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SPS Chapter Research Award Interim Report

Project Title	Feasibility Studies of Dolomites from Phosphatic Pebble for Thermochemical Energy Storage and CO_2 Sequestration]
Name of School	Florida Polytechnic University
SPS Chapter Number	2054
Total Amount Awarded	$2,000.00
Project Leader	Wyatt Lyptak, Dana Velez, Sesha Srinivasan

Abstract

The current proposal 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_2 sequestration assembly by using the dolomites ($CaO/CaCO_3$ and $MgO/MgCO_3$ reactions) in phosphatic pebble matrices is proposed. 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_2 in power plants.

Statement of Activity, Interim Assessments & Results

1. High concentration dolomite pebbles with different pebble sizes, shapes and colors have been obtained from Florida Industrial Phosphate Research Institute (FIPR), a dedicated research Institute of Florida Polytechnic University.
2. The pebbles were then sieved with mesh filter and stored per the sizes (for example large and small)
3. FIPR has provided the chemical analysis of these pebbles as shown in the table below.

High Dolomite Pebble 12-20-2017						
Sample ID	**% P2O5**	**% Insol**	**% MgO**	**% Al2O3**	**% Fe2O3**	**% CaO**
High Dolomite Pebble	20.84	17.74	3.33	1.47	1.08	36.76

4. Since these dolomite samples contains majority chemical composition of Calcium-magnesium carbonates, the thermal decomposition of CO_2 under nitrogen ambient was carried out from room temperature to 800^{o}C using Thermogravimetric Analysis (TGA). Different ramping rates of 10^{o}C/min, 5^{o}C/min and 1^{o}C/min shows the thermogravimetric weight loss on an average of 22 wt%. The on-set and end-set temperature points measured during the weight loss analysis are closed to 580^{o}C and 720^{o}C respectively.

5. Based on our preliminary TGA studies, the low ramping rate provided a clean baseline when compared to the high ramping rate with increasing baseline (see the Figure 1). The sample sizes of all three samples have been normalized to compare their thermogravimetric performance.
6. TGA studies of various color samples of high dolomite concentration (for example white, gray and yellow) demonstrated with different weight loss and since this investigation is underway, the results are not reported here.

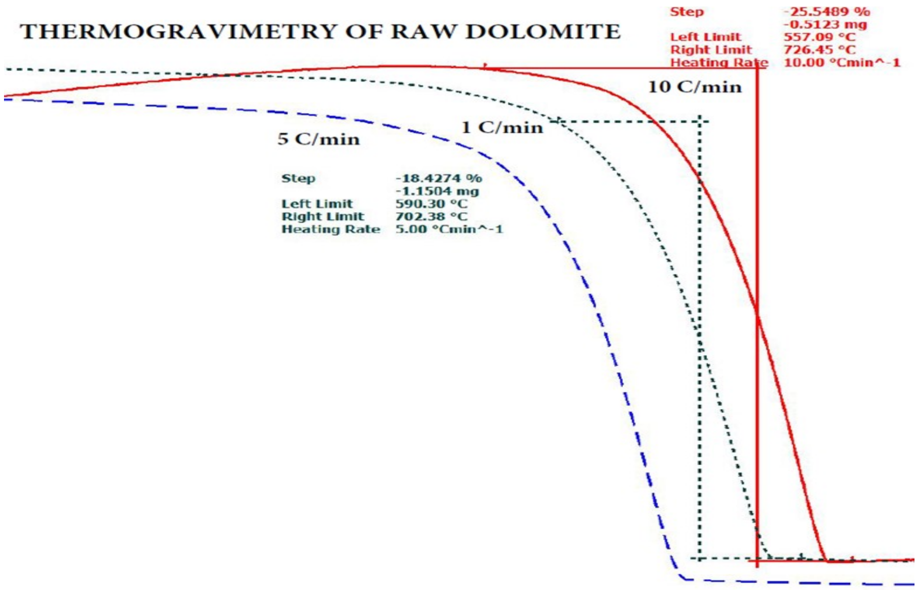

Figure 1: Thermal Gravimetric Analysis or Raw Dolomite at different ramp rates

7. Scanning electron micrographs (SEM) of raw and TGA processed dolomite are shown in Figure 2. The raw materials demonstrated various sizes and shapes, whereas, after TGA thermal decomposition under CO_2 ambient, shows single cluster of dolomite at the same magnification which may reveal the coalescence effects at elevated temperatures. The studies pertaining to understand the elemental composition and their weight percentage are examined by Energy Dispersive Spectroscopy (EDS) feature of back scattered electron imaging as shown in Figure 3. Majority of the composition based on the calcium, magnesium, carbon and oxygen elements, it is partially confirmed the presence of dolomite phases $CaMg(CO_3)_2$.

