Article

Energy Storage in Earth-Abundant Dolomite Minerals

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Featured Application: Thermochemical energy storage via reversible calcination and carbonation in presence of dolomites.

Abstract: Dolomite, a calcium magnesium mineral ($\text{CaMg}(\text{CO}_3)_2$), is considered an undesirable accompanying mineral in the phosphoric acid production process and, as such, large quantities of this mineral are available in Florida. This study is aimed toward the characterization of the high-concentration phosphatic dolomite pebbles (handpicked dolomites) received from the Florida Industrial and Phosphate Research Institute (FIPR) and investigate their feasibility for thermochemical energy storage (TCES). The chemical composition, structural and microstructural characteristics of commercial and handpicked dolomite minerals was studied using a variety of techniques such as X-ray Fluorescence (XRF), Fourier-transform infrared spectroscopy (FTIR), and an automated mineralogy Automated SEM-EDX Mineralogy (or automated scanning electron microscopy) with energy dispersive X-rays spectrometer (SEM-EDX), which confirmed the phosphatic pebbles received contains dolomite ($\text{CaMg}(\text{CO}_3)_2$) phase in a high percentage. Particle size and the surface area were measured using XRD and N_2 adsorption, the Brunauer–Emmett–Teller (BET) methods. Thermogravimetric analysis (TGA) was used to determine the activation energy for the calcination and re-carbonation reactions of the dolomite pebbles in nitrogen (N_2) and carbon dioxide (CO_2) atmospheres at temperatures up to 800 °C. The present results exhibit, for the first time, the potential for using abundant, high phosphatic concentration dolomite possessing long-term cycling behavior for thermochemical energy storage applications in Concentrated Solar Power (CSP) plants.

Keywords: dolomite; thermochemical energy storage; calcination; carbonation; activation energy

1. Introduction

In a 1914 U.S. Geological Survey Bulletin, Van Kauwenbergh et al. [1] presented a detailed study of the mineralogy and chemistry of the phosphates mined in Florida, specifically Polk and Hillsborough counties of Central Florida. From this report, it was understood that the most uneconomical ingredient in the phosphate mineral matrix was the calcium-magnesium mineral $\text{CaMg}(\text{CO}_3)_2$, also known as

earth-abundant “dolomite”, with a purity of at least 60% occurring in combination with sand (Silica or quartz ~30%). The mining industry routinely terminates their mining process, when they encounter the dolomites or “dolostones”, which are the major source of magnesium and are not favorable for phosphate fertilizer processing. The gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) stack is a potential US-EPA sustainability concern for the precipitation of the CO_2 reaction on limestones (calcium carbonate or CaCO_3) or dolostones [$\text{CaMg}(\text{CO}_3)_2$] during the geological sequestration processes, as demonstrated by Garcia et al. [2]. The late Professor of Mineralogy and Geology at Amherst College, Frederic Brewster Loomis, published an e-book, “Field Book of Common Rocks and Minerals” [3], in which he discusses systematic approaches to identifying minerals and rocks using their physical and chemical properties, including the composition of minerals, and their classifications based on metals. The phenomenon of metamorphism in rocks and minerals have been widely analyzed and discussed by Kurt Bucher and Martin Frey [4].

The dolomites are not only difficult to remove from the gangue (phosphatic minerals) but also pose “environmental sustainability” issues due to their deposition in clay settling ponds around these counties. The magnitude of this problem is considered to be multifold if the future mining processes continue growing to other counties such as Manatee, Hardee, and DeSoto in the State of Florida. The problem of dolomite sedimentation (or stockpiling) in mining plants or clay settling ponds is unavoidable, if there is a depletion of mostly wanted “overburden” soil or economic phosphate ores which are the main source of the phosphorous and phosphorites for the fertilizer industry. The presence of the most troublesome magnesium oxide (MgO)-containing dolomites are a major hindrance in the manufacturing of “phosphoric acid” for diammonium phosphate (DAP) fertilizer production. The high magnesium content increases the sulfuric acid consumption, and, therefore, causes a lower production rate and yield of phosphoric acid [5,6]. All of these consequences could be eliminated by a process that utilized the wasted geological resource, dolomite.

High-temperature thermochemical energy storage utilizes reversible reactions that store energy in the chemical potential of the system. This type of energy storage process is thought to be critical for the on-demand energy production and penetration of concentrated solar power (CSP) into the grid. Current storage systems rely on molten salts, which have an operating temperature limit of 550°C and, therefore, the CSP systems operate at that temperature. However, the CSP plants do have the potential to operate at higher temperature ($>600^\circ\text{C}$) if an alternative to molten salt is found [7]. A recent publication by Konstantinos Kakosimos et al. [8] studied the characterization of surface carbonates obtained from various regions of the Qatar peninsula and have shown promising potential for applications in CO_2 capture and thermochemical energy storage. According to this report, dolomites have higher performance in terms of CO_2 sorption and storage capacity when compared to calcite, CaCO_3 [9–11]. In a long-term cyclic stability study, up to 27% thermal energy storage was demonstrated by Perlinger et al. in a groundwater aquifer, which was plausibly due to the presence of minerals (dolomites) [12]. Another vital use of dolomite in producing a most wanted chemical, magnesium sulfate heptahydrate [$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$] to its highest purity of 99.2% could be deployed in medical, textile, tanning and agriculture industries [13].

