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## SPS Chapter Research Award Final Report

Project Title	Feasibility Studies of Dolomites from Phosphatic Pebble for Thermochemical Energy Storage and CO <sub>2</sub> Sequestration]
Name of School	Florida Polytechnic University
SPS Chapter Number	2054
Total Amount Awarded	\$2,000.00
Project Leader	Wyatt Liptak, Sesa Srinivasan

### Abstract

The current SPS Research Project addresses and aims to deploy the highly abundant, uneconomical dolomites (calcium-magnesium carbonates) for the end-use and green technology applications namely, (i) thermochemical energy storage and (ii) carbon dioxide sequestration and capture in fossil fuel power plants. An innovative concept of thermochemical energy storage system and CO<sub>2</sub> sequestration assembly by using the dolomites (CaO/CaCO<sub>3</sub> and MgO/MgCO<sub>3</sub> reactions) in phosphatic pebble matrices is demonstrated. The motivation behind the project is that the Central Florida's phosphate mining produces dolomites which are currently piled up in clay ponds and the proposed study is attempt to establish feasibility study to utilize dolomites for thermochemical energy storage and sequester/capture CO<sub>2</sub> in power plants.

### Statement of Activity, Interim Assessments & Results

**Goals and Objectives:** The central hypothesis of this project is to explore the feasibility of phosphatic pebble sorbents such as high-dolomites (calcium magnesium carbonate) in clean energy applications such as thermochemical energy storage and carbon capture via these sorbents.

Major research accomplishments are listed below:

- QEMSCAN results obtained from Colorado School of Mines for dolomite samples
- BET surface area analysis of commercial and handpicked dolomites performed at USF
- Carbonation and calcination optimization in both the tube furnace (STF) and Bomb reactor
- Wet ball milling of handpicked dolomites under different optimized experimental conditions
- Continuous looping of mix and handpicked dolomites in TGA and determined the sample intake expectancy
- XRD and XRF analysis of handpicked dolomites at various stages
- Life cycle and cyclic stability studies of dolomites

#### **QEMSCAN results obtained from Colorado School of Mines (CSM) for Dolomite Samples**

Seven different dolomite samples (see Table 1) have been prepared and shipped to our collaborating partners from Colorado School of Mines (CSM) for QEMSCAN (Quantitative Evaluation of Materials by Scanning Electron

Microscopy), a system which quietly differs from image analysis systems. The advantage of QEMSCAN that is configured to measure mineralogical variability based on chemistry at the micrometer scale.

**Table 1:** List of dolomite samples prepared and shipped to CSM for QEMSCAN

Sample sets	Samples	Expected QEM SCAN Results
Sample Set I – Commercial Dolomite from Alfa Aesar	1. Hand crushed 2. Hand Crushed STF (N <sub>2</sub> ) Calcined	It is expected to understand the chemical assay, concentration of dolomites (or Ca to Mg ratios), size by size analysis, trace mineral explorations and degrees of mineral species (for example, CO <sub>3</sub> ) locked before calcination and/or liberated after calcination in STF under N <sub>2</sub> ambient.
Sample Set II – Handpicked from Central Florida Phosphate Mining Site (Courtesy: FIPR)	3. Hand Crushed 4. Hand Crushed STF (N <sub>2</sub> ) 5. Hand Crushed STF (Air) 6. Ball Milled (Acetone)	For the hand crushed and hand crushed followed with STF (under N <sub>2</sub> and/or air) samples, we would like do the QEMSCAN studies similar to Sample Set I mentioned above. Additionally, the ball milled under acetone medium of the hand crushed samples, we would like estimate the particle map analysis and trace minerals analysis (to find out the trace amount of Fe or Co which leached out from the balls and ball mill container).
Sample Set III: Mixed Dolomite samples from Central Florida Phosphate Mining Site (Courtesy: FIPR)	7. Ball Milled (Ethanol)	The QEMSCAN similar to sample set II Ball milled under acetone medium. For example Trace Minerals Searches, Quantification of the mineralogy and textural associations between the dolomite (ore) and gangue in the mixed samples.