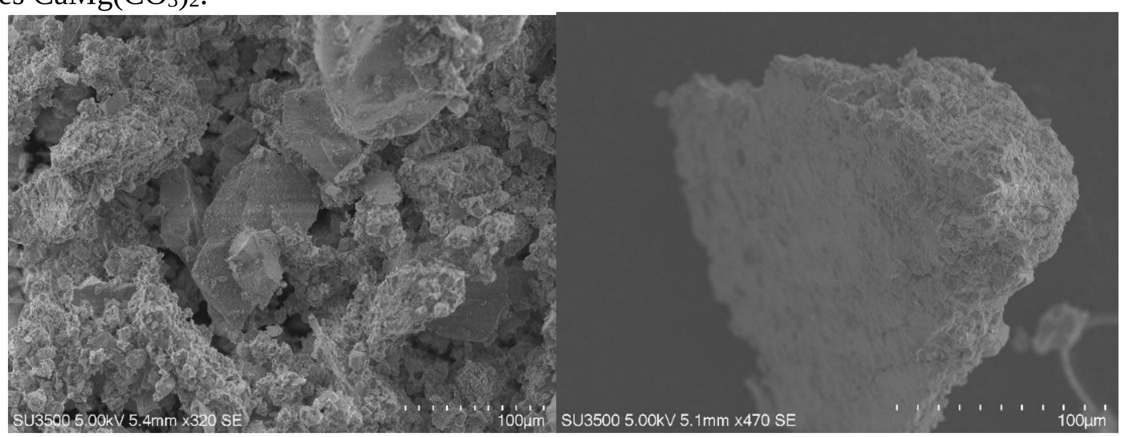

Figure 2: SEM of unprocessed and TGA processed dolomite (100 µ)

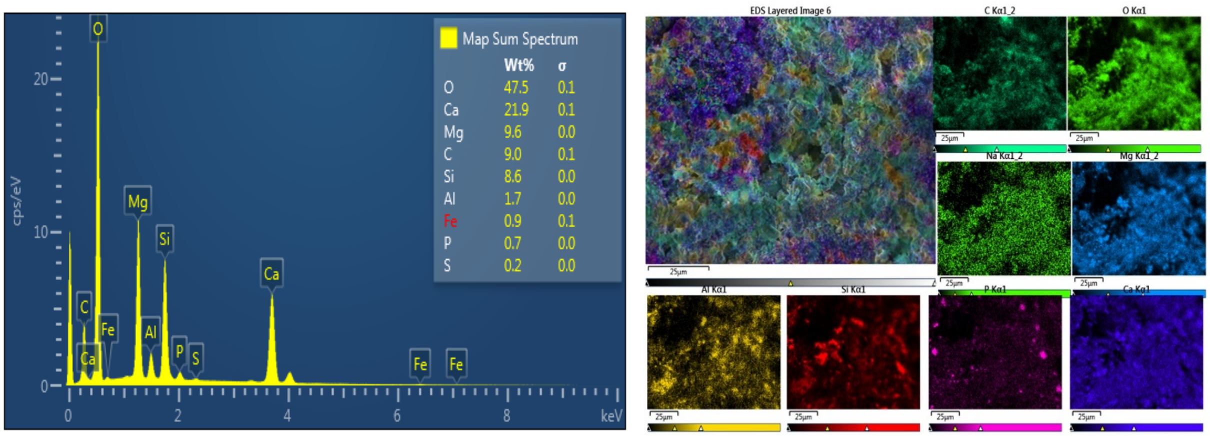

Figure 3: EDS Spectrum and layered EDS mapping of raw dolomite

8. At the end of this interim report, the researchers presented the results obtained from the high dolomite concentration samples supplied obtained from the Phosphate mines in Central Florida. Some of the very important findings are detailed below.

