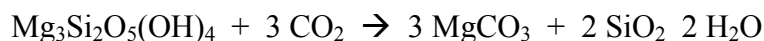
The thermodynamics of the forward reaction are favorable up to 427 C for a CO_2 pressure of one atmosphere and to higher temperatures at higher CO_2 pressures. However, the reaction rate of the gas/solid reaction is extremely sluggish at all temperatures below the thermodynamic phase boundary. To circumvent the slow reaction rates, a variety of high pressure reaction chambers using solvents have been devised[5-7].

The research reported in this paper deals with the question of whether microwave fields enhance reaction rates when applied to silicate reactions. Microwave processing has been widely applied to enhance sintering and other ceramic reactions and there have been some considerations of mineral processing[8,9]. Whether the acceleration of ceramic reactions is simply the result of more effective heat transfer or whether there are effects of the microwave field itself remains an open question. Recent experiments with ferrites suggest that there is more to microwave reactions than heat transfer[10-12].

In the present paper we report the results of a series of experiments on the dehydroxylation of serpentine in which we compare the reaction kinetics in a microwave field with kinetics under conventional heating. The reaction is

$$2 \ Mg_3Si_2O_5(OH)_4 \ \rightarrow \ 3 \ Mg_2SiO_4 \ + \ SiO_2 \ + \ 4 \ H_2O$$

The reaction products are forsterite, which appears in a well-crystallized form easily

recognized by its x-ray powder pattern, and silica which does not appear crystalline. The

equilibrium constant for the reaction is

$$K \ = \ P_{H_2O}^4$$

Values for K at various temperatures were calculated from the thermochemical data of

Robie and Hemingway[13] using both quartz (K = 1.039 x 10^{-23} at 300 K) and silica glass

(K = 6.536 x 10^{-25} at 300 K) as the silica phase. The univariant reaction curves are very

similar (Fig. 1). The minimum temperature at which the reaction should proceed depends

on the water vapor partial pressure as indicated on figure 1.

II. Experimental Methods

(1) Starting Materials

Samples of serpentine were obtained from three sources. Each was characterized

by X-ray diffraction (Table 1). The starting materials were ground to a particle size in

the range of 20 - 100 μm. The dehydration characteristics of the starting materials were

checked by thermogravimetric analysis. The dehydration curves are similar but not

identical (Fig. 2).

(2) Furnaces

The microwave furnace was a commercial device (Amana Radarange) producing

2.0 kW of microwave energy at 2.45 GHz. A horizontal mullite tube was installed

through the middle of the furnace (Fig.3). The tube was insulated with Fiberfrax in the

hot zone in the middle of the furnace. Samples were placed in alumina boats in the hot

zone. Temperatures were measured with an infrared pyrometer which observed the

sample through a window placed on the end of the mullite tube on the outside of the furnace. A gas atmosphere consisting of H_2O-saturated CO_2 was passed through the furnace during the experiments. This gives a water vapor partial pressure of approximately 2.5 kPa.

For conventional firing, a resistance-heated furnace was used. It also contained a horizontal mullite tube. Temperatures were determined with a thermocouple placed near the samples. The furnace atmosphere was also water-saturated CO_2.

(3) Experimental Procedures

About 0.5 grams of powdered serpentine were placed in alumina boats which were in turn placed in the hot zone of either the microwave or the resistance furnace. Power was applied to the microwave system and the temperature tracked by the optical pyrometer. When the sample reached the desired temperature, the temperature was held constant for the prescribed time after which the power was shut off and the furnace allowed to cool. Samples were not quenched. Figure 4 shows a typical firing cycle. Firing in the resistance-heated furnace followed similar procedures.

After reaction, the samples were characterized by x-ray powder diffraction and by scanning electron microscopy. The intensities of the 100 (d = 7.300 Å) reflection of serpentine and the 020 (d = 5.102 Å) reflection of olivine were used for quantitative analysis of the progress of the reaction. The reaction products were packed into hollow slides, and measured carefully for quantitative line intensities. The x-ray peak intensities of the reaction products were compared with the peak intensities of end-member serpentine and end-member olivine to determine the progress of the reactions.