CSM reported that out of 7 samples received, two of them were lost during preparation stages. Therefore only 5 samples (2, 3, 4, 5 and 6) have been examined under QEMSCAN. This meaning the samples are categorized and tabulated in Table 2.

**Table 2:** Samples under QEMSCAN investigations

Sample Category Number(s)	Sample(s) Name	Dolomite Pure or Dolomite (with Fe) Concentration (as Reference Phase)	Other Major Phases
2	Commercial + Hand Crushed STF (N <sub>2</sub> ambient)	0.91%   29.38%	Magnesite: 23.7% Quartz: 0.36%
6	Hand Picked + Ball Milled (Acetone)	74.9%   0.53%	Quartz: 6.42%
4	Hand Picked + Crushed STF (N <sub>2</sub> ambient)	0.5%   3.51%	Quartz: 15.975 Amphibole/Pyroxene: 51.93%
3	Hand Picked + Hand Crushed	49.6%   0.08%	Calcite: 17.46% Quartz: 21.67%
5	Hand Picked + Hand Crushed STF (Air ambient)	1.15%   0.31%	Quartz: 14.26% Anorthite: 8.01%

			Amphibole/Pyroxene: 63.47%
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Based on the QEMSCAN, the following analysis and conclusions are drawn for both the commercial and handpicked samples at various stages of unmodified but hand crushed, after calcination and after ball milling under solvent medium.

- (i) Sample 2, the commercial and hand crushed dolomites though calcined under nitrogen ambient in tube furnace, due to the partial calcination, exhibit the presence of dolomite (both pure and with Fe content) up to 30% and Magnesite up to 24%. This sample clearly indicates the need of calcination optimization which we will work on the future reports.
- (ii) All the handpicked dolomite samples obtained from FIPR are having the concentration of quartz phase between 7-20%, however the commercial dolomites having quartz phase less than 0.5%. This may be the one major difference between commercially available, expensive dolomites when compared to inexpensive handpicked samples, however in terms of calcination or carbonation, this dead weight percentage needs to be subtracted which is again part of our future efforts.
- (iii) The two handpicked and hand crushed samples (samples 4 and 5) calcined under nitrogen and air ambient respectively in tube furnace the phase transformation from dolomite to Amphibole/Pyroxene about 50-65% with addition of quartz phase around 15%. Rest of the small phase contents are due to unclassified phases which are discussed below. Overall the STF process is very effective for the calcination nevertheless done under inert or air atmospheres. We will continue with various experimental conditions to obtain optimum concentrations in this technique.
- (iv) The unclassified phases in all the samples listed in Table 2 varies from 6% to 20% (data are not given in the table) depend on the processing conditions. The present attempts are to minimize the unclassified phases which may be again the dead mass which are not taking part of the reversible calcination and carbonation reactions.
- (v) The handpicked and hand crushed dolomite samples shows (sample 3) the concentrations of pure dolomites around 50% with limestone or calcite and quartz concentrations 20% respectively. Rest of 10-15% may be contributions from unclassified phases. Therefore, the active phase percentage may be involved in the active calcination and carbonation is considered to be about 70%, and this has to take in to account when calculating the actual calcination and carbonation percentages when compared to commercial dolomite samples at the some working conditions.
- (vi) Yet another important conclusions based on our Ball milling process (sample 6) that enhance the pure dolomite concentration to 75% from of 50% and the quartz phase has been reduced by half (for example from 15% to 7% quartz concentration of phases). By reducing the dead weight of quartz thus increased the dolomite concentration to 75% could be beneficial for the high reversibility of calcination and carbonation which needs to be tested in the future work.

Overall, the QEMSCAN studies provide directions for the project in optimizing both the preparation and processing conditions of handpicked dolomite samples in terms of calcination and carbonation for the life cycle stability of the reversible reactions. Figure 1 below shows the representative QEMSCAN analysis of all the five samples discussed in table 2. The conclusions proposed above are based on the phase % in terms of Mass % basis. On the volume % basis, the conversions from dolomite to amphibole is increased to 10-20% more.