9. Figure 1 below shows the TGA (thermogravimetric analysis) profiles of different color high dolomite concentration samples collected as mentioned above. There were different color pebbles and hence the thermogravimetric analysis of these samples demonstrated non-uniform thermal decomposition in perspective to on-set and end-set points. The thermal decomposition of the commercial dolomite sample exhibited with twice mass loss when compared to the Central Florida's phosphatic samples. Additionally, the samples with dark color sample show two step decomposition with lower weight loss.

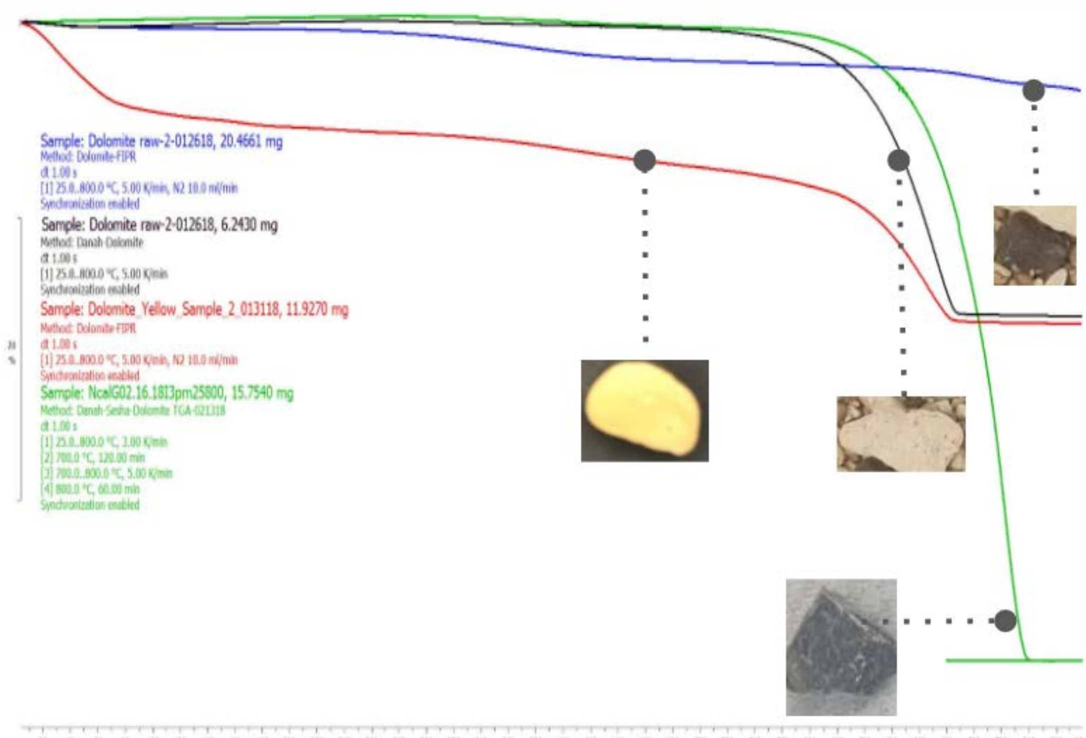

Figure 1: TGA of commercial dolomite sample and the earth obtained samples.

10. The commercial dolomite sample was examined in both calcination and carbonation loop cycles. For the calcination run, nitrogen was used as a carrier gas the ramping rate was fixed to 10°C/min from room temperature to 700°C. For the carbonation cycle, ultrapure CO_2 was used (100 mL/min) for the same

ramping rate and other temperature settings. The commercial dolomite sample in four consecutive calcination and carbonation cycles are shown in Figure 2.

