

**SIMULTANEOUS MECHANICAL AND HEAT ACTIVATION: A NEW ROUTE TO
ENHANCE SERPENTINE CARBONATION REACTIVITY AND LOWER CO₂
MINERAL SEQUESTRATION PROCESS COST**

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ABSTRACT

Coal can support a large fraction of global energy demands for centuries to come, *if* the environmental problems associated with CO₂ emissions can be overcome. Unlike other candidate technologies, which propose long-term storage (e.g., ocean and geological sequestration), mineral sequestration permanently disposes of CO₂ as geologically stable mineral carbonates. Only benign, naturally occurring materials are formed, eliminating long-term storage and liability issues. Serpentine carbonation is a leading mineral sequestration process candidate, which offers large scale, permanent sequestration. Deposits exceed those needed to carbonate all the CO₂ that could be generated from global coal reserves, and mining and milling costs are reasonable (~\$4 to \$5/ton). Carbonation is exothermic, providing exciting low-cost process potential. The remaining goal is to develop an economically viable process. An essential step in this development is increasing the carbonation reaction rate and degree of completion, without substantially impacting other process costs. Recently, the Albany Research Center (ARC) has accelerated serpentine carbonation, which occurs naturally over geological time, to near completion in less than an hour. While reaction rates for natural serpentine have been found to be too slow for practical application, both heat and mechanical (attrition grinding) pretreatment were found to substantially enhance carbonation reactivity. Unfortunately, these processes are too energy intensive to be cost-effective in their present form.

In this project we explored the potential that utilizing power plant waste heat (e.g., available up to ~200-250 °C) during mechanical activation (i.e., thermomechanical activation) offers to enhance serpentine mineral carbonation, while reducing pretreatment energy consumption and process cost. This project was carried out in collaboration with the Albany Research Center (ARC) to maximize the insight into the potential thermomechanical activation offers.

Lizardite was selected as the model serpentine material for investigation, due to the relative structural simplicity of its lamellar structure when compared with the corrugated and spiral structures of antigorite and chrysotile, respectively. Hot-ground materials were prepared as a function of grinding temperature, time, and intensity. Carbonation reactivity was explored using the standard ARC serpentine carbonation test (155 °C, 150 atm CO₂, and 1 hr.). The product feedstock and carbonation materials were investigated via a battery of techniques, including X-ray powder diffraction, electron microscopy, thermogravimetric and differential thermal, BET, elemental, and infrared analysis.

The incorporation of low-level heat with moderate mechanical activation (i.e., thermomechanical activation) was found to be able to substantially enhance serpentine carbonation reactivity in comparison with moderate mechanical activation alone. Increases in the extent of carbonation of over 70% have been observed in this feasibility study, indicating thermomechanical activation offers substantial potential to lower process cost. Investigations of the thermomechanically activated materials that formed indicate adding low-level heat during moderately intense lizardite mechanical activation promotes (i) energy absorption during activation, (ii) structural disorder, and (iii) dehydroxylation, as well as carbonation reactivity, with the level of energy absorption, structural disorder and dehydroxylation generally increasing with increasing activation temperature. Increasing activation temperatures were also associated with decreasing surface areas and water absorptive capacities for the activated product materials. The above decreases in surface area and water absorption capacity can be directly correlated with

enhanced particle sintering during thermomechanical activation, as evidenced by electron microscopy observation. The level of induced structural disorder appears to be a key parameter in enhancing carbonation reactivity. However, particle sintering may contribute to reduced reactivity. The effectiveness of thermomechanical activation at enhancing carbonation reactivity appears to be a complicated function of a variety of process parameters, including grinding intensity, feedstock-to-media ratio, time, temperature, etc. At higher grinding intensities, the incorporation of low-level heat (≤ 250 °C) was found to be substantially less effective in enhancing carbonation reactivity. In the extreme, initial investigations indicate the addition of low-level heat during higher intensity grinding can even result in reduced carbonation reactivity compared with lower temperature mechanical activation, which is likely associated with enhanced particle sintering. Although more work is needed to establish the full potential of thermomechanical serpentine activation, it is clear that temperature control utilizing waste heat can substantially enhance carbonation and reduce process cost. Careful control of all of the process parameters will be essential for process optimization. Optimizing the combined impact of grinding intensity and activation temperature appears to be of particular importance.

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EXECUTIVE SUMMARY

Mineral carbonation is an intriguing large scale candidate carbon sequestration technology that permanently disposes of CO₂ as geologically stable and environmentally benign mineral carbonates. The primary challenge to viability is low-cost process development. Cost-effective enhancement of feedstock carbonation reactivity is critical. Recently, the Albany Research Center (ARC) has accelerated the carbonation of widely available serpentine minerals, which occurs naturally over geological time, to near completion in less than an hour. While reaction rates for natural serpentine were found to be too slow for practical application, both heat and mechanical (attrition grinding) pretreatment were separately found to substantially enhance carbonation reactivity. Unfortunately, these processes are too energy intensive to be cost-effective in present form. A 4-month pilot project collaboration between our CO₂ Sequestration Research Group and the Mineral Carbonation Research Group at the ARC has provided initial process development insight into the potential of combining heat and mechanical activation (thermomechanical activation). The project primarily focused on the potential impact of process parameters (e.g., temperature, grinding system aggressiveness, media size, activation time, media-to-feedstock ratio, and grinding speed) on serpentine carbonation reactivity and provides some preliminary X-ray powder diffraction insight. Adding external heat to mechanical activation was found to have the potential to both enhance and diminish serpentine carbonation reactivity, depending on the other process parameters, underscoring the complex potential offered by thermomechanical activation. This one-year UCR project was performed in collaboration with the ARC and the above pilot study, which was partially supported by a National Research Council Senior Research Associateship Award, to better establish the potential combining low-cost heat (e.g., power plant waste heat available up to 200-250 °C) with mechanical activation offers to enhance serpentine carbonation reactivity and lower process cost. The primary objective of this project is to better understand the mechanisms and material parameters that govern thermomechanical activation. The goal is to provide the necessary insight to engineer enhanced carbonation materials and processes for CO₂ disposal and reduce sequestration process cost.

ACCOMPLISHMENTS

Lizardite was selected as the model serpentine mineral of choice for mechanistic investigations of thermomechanical activation due to its relatively simple lamellar structure compared with the more complex structures of the other serpentine minerals (i.e., antigorite and chrysotile). Two feedstock materials have been investigated: (i) high purity Globe lizardite and (ii) southwest Oregon lizardite. Globe lizardite is phase pure, while the southwest Oregon lizardite was found to contain a minor chrysotile component, as determined by X-ray powder diffraction (XPD) and electron microscopic observation. Southwest Oregon lizardite was selected as the primary feedstock to facilitate comparison with the above pilot process development investigations carried out in collaboration with the ARC.