### **BET Surface Area Analysis of Commercial and Handpicked Dolomite Samples**

Since the calcination and carbonation involves solid-gas reactions, which are primarily surface based than the bulk. The surface area of the solid plays a vital role in locking and/or liberating the CO<sub>2</sub> species from the

dolomites at appropriate temperature driven (calcination) and pressure driven (carbonation) processes. Moreover, the amount of absorbed gaseous nitrogen with monatomic layer is proportional to the surface area of the material, we have carried out BET surface area analysis using the Quantachrome Instruments's Autosorb equipment which is currently available at our collaborator's institution, University of South Florida. Figures 2 and 3 represents the 11 point BET (under liquid N<sub>2</sub>) after outgassing the materials at around 300 °C for two hours. Based on our BET analysis, we have determined the surface area which is approximately 35.45 m<sup>2</sup>/g. From the literature, the pure calcium carbonate calcined at 745 °C, the surface area was reported to be 15.2 m<sup>2</sup>/g (Murthi and Harrison, 1970).

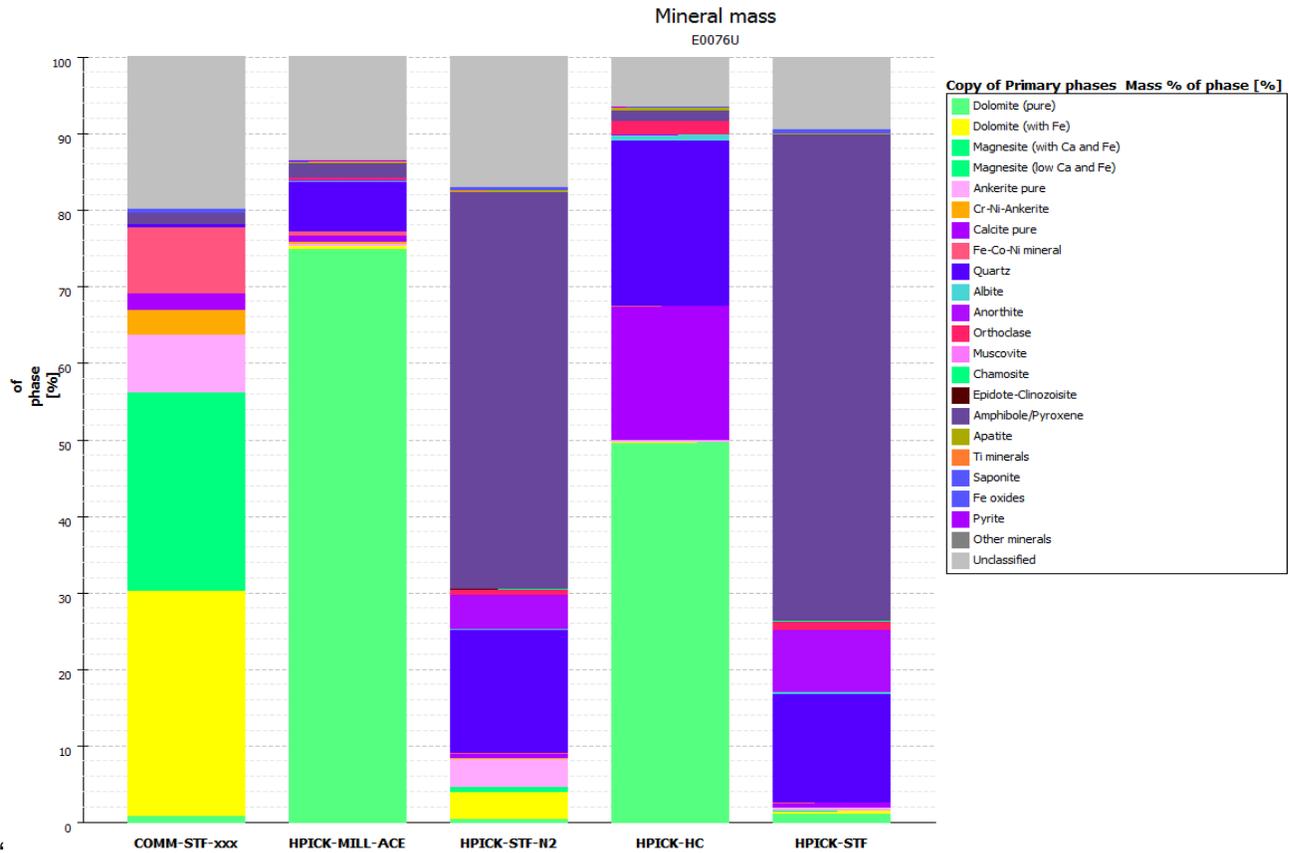
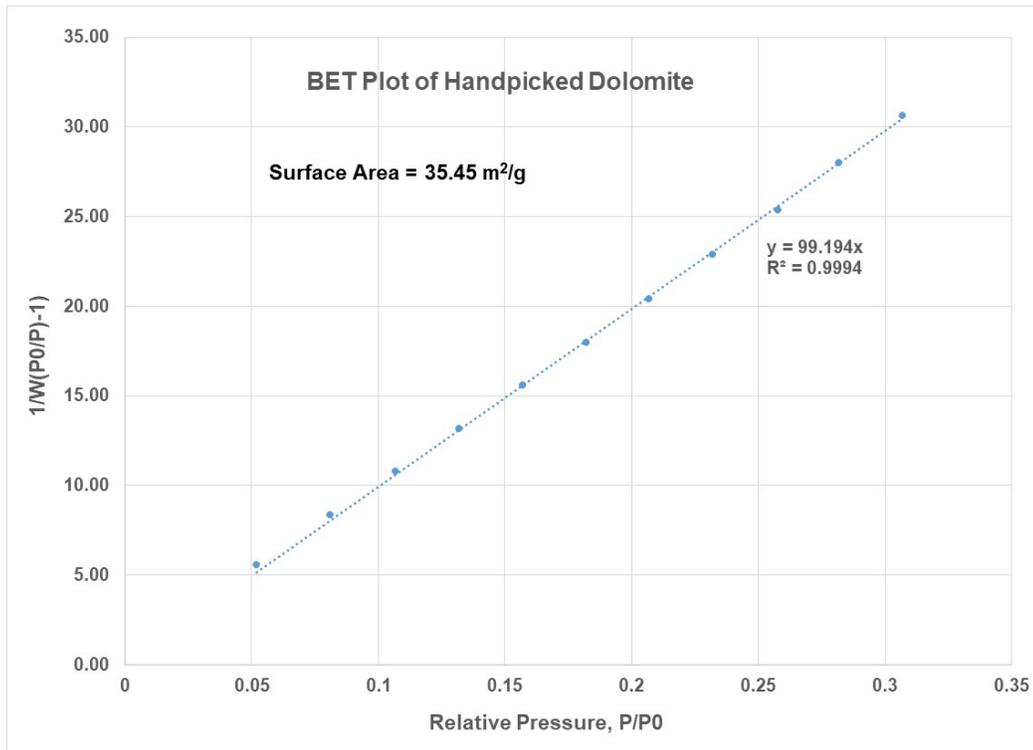