A multi-year research and development by the Southern Research Company, a Sun Shot initiative of the US Department of Energy, was recently demonstrated for high-temperature thermochemical energy storage systems with the Concentrated Solar Power facilities [14,15]. Such high-temperature thermochemical energy storage units are in demand due to the abundant availabilities of heat storage materials such as dolomite in the Central Florida’s Phosphate mining sites [16,17]. The commercial potential for the thermochemical energy storage and its marketable share predicted to be for year 2020 is ~147 GW and for the year 2050, it is of the order of 1089 GW with energy storage cost assumed to be at least 15 USD/kWh. The data for the thermodynamic and kinetic dissociation of dolomites are unambiguously unknown until recently [18]. The role of crystal structure on CO_2 capture by limestone derived CaO subjected to carbonation/re-carbonation/calcination cycles at Ca-Looping conditions were reported in the seminal paper published by Valverde et al. [19]. The equilibrium for the thermodynamic dissociations of dolomite is governed by the two reactions given in equations below [20,21]:

High-temperature impregnation has been carried out on an alumina fabric and was thought to serve two purposes such as cumbersome-free calcination and carbonation looping [22] with a cyclic capacity increase. It has been shown that mechano-chemical synthesis [23] offers a simple, efficient, and inexpensive tool for the synthesis of highly stable CaO-containing sorbents for high-temperature CO₂ capture. The CO₂ capture behavior on the porous MgO material involves a two-stage adsorption process which is not caused by adsorbed products, and the adsorption process is minimized by inter-particle diffusion resistance [24].

An intergovernmental panel on climate change (IPCC) report [25] on reduction of greenhouse gases (GHG) emissions indicated they could be lowered by adhering to two stringent processes: (i) by sequestering and capturing atmospheric CO₂ or in coal power plants as produced CO₂ and (ii) developing thermochemical energy storage systems using earth-abundant materials. Based on such high-level recommendations, our project addresses the fundamental and applied aspects of calcium-magnesium carbonates [CaMg(CO₃)₂] or dolomites which have previously been shown to have potential in thermal energy storage applications [8,12,18–22]. The present study is the first examination of the thermochemical energy storage feasibility in high-dolomite phosphatic pebbles obtained from the Florida Industrial and Phosphate Research (FIPR) Institute that are quite abundant in Central Florida's phosphate mining sites. Besides the earth abundance that makes the system cost effective, these calcium-magnesium carbonates or high dolomite pebbles possesses high enthalpy of reaction which is suitable for their wide usage in sustainable and green technological applications such as thermochemical energy storage (TCES) and carbon dioxide capture (Carbon Capture and Storage, CCS) [26–34].

Applications of Dolomites in Concentrated Solar Power Plants (CSPs)

Cheap, efficient, and non-toxic energy storage technologies are vital to handle the rapidly increasing usage of renewable energy at the power production plants, for example, grid stations, solar power plants and windmills. Solar energy-based power generation in concentrated solar power (CSP) plants often deploy phase change materials (PCMs) for storing the latent heat of the sun either received in parabolic troughs or dish-type configurations [35,36]. Another important method of storing heat is by thermochemical reactions using calcite and dolomite which undergoes reversible reactions of CO₂ cycling at elevated temperatures [37,38]. The added advantage of using dolomites for such CSP applications can not only store the large amounts of energy per unit mass but it also can upgrade the temperature of the heat energy. The highest thermal CO₂ conversion efficiency (above 50%) is reported in these dolomite systems if the upgrading heat at 500 °C to temperatures above 800 °C [37]. It has very recently demonstrated that the calcium looping (CaL) process based on multicycle carbonation/calcination of natural limestone/dolomite for thermochemical storage of CSP [38].

2. Experimental and Theoretical Methods

2.1. Materials Developed and Used

Dolomite is ~90% pure commercial naturally occurring mineral (grain sizes of ~5 mm) form has been procured from Alfa-Aesar and are labeled as CO-Dolo (commercial Dolomite). The handpicked dolomites with white color, pebbles were obtained from phosphate mining sites and are labeled as HP-Dolo (Hand Picked Dolomite). Both CO-Dolo and HP-Dolo are used as such with no further purification processes. The Retsch, PM 400, high energy ball milling under wet condition using DI water, was employed to process the handpicked dolomite, and are labeled as HP-Dolo-BM (Hand Picked Dolomite and Ball Milled). A Single-zone Tube Furnace (STF) from Carbolite is used for both the calcination (under N₂ atmosphere) and carbonation (under CO₂ ambient) and operate at temperature from 25 °C up to 800 °C with ramping rate of 6 °C/min. Two additional samples of both commercial and

handpicked dolomites after their initial calcination stages were chosen and labeled as CO-Dolo-STF (Commercial Dolomite in Single Zone Tube Furnace) and HP-Dolo-STF (Hand Picked Dolomite in Single Zone Tube Furnace). All the samples were used completely in dry condition for characterization.

2.2. Physicochemical Characterizations of Dolomites

In general, multiple metrological and mineralogical techniques have been employed to characterize the different stages (plain commercial and handpicked dolomites and their calcined counterparts) of dolomite samples at room temperatures. Some of these techniques are powder X-ray diffraction, X-ray fluorescence, Fourier-Transform Infrared Spectroscopy (FTIR), automated scanning electron microscopy with energy dispersive X-ray spectroscopy, thermogravimetric analysis, and BET surface area analysis. The experimental conditions of these techniques and the parameters used to study the dolomites are elaborated in detail in the following paragraphs.