The thermomechanically activated materials generated under a variety of process conditions have been investigated via a battery of analytical techniques, as a function of their carbonation reactivity. In particular, simultaneous thermogravimetric and differential analysis (TGA/DTA), X-ray powder diffraction (XPD), infrared spectroscopy (IR), electron microscopy, energy

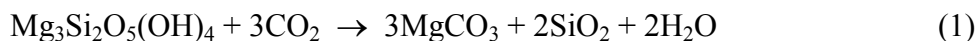
absorption, and surface area analysis have been combined to probe the mechanisms and materials characteristics that govern carbonation reactivity. Activated lizardite carbonation reactivity was assessed using the standard ARC aqueous carbonation process conditions (155 °C, 150 atm CO₂, 1 hr).

Combining low-level waste heat (e.g., ≤ 250 °C) with mechanical activation can substantially enhance carbonation reactivity. However, the effect of temperature is complex and its impact on the absorbed energy, structure, composition, and carbonation reactivity of the resulting activated materials depends on the various mechanical activation parameters that are employed. Combined TGA and DTA of the dehydroxylation process for the host lizardite and the activated lizardite materials indicates both thermal and mechanical energy are absorbed during thermomechanical activation and are generally correlated with enhanced carbonation reactivity for moderately aggressive mechanical activation conditions (e.g., the enthalpy of the associated lizardite/activated lizardite dehydroxylation endotherm generally decreases with increasing carbonation reactivity). TGA indicates that thermomechanical activation induces partial dehydroxylation at substantially lower temperatures than during simple heat activation alone, consistent with simultaneous mechanical and thermal energy absorption during activation. Two TGA steps are observed for the thermomechanically activated materials, (i) a low-temperature step associated with absorbed water (e.g., associated with air exposure after activation) and/or more weakly bound hydroxyls and (ii) a higher-temperature step associated with more strongly bound hydroxyls. Structural lattice defects and disorder are induced during thermomechanical activation, as evidenced by XPD, and generally exhibit a high correlation between the extent of disorder induced and carbonation reactivity. Both a decrease in the residual crystalline grain size and an increase in general structural disorder are induced during activation. Investigation of the thermomechanically activated materials via FTIR suggests the possible presence of activation-induced disordering of the immediate structural environment around the lattice hydroxyls. Thermomechanical activation was also observed to result in increasing levels of particle sintering with increasing temperature via electron microscopy and is consistent with the decreasing surface areas observed by BET with increasing thermomechanical activation temperature.

INTRODUCTION

Coal can fuel a large fraction of the world's energy needs well into the next century *if CO₂ sequestration technology can be developed that is (i) permanent, (ii) environmentally benign, and (iii) economically viable*.^{1,2} CO₂ mineral sequestration permanently disposes of CO₂ as geologically stable mineral carbonates.^{3,4} The process also offers the added benefit that only benign, naturally abundant materials are formed. The remaining hurdle is economic viability. The primary research focus is reducing the cost of the carbonation process. This is one of the goals of the CO₂ Mineral Sequestration Working Group managed by DOE, with members from the Albany Research Center (ARC), Los Alamos National Laboratory, National Energy Technology Laboratory, Science Applications International Corp., and our research group at Arizona State University (ASU).

Mineral carbonation of serpentine [Mg₃Si₂O₅(OH)₄] is a particularly attractive candidate technology. Serpentine (e.g., lizardite, antigorite and chrysotile) deposits exceed those needed to carbonate all the CO₂ that could be generated from global coal reserves.^{4,5} Thus, serpentine-based feedstock materials can support large-scale, permanent CO₂ sequestration. Serpentine can also be cost-effectively mined and milled (~\$4 to \$5/ton)⁵ and its general carbonation process (reaction 1) is exothermic, providing exciting potential for low-cost process development. The



ARC recently made an exciting breakthrough, accelerating serpentine carbonation, which occurs naturally over geological time, to near completion in less than an hour. The process reacts an aqueous slurry of finely ground, pretreated serpentine with CO₂ under relatively modest conditions. Pretreatment is essential, as the carbonation reaction rate for untreated serpentine is too slow for economically-viable process development.^{5,6} Heat and mechanical pretreatment disrupt the serpentine structure, yielding poorly ordered, activated serpentine materials with enhanced carbonation reactivity.⁵⁻⁷ Although these processes greatly enhance carbonation reactivity, they are too energy intensive to be economically viable in present form. An intriguing alternative is combining power plant waste heat, which can be available at up to 200-250 °C,⁸ with mechanical activation (i.e., thermomechanical activation) in an effort to enhance carbonation reactivity and lower process cost.

EXPERIMENTAL

Two feedstock materials were investigated in the course of this project: (i) high purity Globe lizardite collected at the Philips Mine, Arizona and (ii) the non-magnetic fraction of southwest Oregon lizardite, which was obtained in collaboration with the Albany Research Center.⁵⁻⁷ The Globe lizardite was found to be phase pure (containing a trace, ~1%, of chrysotile), while the southwest Oregon lizardite was found to contain a minor chrysotile component, as determined by X-ray powder diffraction (XPD) and electron microscopic observation.

The southwest Oregon lizardite (SWOL) was selected as the primary feedstock in these investigations (i) to facilitate comparison with prior mechanical activation and heat activation

studies at the ARC,⁵⁻⁷ (ii) as it is the most difficult material to carbonate of the serpentine materials previously investigated at the ARC, allowing more room for reactivity improvement, (iii) because it was available in quantities sufficient for the thermomechanical investigations described herein, and (iv) it offers a fairly pure serpentine (lizardite with a minor chrysotile component) with a relatively simple lamellar structure compared to the corrugated and spiral structures of the other serpentine minerals, antigorite and chrysotile, respectively, as seen in Figure 1.⁹ The latter advantage facilitates gaining important fundamental insight into the