III. Results

(1) Characterization

The progress of reaction was tracked by changes in the x-ray diffraction patterns (Fig.5). The patterns shown in figure 5 were all obtained on material that had been reacted in the microwave field for 30 minutes at the temperatures shown. The characteristic powder pattern of serpentine persists up to 535 ˚C. At higher temperatures, the serpentine pattern is replaced by the pattern of olivine. There is no evidence for crystalline intermediate phases in the diffraction patterns. The silica component in the dehydroxylation reaction does not appear as a crystalline phase. Further, considerations of the quantitative intensities of the diffraction peaks suggests that olivine can account for only 10 – 20 percent of the reaction product. The remainder must be present in non-crystalline form.

A comparison of the microstructures resulting from the dehydroxylation reaction is shown in figures 6 and 7. The same crushed Ward's serpentine was used as a starting material. The intent was to compare the structures at the same location on the dehydroxylation curve so the microwave processed samples were prepared at 600 ˚C, the beginning of the reaction, at 650 ˚C, about the mid-point in the reaction, and at 700 ˚C, near the end of the reaction. To get a comparable sequence of images for serpentine dehydroxylated by conventional heating, the images were obtained from materials heated at 700, 750 and 800 ˚C respectively.

The microwave-reacted material retains much of its original texture in spite of the rearrangement of the mineralogy. In contrast, the conventionally heated material shows considerable grain growth. The material completely reacted by microwave was

considerably more compact that the corresponding material reacted by conventional firing.

The BET surface areas were compared for materials prepared by the two reaction techniques (Table 2). The surface areas of the microwave-reacted materials are smaller than those of materials prepared by ordinary firing.

(2) Kinetics

The relative rates of reaction can be compared either as a function of time at constant temperature or as a function of temperature at constant time. For both approaches, the technique was to compare intensities of selected x-ray peaks and normalize these to a fraction of serpentine in the sample.

Remaining serpentine as a function of time at 650 ˚C shows a pronounced contrast between microwave heating and conventional heating (Fig. 8). After 60 minutes in the conventional furnace at 650 ˚C, only a few percent of the serpentine had dehydrated. At the same temperature in the microwave furnace, most of the serpentine had lost its hydroxyl groups after only 15 minutes and at 60 minutes all serpentine had been dehydroxylated.

Reaction rates were compared at a fixed time of 30 minutes (Fig. 9). Both methods of heating produced the expected S-shaped or Avrami type rate curve. However, the curve for conventional heating is offset by about 100 degrees from the microwave heating curve. Both curves show an abrupt onset of dehydroxylation with reaction going to completion over a relatively narrow temperature range.

An obvious consideration is whether the difference in rate curves arises simply from lag in heat flow. The microwave samples would be heated uniformly through the

mass of the powder so that temperature rise would be rapid and the dehydroxylation reaction begin immediately throughout the mass of the sample. Because heat flow in the conventional furnace is from the outside of the sample and the powdered silicate is a good thermal insulator, one might expect the temperature rise in the central portions of the sample to lag and thus the effective reaction time at temperature would be shorter. As one test this possibility, a thermocouple was buried in the center of the mass of powder so that the temperature at the core of the sample could be monitored directly. It was found that, for the size of samples used in this investigation, there is a lag of about 10 minutes before the core of the sample came to full reaction temperature. It was not possible to make a similar measurement in the microwave chamber. As a second test, the reactions were carried out with 0.1, 0.2, 0.5, and 1.0 grams of powder. The reaction rates were essentially the same and independent of the amount of material in the furnace. Overall, it does not seem that the offset between the two reaction curves are primarily an experimental artifact.

V. Conclusions

A comparison of the reaction rates for the dehydroxylation of serpentine between microwave driven reaction and ordinary furnace heating shows that the microwave driven reaction is substantially faster. Both techniques give the expected S-shaped reaction curve but in the microwave driven system the mid-point of the reaction curve is shifted to lower temperatures by about 100 ˚C. The microwave reacted product is of smaller particle size but has a lower surface area then the material prepared by conventional firing.. It appears that microwave processing might be a useful approach to preparing precursor materials for carbon sequestration reactions.

Acknowledgements

We thank David Dahlen of the Albany Research Center for providing the Cedar Hill serpentine.