A number of physicochemical characterizations have been carried out and the results are reported in terms of structural, microstructural, chemical, compositional, and thermal properties during calcination and subsequent carbonation reactions. The chemical composition, structural and microstructural characteristics of the dolomite minerals was studied using different techniques such as X-ray Fluorescence (XRF, Rigaku—NEX/QC/Quantez), Fourier-transform infrared spectroscopy (FTIR), and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM, EDS). All these metrological techniques confirmed the high percentage of dolomite mineral phase in the earth abundant phosphatic pebbles. The Fourier-Transform Infrared Spectra of the dolomite samples have been characterized using Agilent's CARY 600 FTIR spectrometer (Agilent Santa Clara, CA, USA). The Thermogravimetric analyzer (TGA/DSC 1, STAR^e system), from Mettler Toledo (Columbus, OH, USA), was used to calculate the activation energy for calcination and carbonation of the dolomite pebbles in nitrogen (N₂) and carbon dioxide (CO₂) at temperatures up to 800 °C. The structural phase analysis of the dolomite minerals was observed using X-ray diffractometer (XRD) (Rigaku Mini Flex 600, Rigaku, Tokyo, Japan) with the parameters of 40 kV, current of 44 mA, wavelength ($\lambda = 1.540591 \text{ \AA}$) of X-ray beam corresponds to copper K α line, scan speed of 0.1001°/min and step width of 0.0100°. The ball-milling method was used to downsize (to micrometer size particles) the handpicked dolomite samples under DI water or another solvent medium. Not all the samples were milled before subjected to characterization techniques. Particle size and surface area were measured using XRD and N₂ adsorption BET method (Quantachrome Instruments, Autosorb, Acquired by Anton Paar Quanta Tec Inc., Boynton Beach, FL, USA).

The commercial, handpicked, and ball-milled dolomite samples and their carbonated oxide phases via STF were analyzed using automated scanning electron microscopy (automated mineralogy tool manufactured by TESCAN, Brno, Czech Republic, at the Colorado School of Mines (CSM)). Samples were loaded into the TESCAN (Automated SEM-EDX Mineralogy)-VEGA-3 Model LMU VP-SEM platform and analysis was initiated using the control program TIMA3. Four energy dispersive X-ray (EDX) spectrometers acquire spectra from each point or particle with a user defined beam stepping interval (i.e., spacing between acquisition points), an acceleration voltage of 25 keV, and a beam intensity of 14. Interactions between the beam and the sample are modeled through Monte Carlo simulation. The EDX spectra are compared with spectra held in a look-up table allowing a mineral or phase assignment to be made at each acquisition point. The assignment makes no distinction between mineral species and amorphous grains of similar composition. TIMA software was deployed to study the semi-quantitative compositional mapping output results of dolomite minerals at different stages of calcination [39].

2.3. Activation Energy Calculations

Dynamic TGA was performed and analyzed according to ASTM E1641—16 [40] using the method of Ozawa, Flynn, and Wall [41]. The TGA decomposition curves of both CO-Dolo and HP-Dolo for several heating rates were analyzed using a general rate equation given as

$$\frac{d\alpha}{dT} = A(1 - \alpha) \exp[-E_a/RT]/\beta \quad (2)$$

where α = fraction reacted, A = pre-exponential factor, β = heating rate ($^{\circ}\text{C}/\text{min}$), E_a = activation energy (J/mole), R = gas constant (8.316 J/(mol K)), T = absolute temperature ($^{\circ}\text{C}$), and $d\alpha/dT$ = rate of change of α with T . Using the method of Ozawa, Flynn, and Wall Equation (3) yields a relation for the activation energy given as

$$E_a = \left(\frac{R}{b}\right) \frac{\Delta \log[\beta]}{\Delta \left[\frac{1}{T}\right]} \quad (3)$$

Using a fixed decomposition fraction reaction (0.1, i.e., 10% decomposition), an initial activation energy was determined through the slope of a plot of the $\ln[\beta]$ versus $1/T$ with an initial value of b (constant assuming a first order reaction) of 0.457 (from the Doyle approximation). The activation energy was iteratively regressed until its value was constant and these are reported in the present work.

3. Results and Discussion

Sections 3.1 and 3.2 provide the semi-quantitative results based on the XRF and automated SEM-EDX analyses of plain and heat-treated dolomite minerals. Therefore, any correlations made on the compositional percentages are subjected to the limitations of the instrumental parameters and other underlying discrepancies.

3.1. Chemical Make-Up via X-ray Fluorescence (XRF)

The x-ray fluorescence characterization of CO-Dolo, HP-Dolo (see Figure 1) and their calcined counterparts were carried out to explore the chemical constituents in terms of bulk weight percentages. Table 1 below gives the compositional variations of these samples in terms of constituent compounds and their wt%. By reviewing the Table 1, it is very clear that the HP-Dolo has the active content of CaO and MgO combined to be only ~56%, and the other 44% from inert compounds (e.g., SiO_2 ~32% and Al_2O_3 ~7%) which have no value added to the overall calcination and carbonation processes. Whereas, the CO-Dolo counterpart showed ~88% of the mixtures of CaO and MgO that could fully contribute to the bi-metal carbonate $[\text{CaMg}(\text{CO}_3)_2]$ formation. Therefore, our further results of HP-Dolo samples with lower reported values in terms of percentage of mass conversion may be impacted due to their reported lower purity level. More remarks about the XRF are stated in Table 1.