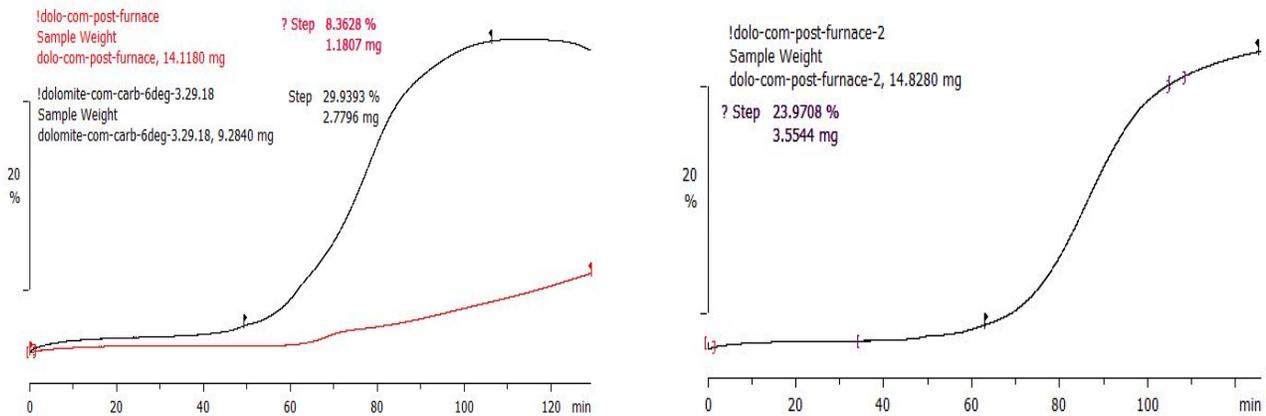
Figure 1: QEMSCAN analysis of five different dolomite samples done at CSM.



**Figure 2:** BET surface area analysis using the nitrogen relative pressure under liquid N<sub>2</sub>

**Calcination in STF and Carbonation via STF or TGA Processes:**

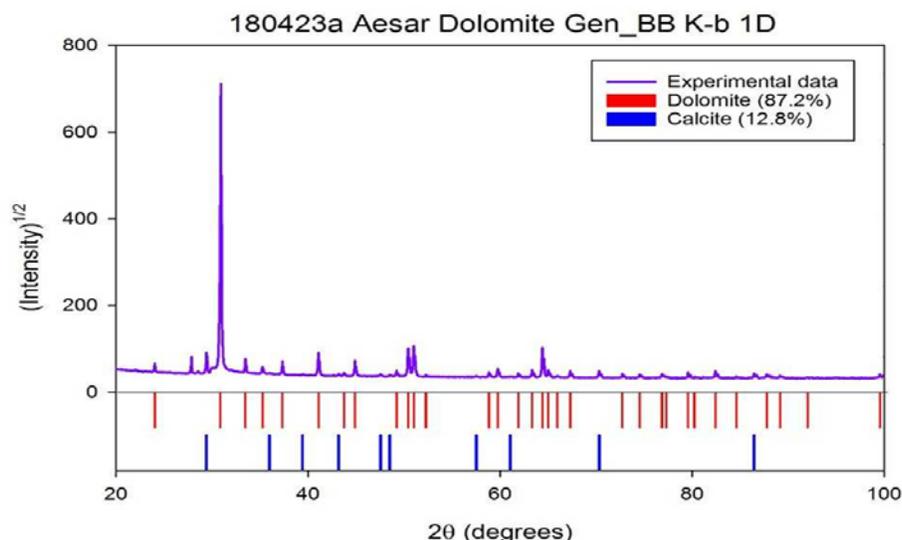
The effectiveness of the calcination process under STF has been validated by the subsequent carbonation step under positive CO<sub>2</sub> atmosphere. Figure 3a shows the TGA profile of low degree carbonation of commercial dolomite sample that was carbonated in STF. However, the TGA carbonation profile demonstrated with high carbonation when it was carbonated in TGA itself (Figure 3b). The downside of the carbonation in STF is due to the lower pressure CO<sub>2</sub> capability compared to the moderate pressure capability in TGA. Moreover, the carbonation process is to recombine the CO<sub>2</sub> gas to reversible the phase of CaMg(CO<sub>3</sub>)<sub>2</sub>.



**Figure 3:** TGA of carbonated commercial dolomites carbonated in (a) STF and (TGA)

### X-ray Diffraction of Commercial Dolomite Samples

The crystal structural characteristics of commercial and handpicked dolomite samples have been investigated via power x-ray diffractometer (Rigaku) with the parameters such as 40 kV, current of 44 mA, wavelength of x-ray beam corresponds to copper  $k_{\beta}$ , scan speed of 0.1001 °/min and step width of 0.0100°. Figure 4 shows the XRD spectrum of commercial dolomite sample fitted with matching peaks. It is observed that ~87% of the phase related to dolomite and around 13% phase related to calcite.