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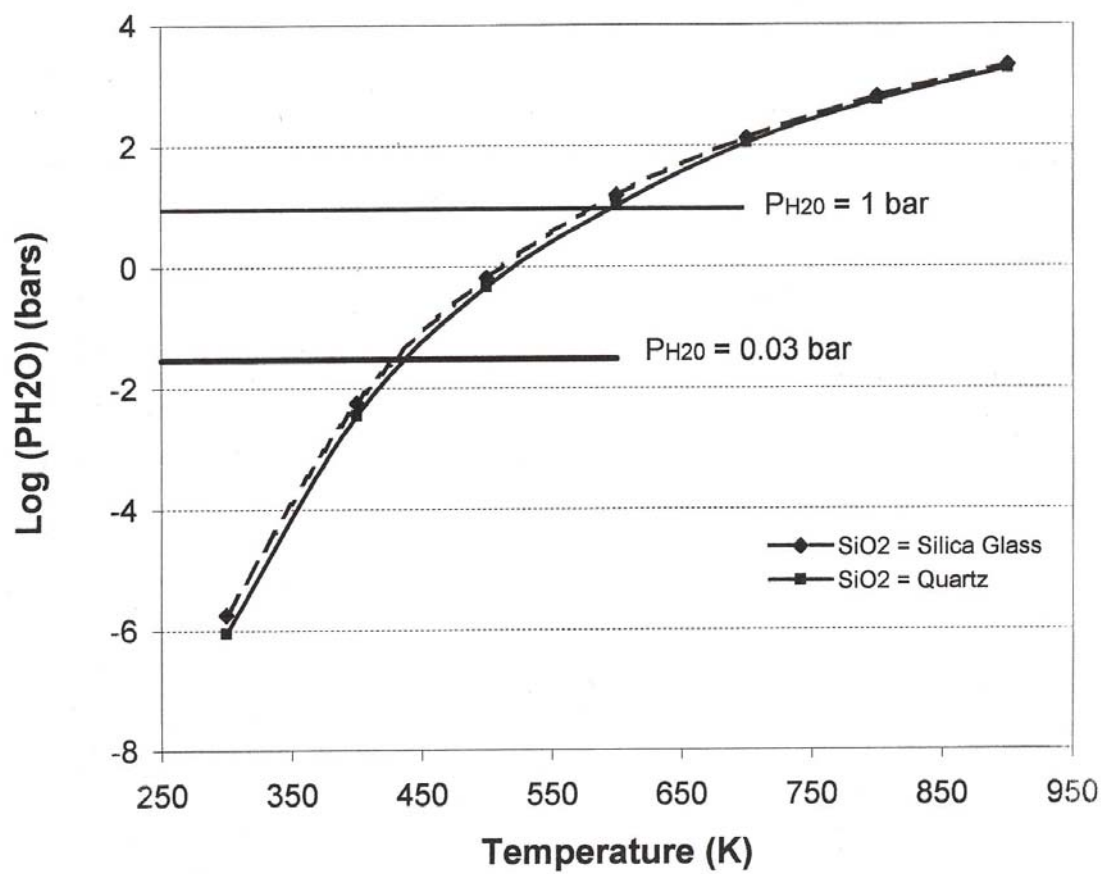
Table I. Properties of Serpentine Starting Materials

Sample	Mineralogy
Welsh	Lizardite + minor dolomite
Wards	Chrysotile + minor antigorite
Cedar Hill	Lizardite + minor antigorite

Table II. BET Surface Areas After Processing (in units of m^2/gram)

Temperature (C)	Conventional	Microwave
600		2.45
650		3.03
700	4.19	0.37
750	2.37	
800	6.95	

Legends for Figures

Fig. 1 Univariant phase boundary for the reaction $2\ Mg_3Si_2O_5(OH)_4 \rightarrow 3\ Mg_2SiO_4 +$

$SiO_2 + 4\ H_2O$ as a function of water vapor partial pressure. Calculations with

two choices of SiO_2 phase are shown.

Fig. 2. Thermogravimetric curves for the three samples of serpentine used in the

dehydroxylation experiments.

Fig. 3 Schematic drawing of the microwave furnace.

Fig. 4 Time-temperature profile for microwave heating chamber.