Figure 1. Snapshot camera pictures of (a) commercial dolomite sample; (b) handpicked dolomite sample.

Table 1. X-ray Fluorescence data for both commercial and handpicked dolomites.

Elements or Compounds	CO-Dolo wt%	CO-Dolo-STF wt%	HP-Dolo wt%	HP-Dolo-STF wt%	Remarks
CaO	67.90	34.26	36.60	32.00	~50% reduction in CaO content in HP-Dolo. After carbonation in STF, the CaO content increased in the range from 3.5 to 17 wt%
MgO	19.60	9.80	19.20	10.90	More or less equal amount of MgO in both samples. After carbonation in STF, the MgO content is reduced in the range from 1.7 to 8.3 wt%
SiO ₂	1.64	0.40	32.00	24.10	HP-Dolo contains large amount of silica (sand type). After carbonation in STF, the SiO ₂ content reduced up to 8 wt%.
P ₂ O ₅	0.52	0.60	1.61	0.83	P ₂ O ₅ in trace amounts in all samples
Fe ₂ O ₃	9.94	9.33	2.53	3.88	Fe ₂ O ₃ is greater in CO-Dolo due to purification procedures.
Al ₂ O ₃	-	-	6.66	5.07	Alumina Al ₂ O ₃ is found in Earth-mined phosphates, HP-Dolo.
CaO + MgO combined	87.50	44.06	55.8	42.90	Added row 1 and row 2 values. ~30% mass reduction in HP-Dolo due to unreactive SiO ₂ . After carbonation in STF, this reactive mixture of CaO+MgO increased by 3–8 wt%.
Loss on Ignition (LOI)	0.00	45.00	0.00	22.00	Loss on Ignition is due to the CO ₂ release during calcination.

3.2. Compositional Mapping via Automated Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDX) Mineralogy

The XRF results as reported in Section 3.1 are at the elemental or compound wt% level. For example, we have given the wt% of CaO and MgO and other oxide phases. The Loss on Ignition (LOI) correction is often needed while analyzing the XRF, in order to account for the volatile compounds, in this case, CO₂ locked in the dolomite [CaMg(CO₃)₂] matrix [42,43]. Therefore, a sophisticated and automated mineralogical tool, Automated SEM-EDX Mineralogy with Variable Pressure-Scanning Electron Microscopy (VP-SEM) coupled with four energy dispersive X-rays (EDX) at the Colorado School of Mines was deployed to study the compositional mapping of all our samples listed in the experimental section and are tabulated in Table 2. Five different samples such as HP-Dolo, ball-milled HP-Dolo-BM, carbonated under nitrogen HP-Dolo-STFN2, carbonated under air HP-Dolo-STFO2 were studied for compositional mapping and are represented in Figure 2.

Figure 2. Automated Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDX) analysis of five different dolomite samples done at Colorado School of Mines (CSM).

Table 2. Semi-quantitative results of samples under automated SEM-EDX Mineralogy (FP-SEM-EDX) at Colorado School of Mines.

Sample Category Number(s)	Sample(s) Name	Dolomite Pure or Dolomite (with Fe) Concentration (as Reference Phase) [wt% of Phase%]	Other Major/Minor Phases [wt% of Phase%]
1	Commercial + Hand Crushed STF (N ₂ ambient) [CO-Dolo-STFN2]	Dolomite (Pure): 0.91 Dolomite (with Fe): 29.38	Magnesite (with Ca and Fe): 23.70 Magnesite (low Ca and Fe) 2.28 Ankerite (pure): 7.56 Cr-Ni Ankerite: 3.19 Calcite: 2.09 Fe-Co-Ni Mineral: 8.69 Quartz: 0.36 Amphibole: 1.46 Unclassified: 19.74
2.	Hand Picked + Hand Crushed [HP-Dolo]	Dolomite (Pure): 49.60 Dolomite (with Fe): 0.08	Calcite: 17.46 Quartz: 21.67 Amphibole: 1.26 Unclassified: 6.36
3	Hand Picked + Ball Milled (Acetone) [HP-Dolo-BM]	Dolomite (Pure): 74.90 Dolomite (with Fe): 0.53	Calcite: 0.82 Quartz: 6.42 Amphibole: 1.85 Unclassified: 13.37
4	Hand Picked + Crushed STF (N ₂ ambient) [HP-Dolo-STFN2]	Dolomite (Pure): 0.50% Dolomite (with Fe): 3.51	Ankerite: 3.71 Quartz: 15.98 Anorthite: 4.42 Amphibole: 51.93 Unclassified: 16.92
5	Hand Picked + Hand Crushed STF (Air ambient) [HP-Dolo-STFO2]	Dolomite (Pure): 1.15 Dolomite (with Fe): 0.31	Ankerite: 0.48 Quartz: 14.26 Anorthite: 8.01 Amphibole: 63.47 Unclassified: 9.33

