

Effect of Pre-Reaction Ball Milling on Kinetics of Lanthanum Phosphate Roasting with Sodium Carbonate

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Abstract

In order to design economic roasting processes for the recovery of rare earth phosphates from coal-derived feedstocks, it is convenient to study model systems of rare earth phosphate plus a reactant. In this work, the kinetics of the high-temperature roasting of lanthanum phosphate with sodium carbonate were studied. It is typically necessary to heat the reaction mixture above the melting point of Na_2CO_3 (851° C) to observe appreciable reaction to form La_2O_3 . However, grinding the reactants reduces the necessary temperature to as low as 625° C. It is believed that this increase in reactivity occurs because the ball milling process reduces the reactant particle size in addition to ensuring that the reaction mixture is thoroughly mixed. XRD hot stage results suggest a two-reaction mechanism is the

route by which La_2O_3 is produced from the ball milled sample upon reaction. Apparent activation energy and Arrhenius pre-factor for each reaction were determined from TGA experiments.

Key Words: Lanthanum Phosphate, Sodium Carbonate, Grinding, Roasting, Kinetics.

1. Introduction

Rare earth (RE) minerals comprise the 14 naturally-occurring lanthanides plus yttrium and scandium. They are vital to industrial operations and are most widely used in the production of magnets, phosphors for video displays, metal alloys, catalysis, and glass production. The industrial world is very dependent on rare earth minerals, yet China controls the vast majority of world production. The price spike following the 2010 cutback in export quotas by the Chinese government indicated the power their decisions had over the worldwide price of RE minerals. The Chinese embargo of RE minerals to Japan illustrates the importance of national self-sufficiency in RE mineral production. To this end, the United States National Energy Technology Laboratory (NETL) seeks to recover RE minerals from coals and coal-derived samples originating from coal mines in the United States.¹ More than 2 billion tons of coal refuse and 100 million tons of ash are produced each year in the United States. Characterization of coal samples from around the world has shown that RE minerals are present at concentrations up to 5000 ppm on an ash-only basis.² The RE minerals present in such coal ash samples are primarily monazite and xenotime at concentrations of 1000 ppm or lower. Within monazite and xenotime the RE minerals are most likely to exist in the form of RE phosphates. Therefore, NETL has interest in the discovery of improved processes for the recovery of RE phosphates from coal-derived samples, especially coal ash.

Typically, the phosphate must be removed from RE minerals before they undergo further processing. If the dephosphorization does not occur prior to metallurgical processing, the presence of phosphates will cause the formation of phosphides which will destroy RE complexes whose formation is necessary in metallurgical processes. Rare earth phosphates are highly stable even at temperatures to

1500° C and do not undergo phase change.^{3,4} Industrial processes involve roasting in the presence of either sulfuric acid⁵ or sodium hydroxide⁶ to convert them into either RE sulfates or RE oxides, respectively. RE phosphates react with NaOH to form RE(OH)₃ and sodium phosphate without undesired side reactions. Such processes have proven their reliability; more than 95% of the RE minerals initially present in an ore can be recovered by NaOH roasting followed by a water leaching step to remove the sodium phosphate byproduct formed.⁷

However, new process technology for the dephosphorization of RE minerals is an active field of research. Current technologies are suited to feedstock minerals that have a substantial concentration of RE minerals (at least ~50%), and are not economical for the coals and coal byproducts which only contain them on the ppm level. Because the RE minerals present in the potential coal and coal-derived feedstocks are primarily present as RE phosphates, the great focus in this section will be new processes to recover RE phosphates. The impetus for such research stems from the desire to (1) Cut the costs associated with processing high-volume feedstocks with a low RE content and (2) Develop “greener” processes (i. e., minimizing or even eliminating the use of corrosive agents such as H₂SO₄ and NaOH as well as the production of toxic byproduct gases).

In Figure 1 is a flowchart representing a proposed experimental system detailing research into the recovery of RE minerals from coal ash that is under active investigation at NETL. In this study the commercially available LaPO₄*H₂O is used as a proxy for the rare earth mineral monazite. The experiments detailed in the flowchart elucidate a sequence for the recovery of the LaPO₄*H₂O after solid-phase roasting with Na₂CO₃ (see red highlights) instead the typical NaOH solution roast. Two questions present themselves:

- (1) Is it possible to eliminate the use of corrosive agents such as NaOH?
- (2) If yes, can the new process ever be made economically feasible?