Fig. 5 Sequence of x-ray diffraction patterns for 30 minute dehydroxylation of serpentine

at various temperatures in a microwave field.

Fig. 6 SEM images of Ward's serpentine after firing in a microwave field for 30 minutes

at the temperatures indicated.

Fig. 7 SEM images of Ward's serpentine after firing in a resistance furnace for 30

minutes at the temperature indicated.

Fig. 8 Rate curves for the dehydroxylation of serpentine at 650 ˚C in a conventional

resistance furnace and in a microwave furnace.

Fig. 9 Rate curves for the dehydroxylation as a function of temperature at a constant time
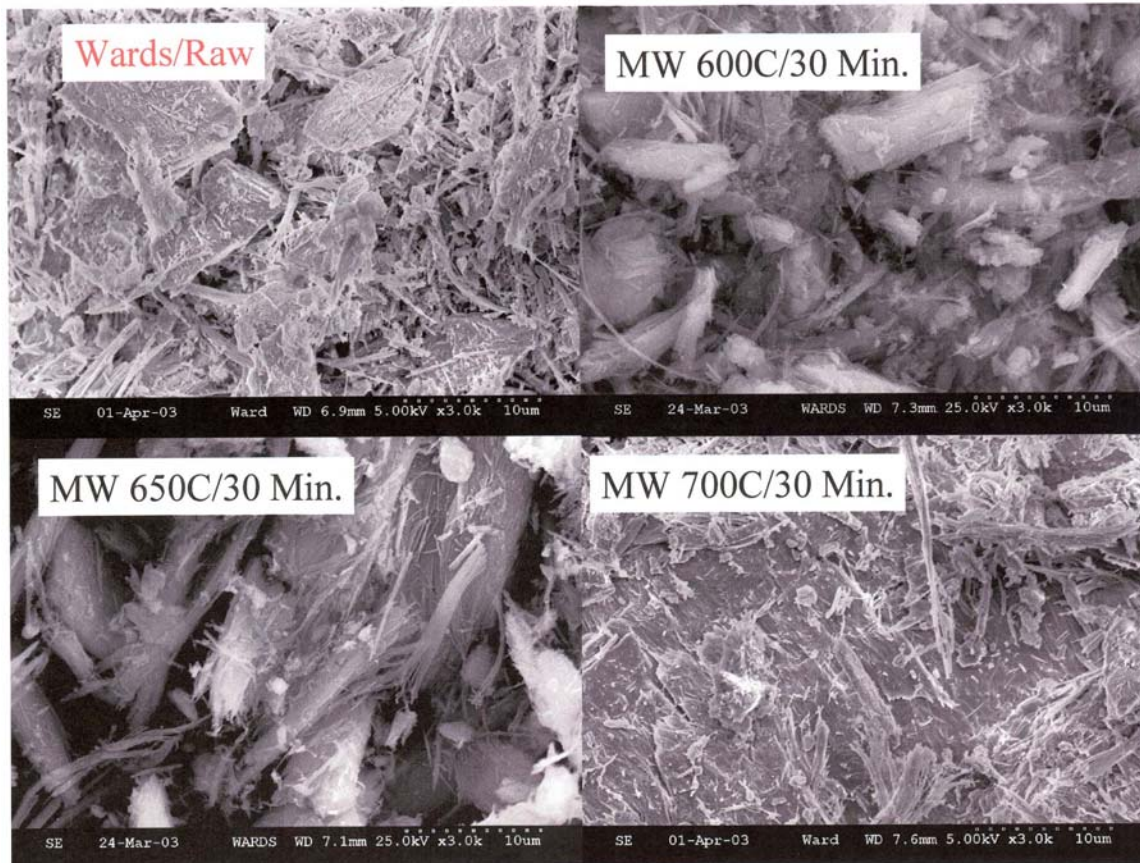