The commercial dolomite in its pristine stage was not examined in the Automated SEM-EDX Mineralogy measurements, but we have evaluated its partial carbonated version under STF/N₂ environment [CO-Dolo-STFN2]. This sample exhibits the majority of phases from the Fe-rich dolomite and magnesite and a few minority phases from Fe-Co-Ni minerals. Therefore, the CO-Dolo-STFN2, Automated SEM-EDX Mineralogy results are agreement with the higher concentration of Fe₂O₃ as previously demonstrated with the XRF results. Another interesting feature noticed based on the Table 2 and Figure 2 results is that the Fe-containing dolomite or Ankerite do occur in low concentration for both the commercial and handpicked samples. However, the Ankerite concentration increases, while heat treatment of these Fe containing dolomites which are commonly referred as Ferroan dolomite/Ankerite phases [44]. It is interesting to note that the quartz phase (SiO₂) is below 0.5%, because of its removal while processing at the industrial scale. The Fe-free dolomite phase, up to 50%, and calcite phase, up to 20%, are predominantly seen in the HP-Dolo samples, which are handpicked at the phosphate mining site in the Central Florida region. At least 22% arises from the quartz, which is considered to be an inert material that does not contribute to the thermochemical reactions. The presence of such high concentrations of SiO₂ in the earth-abundant dolomites, may lead for the de-agglomeration of particles resident during long-term thermal cycling; however, we have not validated this aspect experimentally.

The handpicked dolomite samples are now exposed to the ball milling in the presence of DI water [HP-Dolo-BM] at room temperature. This is carried out to enhance the dolomite reactive species, and to reduce the inert deadweight SiO₂. To our surprise, these HP-Dolo-BM processed materials showed up to 75% of the pure dolomite phase and reduction of calcite to less than 1%. It is unknown how the ball milling enhances the original sample wt% of HP-Dolo from 50% to HP-Dolo-BM, 75% since it is theoretically not plausible. We hypothesize that the ball milling is a highly energy intensive mechanochemical process, with which the calcite phase from 17.5% (HP-Dolo) is fully consumed and that increases the concentration of pure dolomite phase. Another possible reason is the reduction of SiO₂ from 22% to 6% after ball milling which increases the initial concentration of dolomite phase.

The handpicked dolomite samples were calcined in a single-zone tube furnace under nitrogen [HP-Dolo-STFN2] and oxygen (or air) [HP-Dolo-STFO2] atmospheres from 25 °C to 800 °C. This was

to investigate the effect of the calcination process involving CO_2 decomposition. It is observed that the initial dolomite phase of 49.6% and calcite phase of 17.5% was identified in the [HP-Dolo] samples and are considered to be the major contributing phases for thermal decomposition of CO_2 . Therefore, there is an increase of by-product Amphibole phase formation up to 52% in [HP-Dolo-STFN2] and 63% in [HP-Dolo-STFO2]. Approximately 4–8% of a minority satellite phase Anorthite was formed. There was a slight reduction of about 6% quartz phase between the handpicked dolomite sample and its calcined counterparts maybe due to inhomogeneities of the sample or measurement technique error. Moreover, the SiO_2 characterization is of not much interest since this phase does not contribute for any thermochemical reactions, this quartz phase is considered to a dead weight and not further explored.

For samples 4 [HP-Dolo-STFN2] and 5 [HP-Dolo-STFO2], the SiO_2 or quartz phase was identified by the Automated SEM-EDX Mineralogy are 15.975%, and 14.26%, respectively (please see Table 2). These mass percentages in close match with our XRF results as reported in Table 1, for the sample HP-Dolo-STF, the SiO_2 phase is ~24.1 wt%. With this high concentration of SiO_2 phase and the calcination of dolomites, the tube furnace ends up with Amphibole formation. On the other hand, for the non-calcined [HP-Dolo] sample, even though the SiO_2 concentration of 21.67% (sample 2 in Table 2) and 32 wt% in Table 1, there was no Amphibole formation. Yet, another closer look of calcined commercial dolomite, sample 1 [CO-Dolo-STFN2], the Amphibole formation is less than 2 wt%, due to the low concentration of SiO_2 (0.36%). The same is true for the handpicked and ball milled sample 3 [HP-Dolo-BM], without further calcination, the Amphibole phase is less than 2% while the SiO_2 is reported in Table 2, with 6.42%. Based on the above analysis, it is very clear that, for the formation Amphibole phase, a sample composition parameter with a high concentration of SiO_2 (>15 wt%), the sample must undergo high temperature calcination.

There is one unclassified phase which is universally present in all the samples, no matter whether this is in its pristine or calcined form, and this unclassified phase varies from 6% [HP-Dolo] to 20% [CO-Dolo]. Neither the ball milling nor the calcination of HP-Dolo increases the wt% of this unclassified phase. Overall, the Automated SEM-EDX Mineralogy results have identified a number of possible phase compositions of dolomite and other related complex compounds in which the XRF has limited scope. The Automated SEM-EDX Mineralogy supplements and supports the XRF findings that the handpicked dolomites have an intrinsic impurity phase of SiO_2 up to 20–30%.

3.3. Phase Determination and Crystallite Size Analysis via X-ray Diffraction (XRD)

The X-ray diffraction was carried out for the three samples, namely, CO-Dolo, HP-Dolo and HP-Dolo-BM which is shown in Figure 3. The phase matching, peak and hkl planes identification was performed using ICSD database software, Version 4.4.0 that is loaded in the package of Rigaku, PDXL-2.