**Figure 4:** XRD spectrum of commercial dolomite sample procured from Alfa Aesar.

The quantitative results involving lattice constants such as a, b, c and the phase angles  $\alpha$ ,  $\beta$ ,  $\gamma$  and unit cell volumes of the two different phases such as dolomite and calcite are tabulated in Table 3 below. The lattice parameters will be used to calculate the d-planar spacing and hence the (hkl) values of individual peaks which will form parts of our future reporting.

**Table 3:** Quantitative results of XRD spectrum recorded for the commercial dolomite samples.

Quantitative analysis results

Lattice information

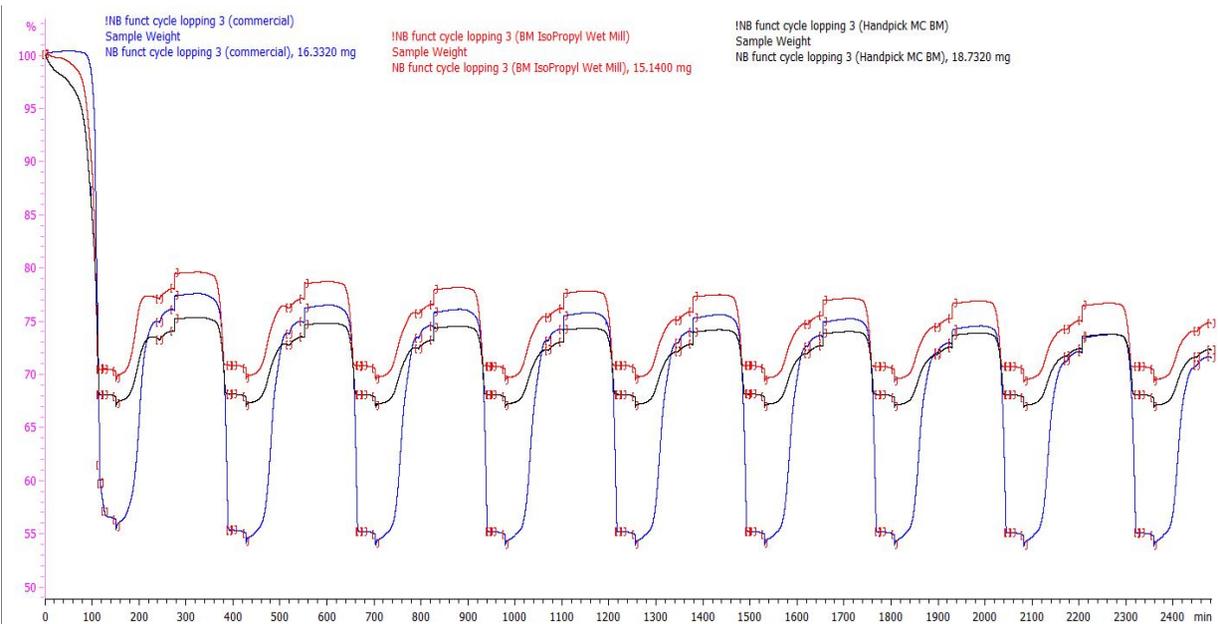
Phase name	a(A)	b(A)	c(A)	alpha(deg)	beta(deg)	gamma(deg)	V(A <sup>3</sup> )
Dolomite	4.813978	4.813978	16.059434	90.000000	90.000000	120.000000	322.306488
Calcite, syn	4.987791	4.987791	17.043972	90.000000	90.000000	120.000000	367.212951

Phase name	Space group	Z	Z'	Calc. density(g/cm <sup>3</sup> )
Dolomite	148 : R-3,hexagonal	3	0.167	2.850
Calcite, syn	167 : R-3c,hexagonal	6	0.167	2.716

### Life Cycle Studies of Handpicked Dolomite Samples

Cyclic stability in terms of reversible calcination and carbonation reaction for the commercial, handpicked and (handpicked + wet ball milled) samples have been examined using thermogravimetric analysis. The TGA looping cyclic methods was formulated in such a way more than 5 continuous cycles were compared for all the samples. Figure 5 demonstrates the continuous looping cycles with calcination under N<sub>2</sub> ambience up to 750 °C, 10 °C/min and carbonation under CO<sub>2</sub> ambience up to 700 °C, 10 °C/min. with cooling in between the cal-carb runs.