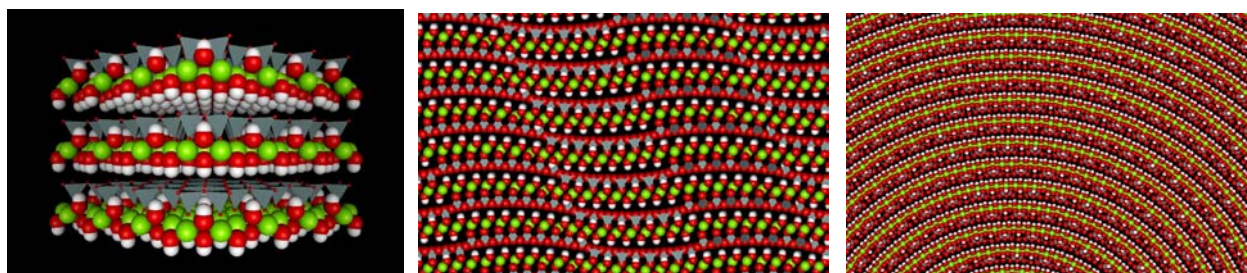


Figure 1) Models of the lamellar, corrugated and spiral structures of the serpentine minerals lizardite, antigorite and chrysotile from left to right. The green, red, and white spheres correspond to the Mg, O, and H atom positions, respectively. The grey tetrahedra with the red spheres at the corners correspond to the silica group positions.

activated feedstock parameters that impact carbonation reactivity via structural, compositional and microscopic investigations. Thermomechanical activation was carried out both at ASU using the system shown in Figure 2 and using the controlled temperature attrition system at the Albany Research Center shown in Figure 3. The materials investigated in this project were



Figure 2) A view of the controlled temperature grinding system used at ASU for initial thermomechanical studies. This system is a rotary type ball mill, which has been outfitted with heating capabilities.

primarily prepared using the latter system, which was developed during a partner (5/02-10/02) pilot project collaboration between the ASU CO₂ Sequestration Research Group (M. McKelvy) and the Mineral Carbonation Research Group at the ARC (D. Dahlin, W. O'Connor, H. Rush,

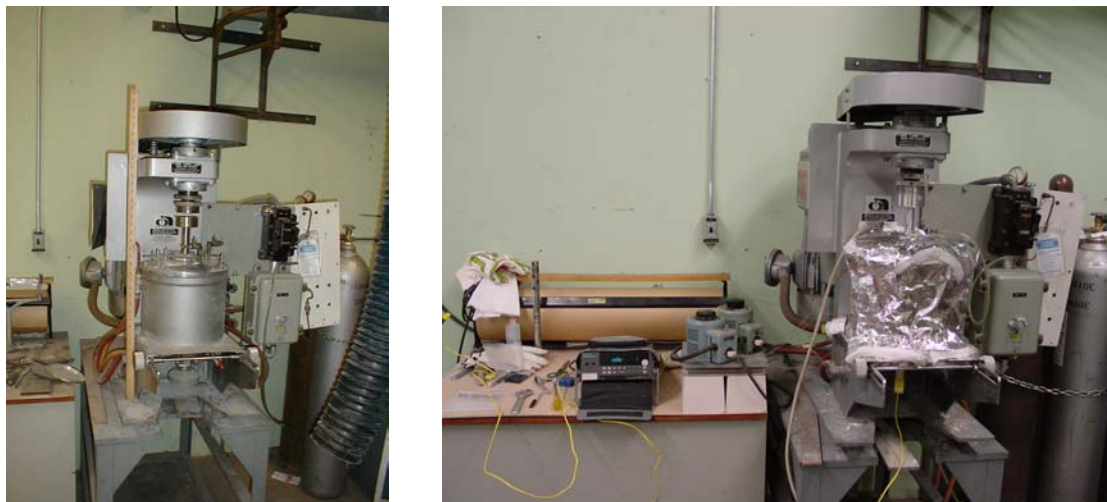


Figure 3) Left: a view of the water-cooled attrition system used for ambient temperature mechanical activation studies. Right: a view of the controlled-temperature system for thermomechanical investigations. Internal system temperatures were determined before and after the attrition runs by inserting a thermocouple in the middle of the media/sample. The controlled-temperature attritor has a thermocouple mounted in the bottom of the attritor shell to monitor the shell temperature during thermomechanical activation. It is also used to compare the shell temperature to the internal media/sample temperatures before, and immediately after, the thermomechanical activation studies.

and S. Gerdemann) that was partially supported by a National Research Council Senior Research Associateship Award. Thermomechanical activation was performed under argon. Controlling humidity during activation was found to be difficult as substantial dehydroxylation was observed to occur during thermomechanical activation. The results reported herein utilize flowing argon during thermomechanical activation to continuously sweep away the water vapor evolved due to dehydroxylation of the feedstock within the vessel during activation. All of the activated materials were found to be extremely fine, free-flowing powders after activation was complete. The standard ARC serpentine carbonation test (155 °C; 150 atm CO₂; 1 hr.) was used to probe the carbonation reactivity (extent of carbonation observed in an hour) of each activated material.⁵⁻⁷ Carbonation tests were carried out using our 100 ml miniature version of the 2 liter batch carbonation reactor developed at the ARC and the ARC batch carbonation system. Comparative carbonation runs in both systems using the same standard feedstock was found to give the same extent of carbonation within experimental error ($\pm 3\%$), allowing direct comparison of results.¹⁰

X-ray powder diffraction patterns were obtained for each of the activated materials using a Rigaku D/MAX-IIIB X-ray diffractometer with Cu K _{α} radiation. Scans were taken from $2\theta = 10^\circ$ to 80° , at a scan rate of $2^\circ/\text{min}$. in steps of 0.01° . Powder transmission infrared (IR) spectra were collected on a Bruker IFS 66/vS Fourier Transform spectrometer in the mid-infrared range ($500\text{--}4000\text{ cm}^{-1}$), utilizing a liquid nitrogen cooled MCT detector. IR samples were prepared by suspending a small amount of finely ground material in a thin window of FTIR grade KBr (Alfa Aesar). A controlled atmosphere glovebox (M. Braun, Inc.; $< 1\text{ ppm}$ total O₂ + H₂O) was utilized to minimize exposure to air and moisture. Samples were prepared both as received and after being dried overnight in a drying oven to remove moisture adsorbed from handling in air.

The spectrometer chamber was evacuated during scanning to further guard against water exposure.

Thermal Gravimetric Analysis (TGA) was performed using a Perkin Elmer Pyris 1 TGA. Combined thermogravimetric and differential analysis (TGA/DTA) studies were carried out under helium using a Setaram TG92 thermal analysis system. The field emission scanning electron microscope (FESEM) system used for morphological observations was a Hitachi 4700. BET surface area analysis was performed at the Albany Research Center. Composition and extent-of-carbonation analyses utilized TGA, CHNS analysis, LECO, and wet-gravimetric methods.