The commercial dolomite [CO-Dolo] exhibits a single phase compound with hkl indices matching $\text{CaMg}(\text{CO}_3)_2$, ICSD PDF Card no. 202162. There is one diffraction peak at 29.34° , d-value 3.026 that is assigned to the maximum intensity XRD peak of calcite (ICSD PDF Card No. 164935) with angle and d-values (29.34° , $d = 3.042$) matching with miller index correspond to (104). On the other hand, the handpicked dolomite sample and its ball milled counterpart, showed $\text{CaMg}(\text{CO}_3)_2$ similar to the pristine dolomite, CO-Dolo sample. Since the pure dolomite mineral phases are predominant (49.6%—sample 2 and 74.9%—sample 3) than the Fe-containing dolomite phases (0.08%—sample 2 and 0.53%—sample 3), as reported in Table 2; the XRD profiles show no indication of Fe in the dolomite structure. The Fe containing dolomite phase increase to 3.51% for calcined, handpicked dolomite (sample 4) and 29.38% for partially calcined, commercial dolomite (sample 1), for which the XRD was not performed. Additionally, an impurity phase, quartz (SiO_2) with ICSD PDF Card no. 42498 is matched with three diffraction peaks at 2θ angles of 27° , 42° and 69° , respectively. The relative intensities of the majority peak at $\sim 30.9^\circ$ is much smaller for the handpicked dolomites when compared to the commercial samples, thus indicating the handpicked versions are at the smaller average crystallite sizes. Table 3 represents the XRD data (few prominent peak positions) of all three samples mentioned

above with respect to the shift in 2θ , d spacing and full-width at half maximum (FWHM) values corresponding to the assigned dolomite phase with hkl Miller indices.

Figure 3. X-ray Diffraction (XRD) spectrum of commercial dolomite, handpicked dolomite, and ball-milled dolomite.

Table 3. Comparison of X-ray Diffraction (XRD) peaks of dolomite of Commercial Dolomite (CO-Dolo), Hand Picked Dolomite (HP-Dolo), and Hand Picked Dolomite and Ball Milled (HP-Dolo-BM).

Co-Dolo			HP-Dolo			HPO-Dolo-BM			Dolomite
Average Crystallite Size = 552.5 nm			Average Crystallite Size = 448.3 nm			Average Crystallite Size = 354.0 nm			ICSD—202162
2θ	d-value	FWMH	2θ	d-value	FWMH	2θ	d-value	FWMH	(hkl)
30.909	2.89075	0.1344	30.9	2.89125	0.188	30.906	2.89099	0.2253	104
41.078	2.19557	0.1932	41.076	2.19565	0.1856	41.072	2.19588	0.2378	113
44.841	2.01966	0.1696	44.878	2.01805	0.1829	44.868	2.01849	0.2226	202
50.430	1.80814	0.1463	50.450	1.80746	0.2309	50.458	1.80721	0.2937	018
50.982	1.78985	0.1809	51.008	1.7890	0.2195	51.005	1.78911	0.3062	116
Lattice Parameters (Calculated for hkl = (300) and (006))			Lattice Parameters (Calculated for hkl = (300) and (006))			Lattice Parameters (Calculated for hkl = (300) and (006))			a = b = 4.811 Å
a = b = 4.8163(2) Å			a = b = 4.8146(5) Å			a = b = 4.8187(8) Å			c = 16.0462 Å
c = 16.0748(7) Å			c = 16.0504 Å			c = 16.0513 Å			Volume = 321.659 (Å) ³
Unit Cell Volume = 322.93 (Å) ³			Unit Cell Volume = 322.22 (Å) ³			Unit Cell Volume = 322.78 (Å) ³			

From Table 3, it is evident that the HP-Dolo samples show an increase in FWHM compared to the commercial dolomite sample, showing that the HP-Dolo has a less crystalline structure form when compared to the CO-Dolo sample. The handpicked ball milled samples on the other hand, have increased FWHM compared to their pristine, handpicked counterparts. This indicates a reduction in average crystallite sizes. The average crystallite sizes based on the Scherrer's equation is found to be 552.5 nm for CO-Dolo, 448.3 nm for HP-Dolo and 354 nm for HP-Dolo-BM. The FWHM shift in terms of the quartz phase has not been explored since this phase does not contribute for the thermochemical reactions during the calcination and carbonation processes.

The most useful information such as lattice constants and unit cell volume of these dolomite samples have been calculated and compared with PDF Card no. 202162 for $\text{CaMg}(\text{CO}_3)_2$. The crystal

system with space group R-3:H(148) is adopted [45]. The lattice parameters (a and c) and the unit cell volume of the commercial dolomite samples are slightly larger than the handpicked dolomites and it supports the average crystallites calculations. On the other hand, the ball milling though downsizes the crystallites about 94.3 nm, the lattice constants, and the unit cell volume slightly higher in HP-Dolo-BM when compared to pristine HP-Dolo. This increase in both lattice parameters ($\Delta a/a_0 = 0.085\%$; $\Delta c/c_0 = 0.0056\%$) and unit cell volume ($\Delta V/V_0 = 0.18\%$) for the HP-Dolo-BM are due to the ball mill-induced deformation in the crystal lattice [46]. Additionally, since the ball milling was done in DI water and with only 10 min, the possibility of Fe incorporation into the sample highly unlikely. The preciseness of the sample preparation and repeating of measurements are within the error limit of less than 1%. Since the commercial and handpicked dolomite samples are as used without further purification the preciseness in preparation is almost 100%. For the ball-milled, handpicked dolomites, we have followed same experimental conditions, such as ball to powder weight ratio, time duration and medium of milling; the preciseness of preparation is within 5% experimental and human error. The repeating of characterization measurements has been done with the standard operating procedure, so the preciseness was ensured, and it was within the error limit of less than 1%.