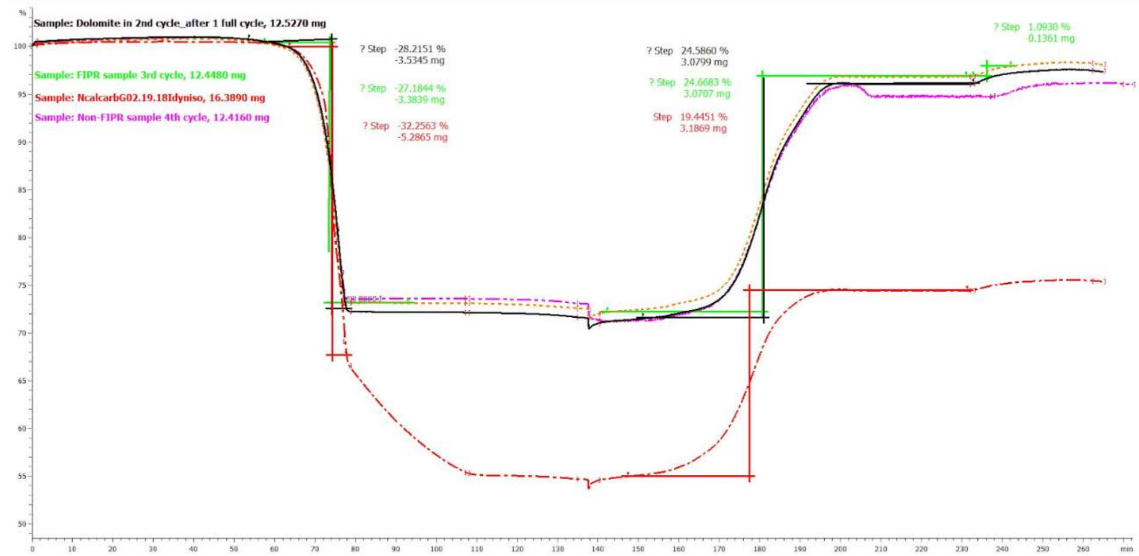

Figure 2: Calcination and Carbonation TGA profiles of commercial dolomite.

11. We have observed, reversible cycles of calcination and carbonation on the earth obtained high dolomite pebble samples. We have picked up the white color pebble since this has decomposed thermally with high mass loss% when compared to other color samples such as gray and black. The Table 1 shows the sample name, initial mass in grams, mass loss% due to calcination and mass gain% due to carbonation cycles. Though the first cycle of calcination demonstrated with ~25% mass loss, however the consecutive carbonation showed less than half of its value. In subsequent runs, the capacity was maintained to 10-12% with mass gain average of ~7%. The X-ray fluorescence of these white samples shows the distribution of different compounds, oxides is shown in Table 2.

Table 1: TGA of FIPR White Dolo-sample

Sample Name	Initial Mass (mg)	%mass drop	%mass gain
FIPR-Dolo-White	4.8610	25.3637	8.2509
FIPR-Dolo-White-2nd-Run	3.5271	12.6450	11.361
FIPR-Dolo-White-3rd-Run	3.4200	13.6710	11.7977
FIPR-Dolo-White-4th-Run	3.3320	13.7602	6.9190
FIPR-Dolo-White-5th – Run (cycle 1)	3.0120	10.022	7.592
FIPR-Dolo-White-5th – Run (cycle 2)	3.0120	11.8684	7.9114
FIPR-Dolo-6th-Run	2.8030	0.5908	7.1854

Table 1: XRF of FIPR's White Sample

Compound	Mass%
Al_2O_3	5.22
SiO_2	24.6
P_2O_5	6.31
SO_3	0.404
K_2O	1.21
CaO	48.7
TiO_2	0.353
Fe_2O_3	4.08
MgO	8.70

Plan for Carrying Out Remainder of Project (including Timeline)

a. Received hand-picked dolomite pebbles from FIPR.
b. Systematic TGA Calcination and Carbonation separate runs have been conducted at various ramping rates, for example 2, 4, 6, 8 and 10ºC. We will analyze these TGA profiles to determine the reaction kinetics and activation energy.
c. Ball milling was utilized to pulverize the new hand-picked dolomites for further characterization and property measurements.
d. High pressure and high temperature PARR type reactor is under testing for loading the FIPR dolomites for high pressure calcination/carbonation at moderate temperatures.
e. High temperature tube furnace with accessories are under construction for the thermal decomposition procedures for the calcination and carbonation.
f. Thus calcined and carbonated dolo-samples will be routinely characterized using metrological suite at Florida Polytechnic University.
g. BET surface area for both the commercial and FIPR supplied samples currently under investigation at collaborator's lab at University of South Florida.