RESULTS AND DISCUSSION

Thermomechanical Activation Studies Utilizing Materials Prepared in the ASU system: Initial studies at ASU focused on determining if low-level heat (≤ 250 °C) can facilitate meta-serpentine formation, which has been associated with substantially increased carbonation reactivity.¹¹ As seen in Figure 4, controlled- temperature grinding (intense ball milling) at 250 °C can

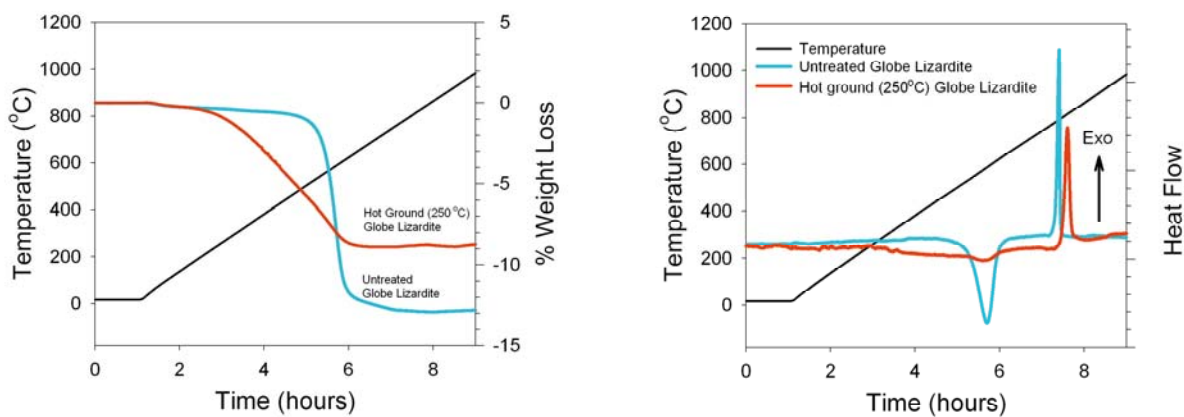


Figure 4) Thermogravimetric analysis (TGA) of hot ground and untreated Globe lizardite heated at 2 °C/min. (left). Simultaneous differential thermal analysis (DTA) of the same hot ground and untreated lizardite samples (right).

substantially reduce the dehydroxylation temperature and hydroxide content of lizardite, while slightly increasing the temperature at which crystallization (i.e., forsterite/enstatite formation) occurs. The decrease in the magnitude of the dehydroxylation endotherm compared to the residual hydroxide in the hot-ground material (Figure 4: TGA) suggests significant energy is absorbed during hot grinding. XPD shows the resulting material to be primarily poorly ordered/amorphous, as are lizardite heat-activated at ~ 640 – 680 °C and attrition ground materials.^{7,11} By comparison, lizardite ground at ambient temperature, under otherwise identical conditions, remained primarily lizardite, suggesting low-level waste heat can facilitate mechanical serpentine activation.

Investigations of Materials Prepared Using the Controlled Temperature Attrition System developed in Collaboration with the ARC: The impact of a variety of thermomechanical process parameters on carbonation reactivity were explored in collaboration with the ARC. Serpentine

carbonation reactivity was found to increase with increasing attrition speed, time and aggressiveness and decreasing charge to media ratio. A range of thermomechanically activated materials were produced as a function of attrition temperature for this project. These materials were investigated in detail in our laboratories at Arizona State University to explore the mechanisms and characteristics that govern thermomechanical activation, as described below. Under moderate mechanical activation conditions (e.g., 300 rpm attrition for one hour), increasing carbonation reactivity showed a strong correlation with increasing activation temperature, as shown in Figure 5. However, BET surface area measurements indicate that the

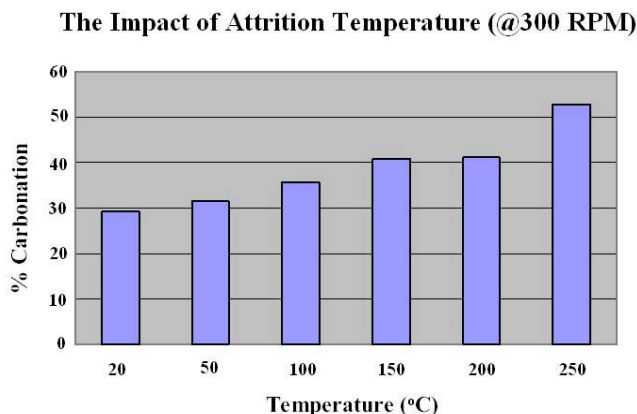


Figure 5) Extent of carbonation observed as a function of attrition temperature for southwest Oregon Lizardite thermomechanically activated at 300 rpm for one hour under argon.

enhanced carbonation reactivity observed is not associated with a simple increase in surface area. Indeed, the surface area for the associated materials was found to decrease with increasing thermomechanical activation temperatures, as seen in Figure 6. Increasing activation temperature

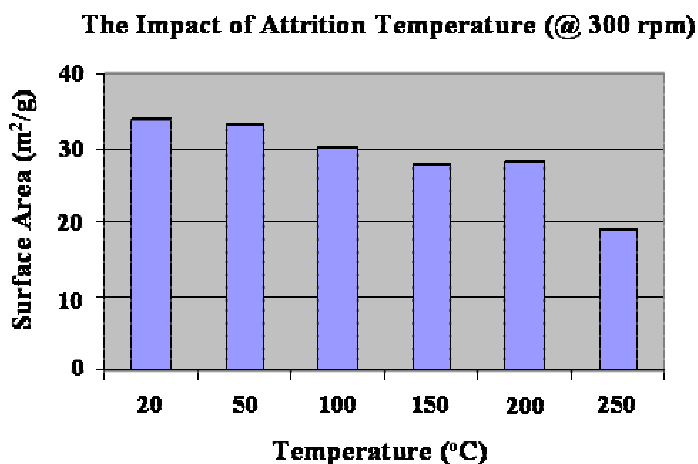


Figure 6) Surface area (BET) as a function of attrition temperature for southwest Oregon Lizardite thermomechanically activated as a function of temperature at 300 rpm for one hour under argon.

is also apparently correlated with increasing particle size, as seen in Figure 7. Figure 7a shows the lamellar character of the original southwest Oregon lizardite feedstock that was used for