3.4. Chemical Environment via FTIR

FTIR profiles of commercial dolomite (CO-Dolo), handpicked dolomite (HP-Dolo) and handpicked, ball-milled dolomite (HP-Dolo-BM) samples have been recorded for IR transmittance with wave numbers in the mid-IR region, ranging from 500 to 4000 cm^{-1} (see Figure 4). In general, the lower energy peaks, for example around 727, 876, 1023, 1418 and 1823 cm^{-1} matches with dolomite bands reported elsewhere [47,48]. The handpicked dolomites, both in its pristine and ball-milled stages, follow the same spectral trends as the commercial dolomites in the lower energy region. The dolomite stretch around 1023 cm^{-1} is, however, not prominently shown in the ball-milled HP-Dolo BM sample, whereas the sharpness of the 1418 cm^{-1} is increased. An additional peak around 2358 or 2362 cm^{-1} appears in the handpicked dolomite and its ball-milled counterpart, which indicates the stretch due to the quartz (SiO_2) phase [49] previously mentioned in the XRF, Automated SEM-EDX Mineralogy and XRD sections.

Figure 4. Fourier Transform Infrared (FTIR) spectra of CO-Dolo, HP-Dolo and HP-Dolo-BM samples in transmittance mode.

3.5. Surface Area via Brunauer-Emmett-Teller (BET) Apparatus

Since the calcination and carbonation involves solid-gas reactions, they are primarily surface based rather than bulk reactions. The surface area of the solid plays a vital role in locking and/or liberating the CO₂ species from the dolomites at appropriate temperature- (calcination) and pressure-driven (carbonation) processes. Moreover, the amount of adsorbed gaseous nitrogen with monatomic layer is proportional to the surface area of the material. Figure 5 represents the 11-point BET (under liquid N₂) after outgassing the materials at 300 °C for two hours.

Figure 5. Brunauer-Emmett-Teller (BET) surface area analysis of CO-Dolo and HP-Dolo samples in liquid N₂.

Based on the BET analysis, we have determined the surface area which is approximately 35.45 m²/g for the handpicked dolomite, [HP-Dolo]. From the literature, pure calcium carbonate calcined at 745 °C had a reported surface area of 15.2 m²/g [50] and the surface area of dolomite, from Carl Pool Co. 200+ mesh, is around 0.97 m²/g [51]. We have carried out the BET of the Alfa Aesar commercial dolomite sample, [CO-Dolo] and the surface area is found to be 0.7 m²/g. Therefore, the higher surface area of HP-Dolo obtained from the BET measurements support the smaller crystallite size (increased FWHM) as evidenced from the XRD results in the Section 3.3.

3.6. Activation Energy from Calcination via Thermogravimetric Analyzer (TGA)

The TGA profiles of commercial dolomite (CO-Dolo) at different ramping rates of 2, 4, 6, 8, 10 and 20 °C/min are shown in Figure 6a. Based on TGA kinetic profiles, the activation energy parameters for the calcination of the commercial dolomite sample is plotted in the inset of Figure 6a and the straight line determined by method ASTM 1641-16 [40] yielded the activation energy, Ea = 465 kJ/mol. For handpicked dolomite (HP-Dolo), a similar activation energy determined using different calcination ramping rates, is shown in Figure 6b. The HP-Dolo sample shows a lower activation energy of 323 kJ/mol when compared to the commercial dolomite sample and thus, may be due to its secondary impurity phase, notably, SiO₂. The tables below Figure 6a,b denote the parametric values used based on the literature [40,41].

Figure 6. (a): TGA profiles (left) showing the calcination of commercial dolomite at different ramping rates, and the Arrhenius plot (right) based on Equation (3) [41]. (b): TGA profiles (left) showing the calcination of handpicked dolomite at different ramping rates, and the Arrhenius plot (right) based on Equation (3) [41].

3.7. Activation Energy from Carbonation via TGA

The effectiveness of the calcination process as reported in Section 3.6 was validated by the subsequent carbonation step under positive CO₂ atmosphere in a single-zone tube furnace and the samples we have labeled as CO-Dolo-STFN2. The carbonation was also studied in TGA at temperatures up to 800 °C under a flow of CO₂ (100 mL/min) with different ramping rates (2, 4, 6, 8, and 10 °C/min). Based on TGA kinetic profiles, the activation energy parameters for the carbonation of CaO and MgO to form CaMg(CO₃)₂, is plotted in the inset of Figure 7 and the straight line determined by ASTM 1641-16 [38] yielded the activation energy, Ea = 38.7 kJ/mol. The activation energy of the handpicked dolomite was not performed due to poor carbonation and the lack of high pressure TGA.

dy/dx	-4932	K/min
R	8.316	J/molK
Ea*b	81.2421	kJ/mol
b	0.4495	k/min
Ea	38.73659	kJ/mol

Figure 7. TGA profiles (a) showing the carbonation of commercial dolomite at different ramping rates. (b) The Arrhenius plot based on Equation (3) [41].