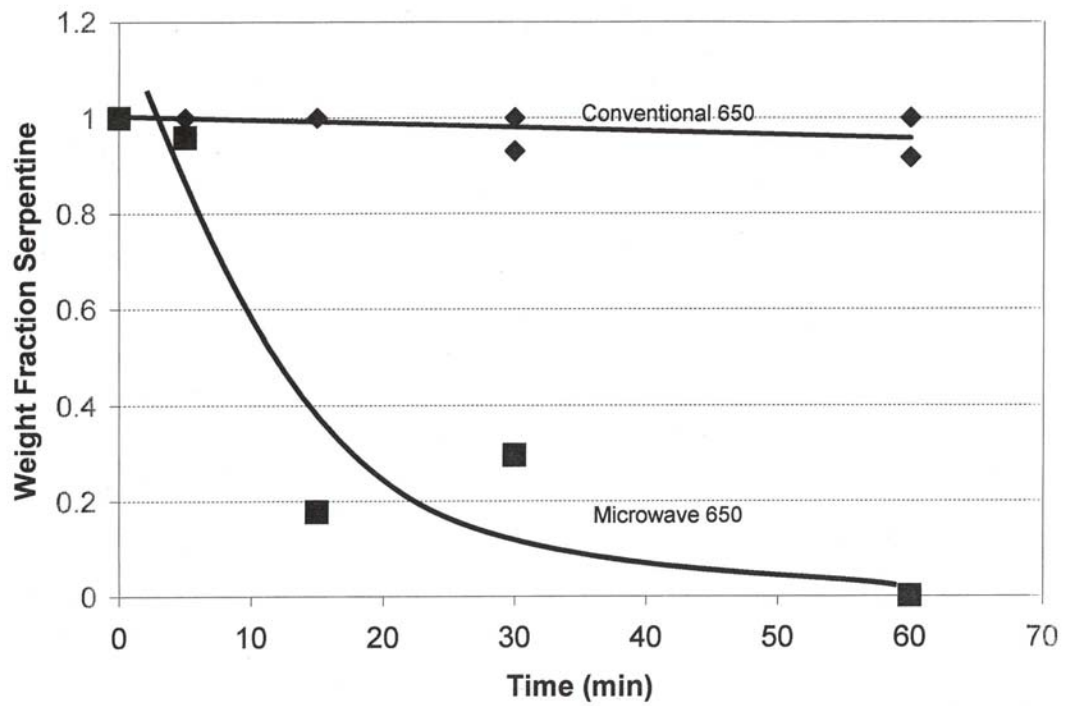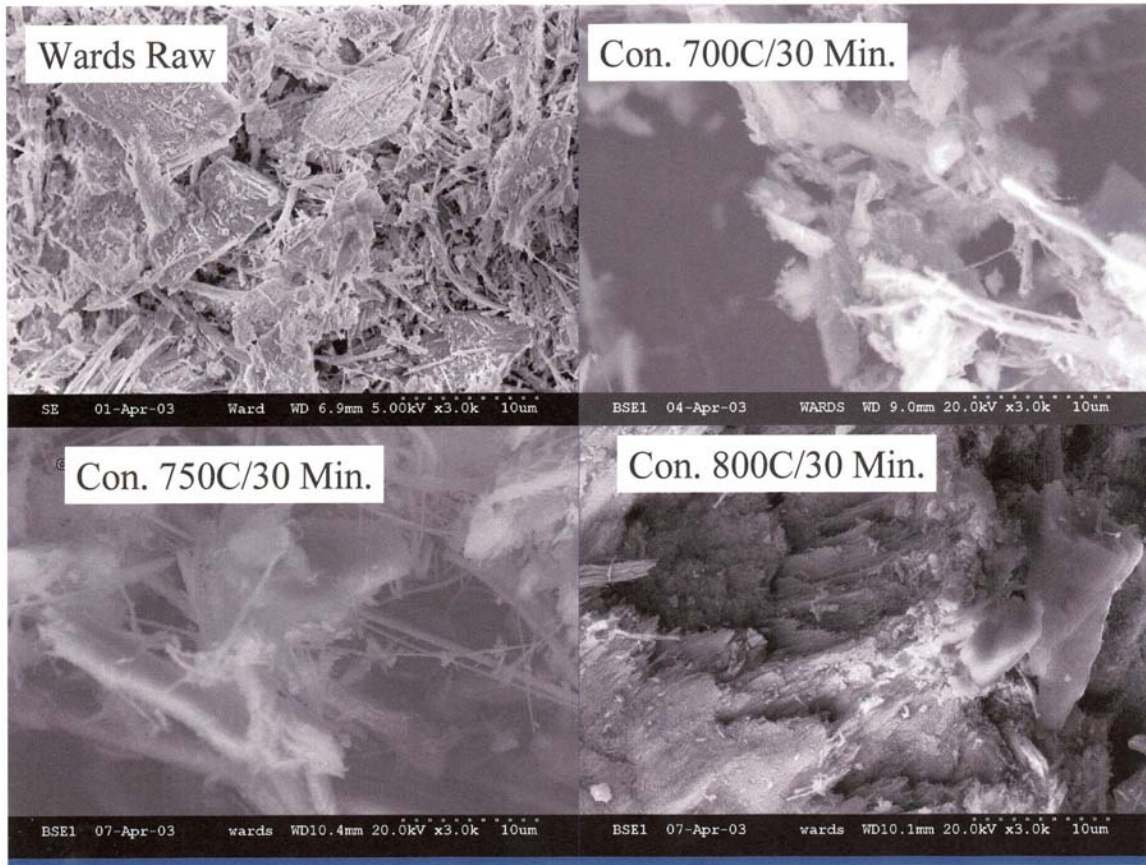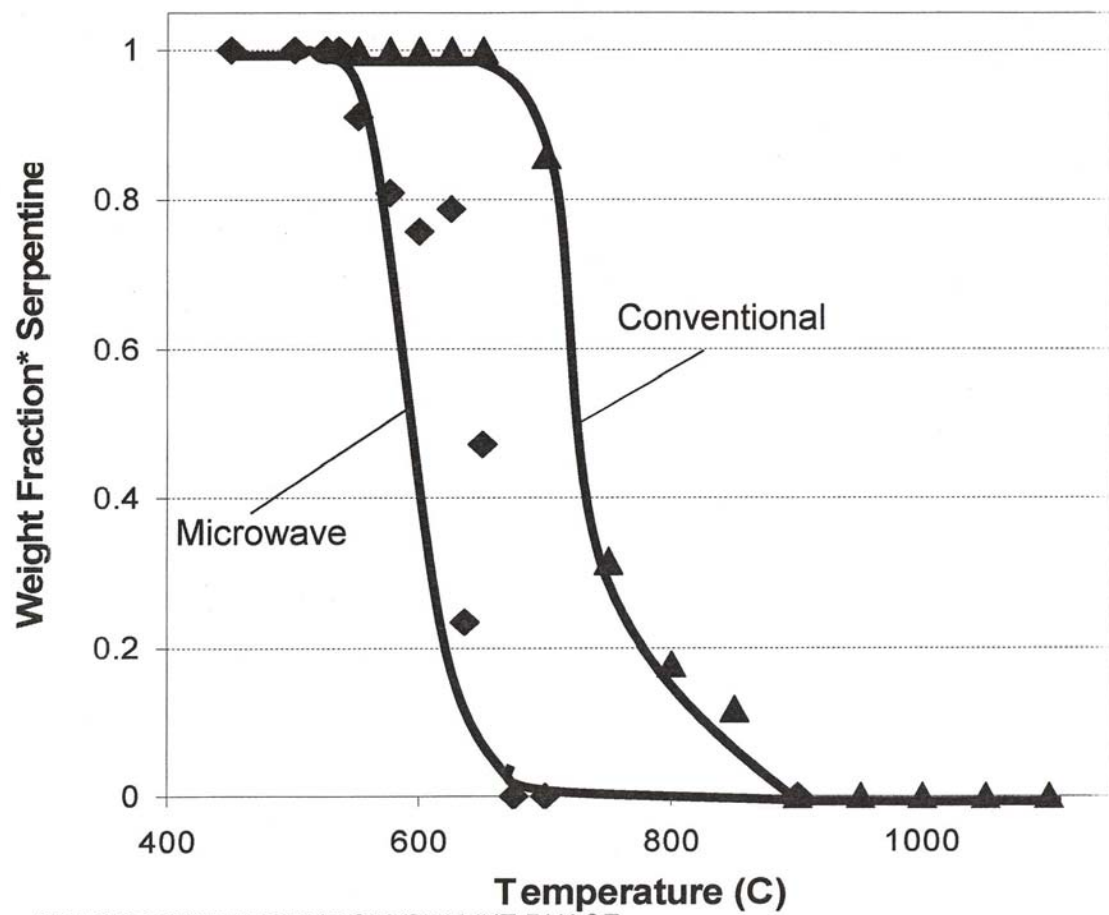
of 30 minutes.
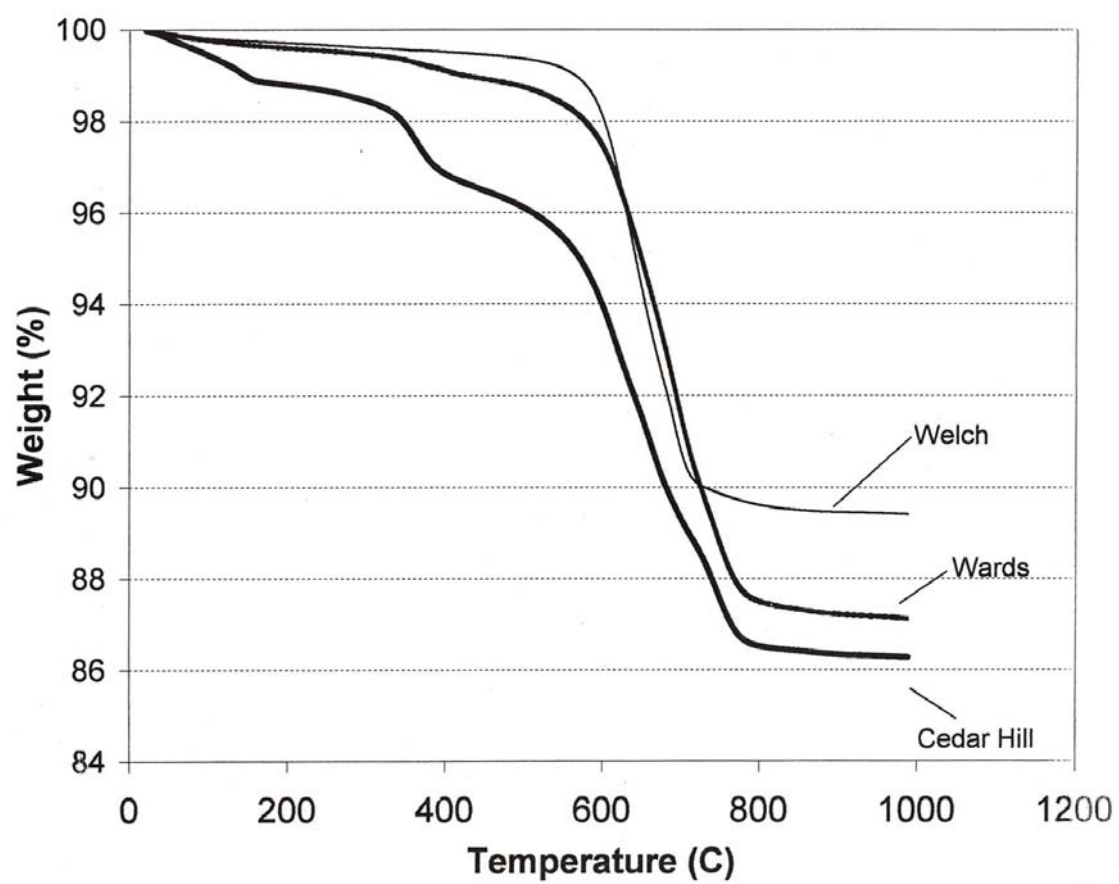
Scheme of the Tube Microwave Processing Setup

Amana Radarange Commercial Microwave Oven (2.0 kW)

Stainless Steel Tube Joints

Forming Gas

Infrared Pyrometer

Mullite Tube

Fiberfrax Insulation Package

Wards Raw — SE 01-Apr-03 Ward WD 6.9mm 5.00kV x3.0k 10um

Con. 700C/30 Min. — BSE1 04-Apr-03 WARDS WD 9.0mm 20.0kV x3.0k 10um

Con. 750C/30 Min. — BSE1 07-Apr-03 wards WD10.4mm 20.0kV x3.0k 10um

Con. 800C/30 Min. — BSE1 07-Apr-03 wards WD10.1mm 20.0kV x3.0k 10um

* BASED ON PERCENT CRYSTALINE PHASE