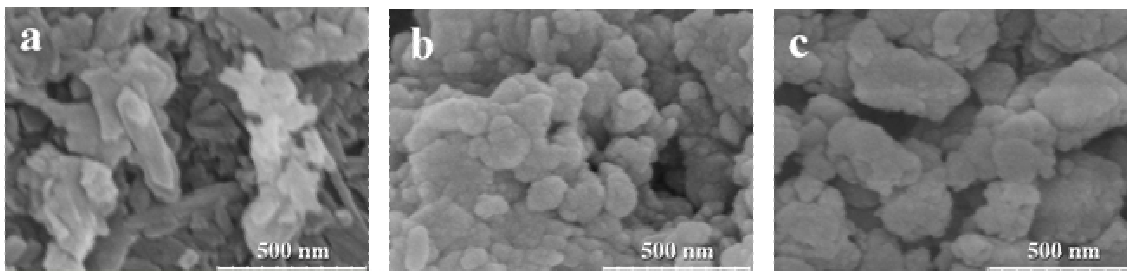


Figure 7) FESEM images of (a) the southwestern Oregon feedstock material before thermomechanical activation, (b) after ambient temperature attrition for an hour, and (c) after attrition at 250 °C for an hour. Note the apparent increase in aggregate particle size for an attrition temperature of 250 °C.

thermomechanical activation sample preparation. Attrition grinding appears to result in cold welding of the particles that are formed, with the resulting aggregate particles increasing in size with increasing temperature, as seen in Figure 7. Such a process is consistent with the enhanced sintering expected to occur at progressively higher activation temperatures, which can also explain the observed decrease in surface area with increasing thermomechanical activation temperature.

Thermogravimetric analysis of the materials activated at 50, 100, 150, 200 and 250 °C is shown in Figure 8. The activated materials generally exhibit a two-step decomposition process, (i) a low-temperature step associated with adsorbed water (e.g., associated with air exposure after activation) and/or much more weakly bound hydroxyls and (ii) a higher-temperature step associated with more strongly bound lattice hydroxyls. The mass loss associated with the first step decreases rapidly with increasing activation temperature, which is consistent with the relatively high surface area materials that form during activation, water adsorption from the atmosphere, and the decrease in surface area with increasing activation temperature observed in Figure 6. Substantial water adsorption was also confirmed by infrared analysis, as described below.

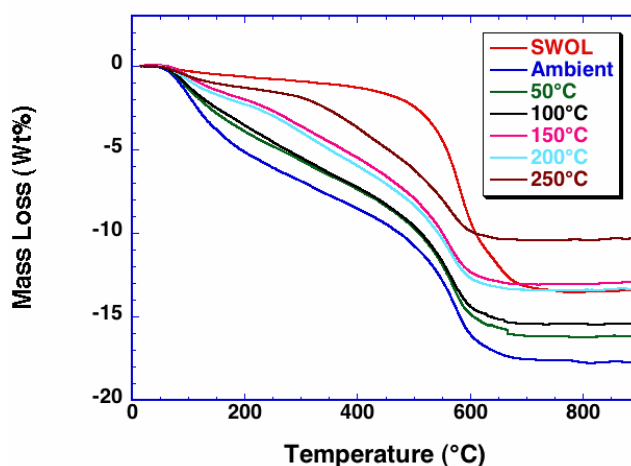


Figure 8) Thermogravimetric analysis of the thermomechanically activated SWOL materials under a helium atmosphere, with a heating rate of 2°C/min. Although lizardite has a theoretical mass loss of 13 wt%, some of the attritted samples show a larger amount of mass loss upon decomposition, indicating substantial uptake of adsorbed water for the lower temperature attritted samples.

In order to better probe the strongly bound hydroxyl groups that remain after thermomechanical activation, the materials investigated in Figure 8 were preheated to 150 °C under dry He for 5 hours to remove adsorbed water. Immediately following this *in situ* drying procedure, the samples were heated at a rate of 2 °C per minute to 900 °C, as shown in Figure 9. The starting

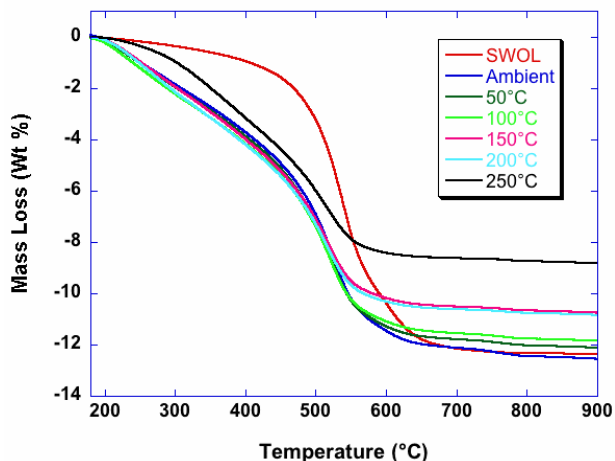


Figure 9) Thermogravimetric analysis under He of the SWOL materials attrited at 300 rpm as a function of attrition temperature. The activated materials were initially held at 150°C for 5 hours to remove water adsorbed to the surface of the material before heating at 2°C/min. The TGA curves show the mass loss, after the *in situ* drying cycle is complete. The samples show a reduction in total mass loss with increasing activation temperature, indicating that partial hydroxyl decomposition (water formation and loss) occurs during heated attrition and is facilitated by higher activation temperatures.

mass of the samples in these investigations is taken as the measured mass at the end of the 150 °C drying cycle. The activated materials begin to decompose at approximately 200 °C, whereas the unactivated SWOL shows slow initial decomposition followed by a much more rapid decomposition once the material has been heated to higher temperatures. The total mass loss for the SWOL feedstock material is slightly less than 13%, consistent with the ideal serpentine composition $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$, which contains 13 wt% hydroxyl groups. The weight loss slows rapidly as the decomposition process nears completion at approximately 650 °C. The sample activated at room temperature, while showing almost identical mass loss, generally decomposes at substantially lower temperatures. Indeed, lower decomposition temperatures are generally observed for all of the activated materials, suggesting significant energy absorption and structural disruption occurred during activation, which facilitates lower temperature dehydroxylation.

As the activation temperature increases, the overall mass loss associated with each sample during TGA decreases, indicating that the materials lose some of their OH content during the heated attrition process. The effect is slight for the materials generated through attrition at 100 °C or less, however higher temperature activation results in significant dehydroxylation. Approximately 1/6 of the hydroxide is removed from the host lizardite via thermomechanical activation at 150-200 °C and over 1/4 of the hydroxide is removed at 250 °C. As substantial hydroxyl loss is not observed until significantly higher temperatures are reached during heat activation alone, it is apparent that the thermal and mechanical energy associated with thermomechanical activation combine to enhance lower temperature dehydroxylation.