3.8. Calcination-Carbonation Looping Cycle via TGA

Cyclic stability in terms of the reversible calcination and carbonation reactions for the commercial, handpicked, and handpicked ball milled dolomite samples have been examined using thermogravimetric analysis. The TGA looping cycle methods were formulated to provide more than five continuous cycles for all the samples examined. Figure 8 demonstrates the continuous looping cycles with calcination under N_2 up to 750 °C at a heating rate of 10 °C/min and carbonation under CO_2 up to 700 °C at a heating rate of 10 °C/min. with cooling in between the calcination–carbonation cycles.

Figure 8. Calcination and carbonation looping cycles for dolomite samples including commercial (purple), handpicked (blue) and handpicked + ball milled (brown).

All three samples showed good cyclic stability from the 2nd cycle onwards due to the absorption and release of CO₂ as shown in Figure 8. Compared to commercial dolomite samples, both handpicked and ball-milled samples showed less calcination and carbonation. It is obvious from the automated SEM-EDX Mineralogy, XRF and XRD analyses, that there is a presence of at least 30% of SiO₂ in handpicked samples, which is inert to thermochemical reaction under CO₂. The XRDs of the de- and re-carbonated samples during the life cycle measurements were not performed due to the limitation of sample size (<15 mg); however, we will execute such studies using a zero-background single-crystal Si sample holder, and the XRD results will be submitted for forthcoming publication.

4. Conclusions

It is concluded that the earth-abundant dolomite materials (handpicked dolomite, labeled as hp-dolo) as obtained from Central Florida's Phosphate Mines have demonstrated the energy storage behavior comparable to the commercial dolomite. The automated SEM-EDX Mineralogy and X-ray Fluorescence experiments were performed to obtain the quantitative measurements in terms of various mineral phases in dolomites during its various stages. The BET results the surface area of handpicked shows about 36 m²/g which is larger than the commercial samples. The XRD of handpicked samples showed two phases which included dolomite and impurity like quartz present. The lattice parameters, the unit cell volume and the average crystallite sizes of the handpicked dolomites are lower than the commercial materials because of its natural abundancy with no further purification. The FTIR spectra of all samples exhibit typical dolomite stretches as previously observed in the literature. The activation energy during calcination for both the commercial and handpicked dolomites, has been calculated using ASTM E1641-16 method. The carbonation activation energy for the commercial dolomite was lower in value compared to the calcination process. This may be due to the effect of positive CO₂ pressure during the carbonation. The cyclic looping studies demonstrated stable cycling after the 2nd calcination-carbonation loop and continued for longer durations. Overall, the handpicked, Earth-abundant dolomites in its pristine, or ball milled powder form, are very comparable to the commercial dolomites, in terms of thermal energy storage, at high-temperature and -pressure conditions.

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Abbreviations

CaMg(CO ₃) ₂	Calcium Magnesium Carbonate
FIPR	Florida Industrial Phosphate Research Institute
TCES	Thermochemical Energy Storage
XRF	X-ray Fluorescence
XRD	X-ray Diffraction
FTIR	Fourier-Transform Infrared Spectroscopy
Automated SEM-EDX Mineralogy	Manufacturing Company for Scanning Electron Microscopes to study Minerals
SEM	Scanning Electron Microscopy
EDX	Energy Dispersive X-ray analysis

BET	Brunauer–Emmett–Teller Surface Area Measurement Technique
CSP	Concentrated Solar Power
CaCO ₃	Calcium Carbonate or Calcite
CaO	Calcium Oxide
MgO	Magnesium Oxide
DAP	Diammonium Phosphate
MgSO ₄ 7H ₂ O	Magnesium Sulfate Heptahydrate
Al ₂ O ₃	Aluminum Oxide or Alumina
SiO ₂	Silicon Dioxide or Silica
Fe ₂ O ₃	Ferrous Oxide
GW	Giga Watts
kWh _{th}	Kilo Watt Hour Thermal
IPCC	Intergovernmental Panel on Climate Chang (IPCC)
CCS	Carbon Capture and Storage
CO-Dolo	Commercial Dolomite (from Alfa Aesar)
HP-Dolo	Handpicked Dolomite
HP-Dolo-BM	Handpicked Dolomite and ball milled
STF	Single-zone Tube Furnace
CO-Dolo-STF	Commercial Dolomite Calcined in Single-zone Tube Furnace
HP-Dolo-STF	Handpicked Dolomite Calcined in Single-zone Tube Furnace
HP-Dolo-STFN2	Handpicked Dolomite Calcined in Single-zone Tube Furnace under Nitrogen
HP-Dolo-STFO2	Handpicked Dolomite Calcined in Single-zone Tube Furnace under Oxygen or air
KBr	Potassium Bromide
TGA	Thermogravimetric Analyzer
DSC	Differential Scanning Calorimetry
ASTM	American Society for Testing and Materials
CSM	Colorado School of Mines
PDXL-2	Powder X-ray Diffraction software
ICSD PDF	Inorganic Crystal Structure Database Powder Diffraction File
FWHM	Full Width at Half Maximum
kJ/mol	Kilo Joule per mole
J/molK	Joules per mole Kelvin

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