**Figure 5:** Calcination and carbonation looping cycles for dolomite samples; commercial (blue), handpicked (black) and handpicked + wet ball milled (red)

It is observed that all the three samples showed good cyclic stability from the 2<sup>nd</sup> cycle onwards, however the very first cycle, huge amount of weight loss is due to the combination of CO<sub>2</sub> liberation, and solvent or water or moisture evaporation etc. Compared to commercial dolomite samples, both handpicked and wet ball milled samples showed less calcination and carbonation and it is obvious that from the QEMSCAN, we have claimed the presence of quartz phases in the handpicked samples. Hence the normalization and optimization is required to actually calculate the loss or gain of CO<sub>2</sub> which is part of our future plans and report submission.

### Summary:

In summary, we have in collaboration with CSM conducted QEMSCAN experiments and obtained quantitative measurements of concentration of various minerals in dolomites during its various stages. The BET results showed the surface area of handpicked shows about 36 m<sup>2</sup>/g. The cyclic looping studies demonstrated the stable cycling after the 2<sup>nd</sup> calc-carb runs. The XRD of commercial samples showed two phases of dolomite and calcite present in the samples.

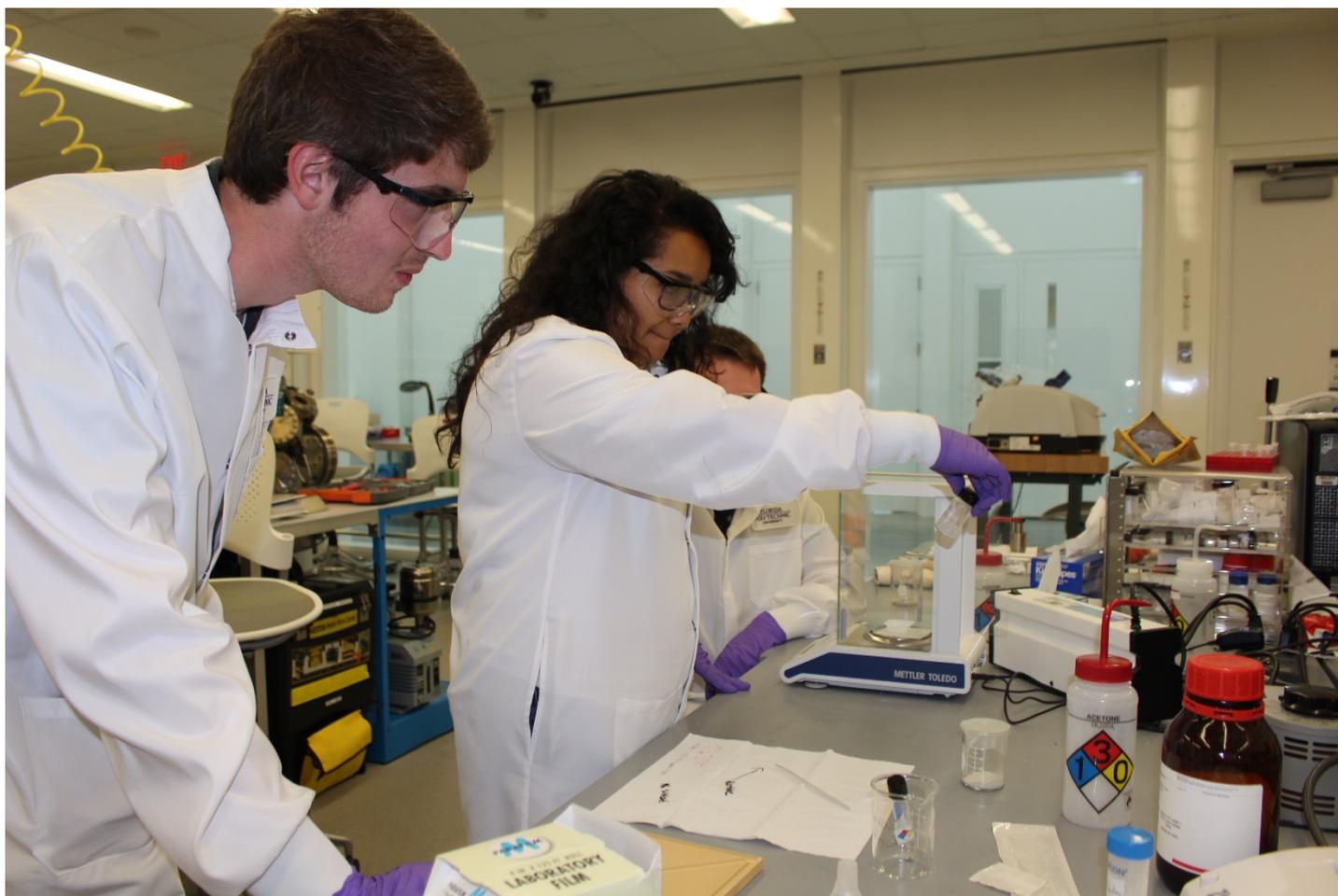
### Future Work:

The future work is based on the results we have obtained so far. More focus will be given to the wet balling to optimize the dolomite concentration and reduce the dead weight minerals. XRD, XRF, SEM, EDS, BET and TPD will be carried out and correlated with the life cycle analysis data.

### Publications and Presentations:

1. **Project Report Presentation entitled** "Feasibility studies of dolomites from phosphatic pebble for thermochemical energy storage and CO<sub>2</sub> sequestration", Danah Velez, Dominic Dodson, Mc Ben Joe Charles, FIPR Board Meeting, June 8<sup>th</sup>, 2018 at FIPR Institute, Bartow, FL
2. **Poster presentation** entitled "Feasibility of high dolomite pebbles for thermochemical storage and carbon capture", Danah Velez, Charles Mc Ben Joe, Dominic Dodson, Scott Wallen, Sessa Srinivasan, Gary Albarelli, Brian Birky, Jaspreet Dhau, USA-India Workshop on Next Generation Green Chemistry/Engineering and Technologies Graduate Program on July 19<sup>th</sup>, 2018 at Florida Polytechnic University, Lakeland, FL, USA.
3. **FIPR Project Report for the period Jan 01, 2018 - Feb 12, 2018**; Submitted on Feb. 12, 2018.
4. **First Quarterly Report for the period Jan 01, 2018 - Mar 31, 2018**; Submitted on April 18, 2018.

5. **Second Quarterly Report for the period Apr 01, 2018 - June 30, 2018**; Submitted on July 21, 2018.
6. Feasibility Studies of Using Dolomite as Thermal Energy Storage for CSP Applications, Dominic Dodson, Mc Ben Joe Charles, Shirley Garcia, Scott Wallen, Gary Albarelli, Brian Birky, Katharina Pfaff, Sessa Srinivasan, **APS Bridge-NMC Conference, Stanford University, November 16-18, 2018 (Abstract Submitted)**
7. Feasibility and Life Cycle Studies of Dolomites for Carbon Capture, Mc Ben Joe Charles, Dominic Dodson, Shirley Garcia, Scott Wallen, Gary Albarelli, Brian Birky, Katharina Pfaff, Sessa Srinivasan, **APS Bridge-NMC Conference, Stanford University, November 16-18, 2018 (Abstract Submitted)**



Wyatt Liptak and Shirley Garcia measuring the FIPR dolomite sample for Thermogravimetric analysis