X-ray powder diffraction patterns were collected for each of the thermomechanically activated materials as well as the host lizardite feedstock, as shown in Figure 10. The powdered feedstock is reasonably well crystallized, while the activated materials exhibit decreasing levels of crystallinity with increasing activation temperature. The associated diffraction peaks broaden with increasing temperature, indicating the residual crystalline grain size decreases with

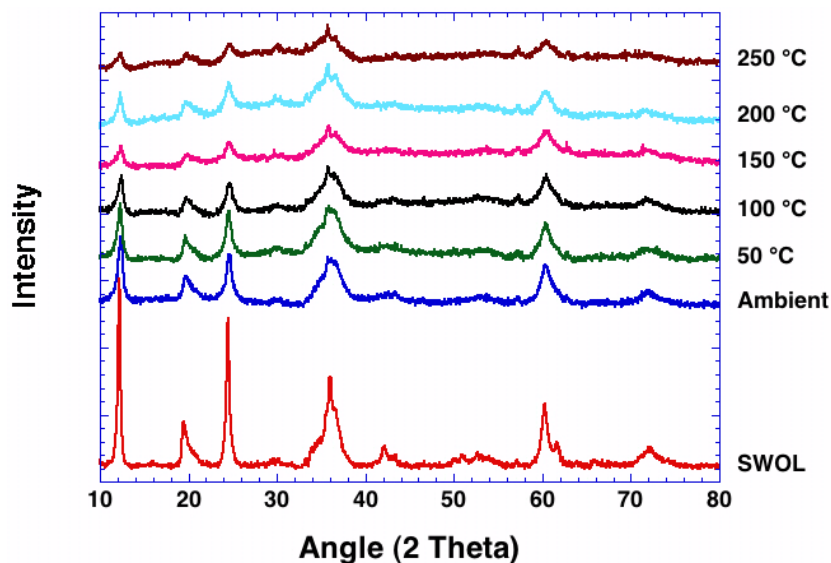


Figure 10) X-ray powder diffraction patterns for southwest Oregon lizardite (SWOL) attrited at 300 rpm for one hour under argon as a function of attrition temperature. The bottom pattern is the reference starting material, while the other patterns are for the ground materials produced at increasing temperatures, as noted. The reduction of the peak intensities and broadening of the peaks is indicative of increasing structural disorder. Increasing disorder in the crystalline phase is apparent with increasing temperature, together with the emergence of a broad amorphous scattering region.

increasing temperature. There is also an underlying broad region of increasing diffuse scatter intensity, which begins to emerge with increasing activation temperature and is consistent with increasing levels of amorphous material formation. This very broad region is visually evident in the higher temperature activated samples and the amorphous material appears to account for a substantial amount of the sample by this stage. Higher resolution, background subtracted XPD investigations are currently underway to better elucidate the nature of the amorphous material that forms.

Powder transmission Fourier transform infrared spectroscopy (FTIR) analysis of the lizardite feedstock material exhibited the expected experimental features from 500 to 4,000 cm^{-1} .¹²⁻¹⁴ Analysis of the thermomechanically-activated materials confirmed the presence of adsorbed water, which decreases with increasing attrition temperature. The water determination was made by examining the intensity in the H_2O bending region, at approximately 1650 cm^{-1} . That the observed water is adsorbed, rather than a part of the sample structure, is consistent with (i) the above surface area analysis, (ii) the sample morphology observed via FESEM, and (iii) the observation that low-temperature heating (e.g., 150 °C) is sufficient to remove the observed water.

In order to probe the impact of the thermomechanical activation temperature on the local hydroxide structural environment in the absence of adsorbed water, samples were dried overnight in a drying oven and prepared for infrared analysis under anhydrous conditions. The dried samples displayed no or only trace features in the 1650 cm^{-1} region, indicating that overnight drying was sufficient to essentially remove all of the water that was adsorbed to the surface of the powdered material. Without H_2O present on the material's surface, the OH stretching features, appearing at $\sim 3650\text{--}3700\text{ cm}^{-1}$, can be associated with the structural hydroxide groups in the activated materials.^{11,15} Although the observed peak positions do not appear to clearly shift during ambient temperature activation or with increasing activation temperature, the spectral intensity appears as though it may be broadening to lower cm^{-1} , suggesting the presence of possible activation induced disordering of the local structural environment of the hydroxyls, as seen in Figure 11. Overall, the OH stretch region exhibits reduced intensity with increasing activation temperature. Although these observations are not quantitative, they are consistent with the increasing levels of dehydroxylation observed with increasing activation temperature.

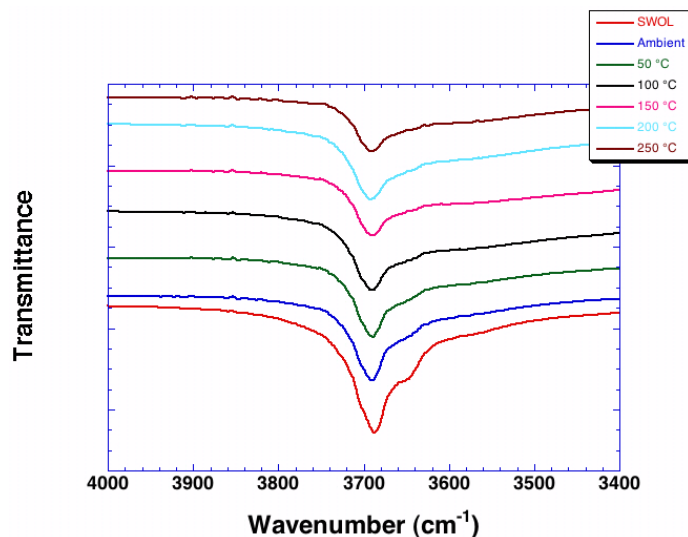


Figure 11) FTIR of the thermomechanically activated materials as a function of activation temperature showing the OH stretching band region. Analysis of the H_2O bending region near 1650 cm^{-1} indicates that there is essentially no water present in the material.

The energy absorbed during thermomechanical activation was explored as a function of activation temperature via simultaneous TGA/DTA, as shown in Figure 12. Figure 13 shows expanded views of the endotherms and exotherms observed as a function of thermomechanical activation temperature compared with those observed for the southwest Oregon lizardite (SWOL) feedstock. Ambient temperature mechanical activation resulted in a substantial decrease and increase in the size of the endothermic and exothermic response, respectively. This can be associated with the energy absorbed (and the structural disorder induced) during activation, which serves to destabilize the activated SWOL product material. These qualitative observations suggest that energy absorption may serve to (i) reduce the hydroxyl decomposition energy within the activated material, leading to the lower endothermic enthalpy observed and (ii) increase the energy of the disordered meta-serpentine material that is produced on heating the activated material past endothermic decomposition, consistent with the increased crystallization energy

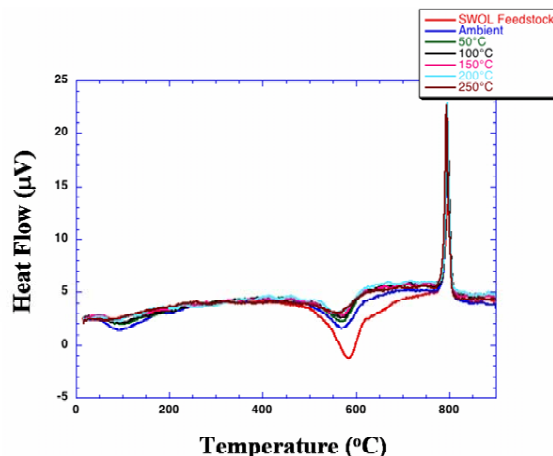


Figure 12) Simultaneous TGA/DTA of SWOL thermomechanically activated at 300 rpm for an hour under argon as a function of activation temperature. The endotherm slightly below 600 °C corresponds to hydroxyl decomposition and water loss. The exotherm near 800 °C is associated with forsterite/enstatite crystallization from the amorphous meta-serpentine material formed via dehydroxylation.¹¹ The weak endotherm near 100 °C is associated with the desorption of water adsorbed from the atmosphere.

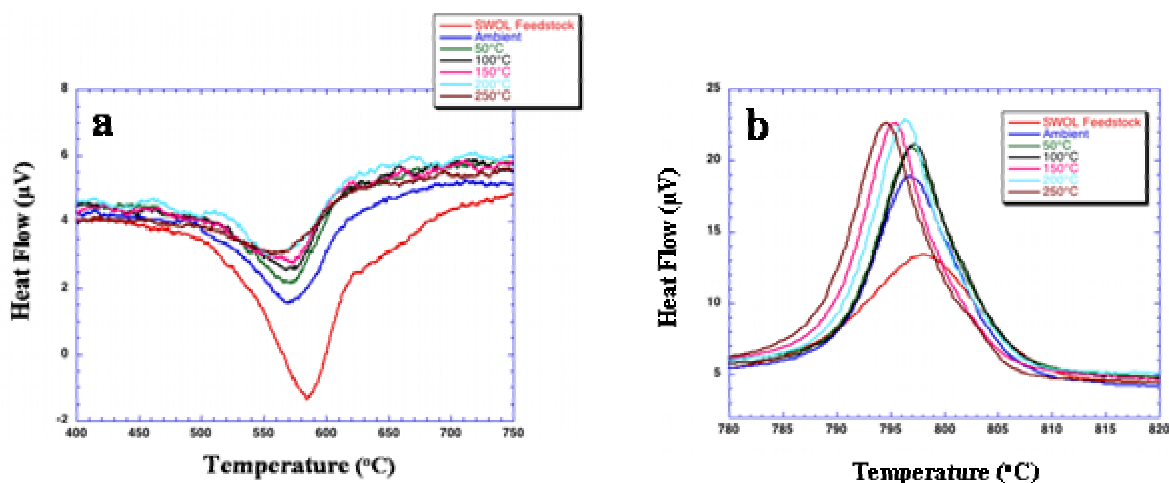
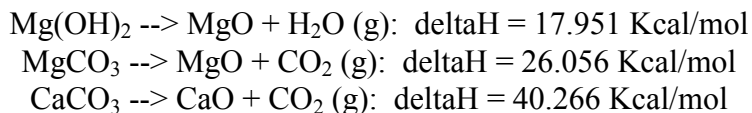


Figure 13) Expanded views of the endotherms and exotherms observed as a function of thermomechanical activation temperature in Figure 12.

observed in Figure 13b. Increasing the mechanical activation temperature was generally found to further decrease and increase the endothermic and exothermic intensities, respectively, suggesting that more energy can be adsorbed during elevated temperature mechanical activation.

In order to better quantify the energy absorption during activation as a function of activation temperature for comparison with the carbonation reactivity observed for the resulting thermomechanically activated materials, the DTA enthalpies observed were calibrated using high purity brucite, calcite and magnesite as reference standards to convert the instrument measured microvolts to Kcal over the temperature range of interest. The standard enthalpies of

decomposition used for calibration (below) were determined via *ab initio* quantum mechanical modeling at their observed decomposition temperatures. The resulting transition energies are



given in Table 1. Simultaneous TGA data taken during each DTA analysis was used to determine the hydroxide content for each activated sample and derive the observed Kcal/mol OH for the endothermic dehydroxylation transition.

Table 1) Comparison of the Energies Observed via TGA/DTA with Carbonation Reactivity

Activation Temp (°C)	Sample Mass (mg)	Endotherm (cal/g)	OH Mass Loss (mg)	Kcal/mol(OH)	Exotherm (cal/g)	Percent Carbonation
SWOL	65.45	141.14	7.09	22.17	37.80	2.5%
Ambient	65.42	79.77	5.37	16.53	46.55	29.4%
50 °C	65.36	81.14	5.22	17.27	46.18	31.5%
100 °C	65.28	74.34	4.84	17.03	48.70	35.7%
150 °C	65.12	64.89	4.48	16.03	51.20	40.8%
200 °C	65.40	60.91	4.42	15.31	48.15	41.4%
250 °C	65.47	52.08	4.03	14.40	54.44	53.0%

The observed energy of dehydroxylation was combined with the total mass loss of the sample during dehydroxylation to determine the energy per mol hydroxide needed for dehydroxylation for the SWOL feedstock and each activated material. Ambient temperature attrition was found to substantially reduce this energy (~25%), consistent with substantial energy absorption during attrition. Furthermore, the observed dehydroxylation energy (Kcal/mol OH) was found to generally decrease with increasing activation temperature, confirming the qualitative suggestion above that the energy absorption associated with thermomechanical activation generally increases with increasing activation temperature.

The per gram energy associated with the crystallization exotherms was determined using the average (essentially constant) mass present during crystallization. Significantly more energy (~20%) is released during crystallization for the ambient temperature activated material than the SWOL feedstock, further demonstrating that mechanical activation imparts substantial energy into the product material. The energy released during crystallization generally increases with increasing activation temperature, further confirming that increasing activation temperature increases the energy absorbed during activation.

The extent of carbonation observed for the SWOL feedstock and the activated materials shown in Table 1 exhibits a strong increase via ambient temperature activation, which generally continues to increase with increasing activation temperature. This suggests a strong correlation between the energy absorbed during mechanical activation and the extent of carbonation observed.

CONCLUSIONS

The incorporation of low-level heat with moderately intense mechanical activation was found to be able to substantially enhance lizardite carbonation reactivity in comparison with moderate mechanical activation alone. Increases in the extent of carbonation of over 70% have been observed in this feasibility study, indicating thermomechanical activation offers substantial potential to lower process cost. Investigations of the thermomechanically activated materials that formed indicate adding low-level heat during moderately intense lizardite mechanical activation promotes (i) energy absorption during activation, (ii) structural disorder, and (iii) dehydroxylation, as well as carbonation reactivity, with the level of energy absorption, structural disorder and dehydroxylation generally increasing with increasing activation temperature. Increasing activation temperatures were also associated with decreasing surface areas and water absorptive capacities for the activated product materials. The above decreases in surface area and water absorption capacity may be directly correlated with enhanced particle sintering during thermomechanical activation, as evidenced by electron microscopy observation. The level of induced structural disorder appears to be a key parameter in enhancing carbonation reactivity. However, particle sintering may contribute to reduced reactivity. The effectiveness of thermomechanical activation at enhancing carbonation reactivity appears to be a complicated function of a variety of process parameters, including grinding intensity, feedstock-to-media ratio, time, temperature, etc. Preliminary thermomechanical activation studies using less and more aggressive (e.g., 500 rpm) mechanical activation suggest that the effectiveness of adding low level heat in enhancing carbonation reactivity is strongly correlated with the intensity of the mechanical activation process used. At higher grinding intensities, the incorporation of low-level heat (≤ 250 °C) was found to be substantially less effective in enhancing carbonation reactivity. In the extreme, initial investigations indicate the addition of low-level heat during higher intensity grinding can even result in reduced carbonation reactivity compared with lower temperature mechanical activation, which may be associated with enhanced particle sintering.

Although more work is needed to establish the full potential of thermomechanical serpentine activation, it is clear that temperature control utilizing waste heat can substantially enhance carbonation reactivity and reduce process cost. Careful control of all of the process parameters will be essential for process optimization. Optimizing the combined impact of grinding intensity and activation temperature appears to be of particular importance.

REFERENCES

1. *Novel Approaches to Carbon Management* (Wash. D.C., National Academies Press, 2003).
2. *Carbon Sequestration Research and Development*, Offices of Science and Fossil Energy, U.S. Department of Energy (December 1999), and references therein.

3. Seifritz, W. *Nature* **345**, 486 (1990).
4. Lackner, K.; Wendt, C.; Butt, D.; Joyce Jr., E.; Sharp, D.; *Energy* **20**, 1153-70 (1995).
5. O'Connor, W.; Walters, R.; Dahlin, D.; Rush, G.; Nilsen, D.; Turner, P. *Proc. 26th Int. Tech. Conf. Coal Util. & Fuel Syst.* pp. 765-76 (2001).
6. O'Connor, W.K.; Dahlin, D.C.; Nilsen, D.N.; Walters, R.P.; Turner, P.C.; *Proc. 25th Int. Tech. Conf. Coal Util. & Fuel Syst.* pp. 153-64 (2000).
7. O'Connor, W.K.; Dahlin, D.C.; Nilsen, D.N.; Gerdemann, S.J.; Rush, G.E.; Walters, R.P.; Turner, P.C.; *Proc. 18th International Pittsburgh Coal Conference*, **35-1**, 1-11 (2001).
8. "Steam: Its Generation and Use," 40th edition, S.C. Stultz and J.B. Kitto, eds. (Babcock & Wilcox Company, Barberton, Ohio, 1992).
9. Wicks, Fred, J. *Powder Diffraction* 15 (1) (2000), 42-50, and references therein.
10. Béarat, H., McKelvy, M., Chizmeshya, A., Nunez, R. and Carpenter, R.W. *Proc. 28th International Technical Conference on Coal Utilization & Fuel Systems* (2003) 307-318.
11. McKelvy, Michael J.; Chizmeshya, Andrew V.G.; Diefenbacher, Jason; Béarat, Hamdallah; Wolf, George; *Environmental Science & Technology* 38 (24), 6897-903 (2004).
12. Tartaj, P.; Cerpa, A.; Garcia-Gonzalez, J.; Serna, C. *J. of Colloid and Interf. Sci.* **2000**, 231, 176.
13. Fuchs, Y.; Linares, J.; Mellini, M. *Phys Chem Minerals* **1998**, 26, 111.
14. Post, J.L.; Borer, L. *Applied Clay Science* **2002**, 16, 73.
15. Lemaire, C.; Guyot, F.; Reynard, B. *European Union of Geosciences 10, Journal of Conference Abstracts* **1999**, 4, 654.; Auzende, A-L.; Lemaire, C.; Daniel, I.; Reynard, B.; Guyot, F.; Devouard, B. *European Union of Geosciences 11, Journal of Conference Abstracts* **2001**, 5, 462.

ARTICLES, PRESENTATIONS, AND STUDENT SUPPORT

Articles and Presentations

- "Simultaneous Mechanical and Heat Activation: a New Route to Enhance Serpentine Carbonation Reactivity and Lower CO₂ Mineral Sequestration Process Cost," Michael J. McKelvy, Jason Diefenbacher, R.W. Carpenter, Andrew V.G. Chizmeshya, and R. Nunez, presented at the University Coal Research Contractors Review Conference, Pittsburgh, Pennsylvania, June 3-4, 2003.
- "Simultaneous Mechanical and Heat Activation," Michael J. McKelvy, Jason Diefenbacher, R.W. Carpenter, Andrew V.G. Chizmeshya, and R. Nunez, an invited presentation at the Ninth Carbon Dioxide Mineral Sequestration Forum, Pittsburgh, Pennsylvania, June 4, 2003.
- "Thermomechanical Activation using Waste Heat: a New Route to Enhance Serpentine Mineral Carbonation Reactivity and Lower Carbon Sequestration Process Cost," J. Diefenbacher, M. J. McKelvy, A.V.G. Chizmeshya, D. Dahlin, W. O'Connor, and H. Rush (in preparation).

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- Ryan Nunez, graduate (Ph.D.) student in the Science and Engineering of Materials Graduate Program, Arizona State University.