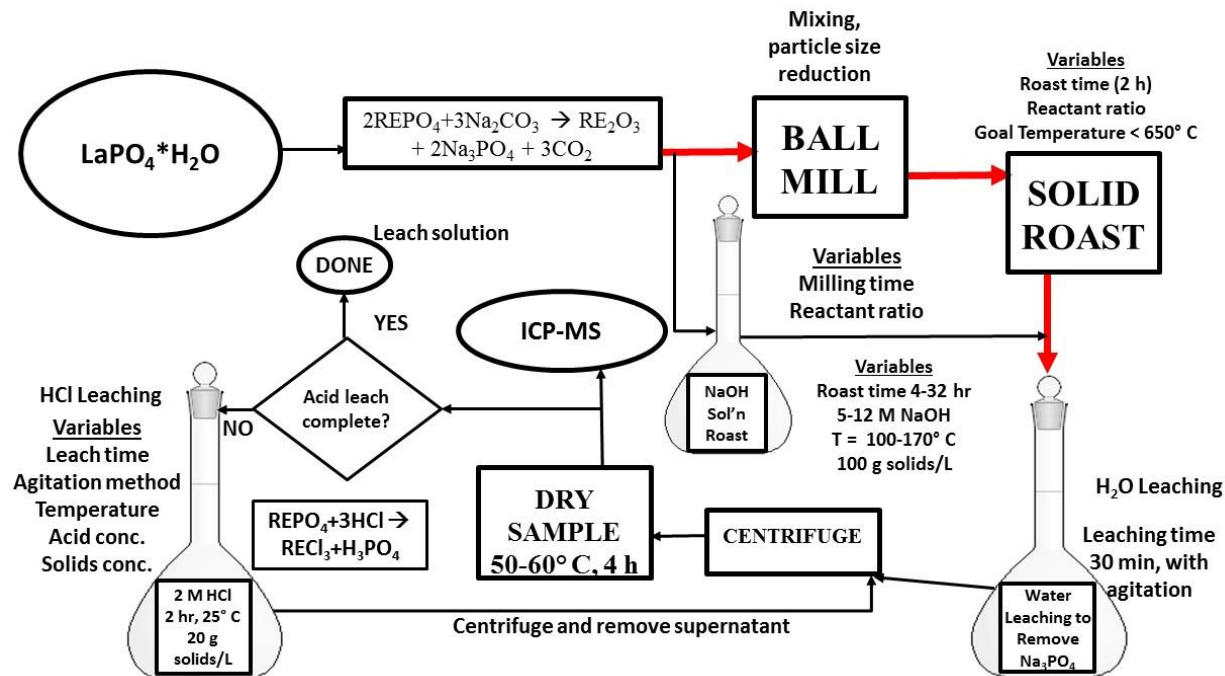


Figure 1. Flowchart for alternate process under investigation at NETL for RE mineral recovery from coal ash. The new proposed ball milling + solid roasting pathway is highlighted in red to distinguish from the typical NaOH solution roasting step.

To eliminate the need for corrosive agents in the roasting process, solid, non-corrosive species have been reacted with rare earth minerals instead. The most prevalent research to date concerning alternative roasting processes has been with NaOH, CaO, and Na_2CO_3 . As will be elucidated in the upcoming sections, Thermogravimetric analysis (TGA) is a relatively rapid, low-volume (only 10-20 mg of sample required per run) aid in the assessment of optimum roasting reaction conditions and, ultimately, reaction kinetics. It has been used to assess the feasibility of RE mineral calcination with CaO.^{8,9,10,11} Recent research on processing RE minerals is concerned either with improving the NaOH roasting process or replacing the NaOH with an alternate reactant. It is summarized in Table 1 and discussed in the following paragraphs.

Table 1. Various studies have attempted to improve the roasting reaction by varying reactant, method of reaction, or reaction temperature.

Reactant	T (°C)	Time (hrs)	REPO ₄ Source	REPO ₄ :Reactant Ratio	Ref.
NaOH(s)	25	2-4	Monazite	1.67:1	12
NaOH(aq), 50 w/v%	170-180	4	Korean monazite	1:7.65	13
NaOH(s)	300-400	2	Korean monazite	1:1	14
CaO:NaCl:CaCl ₂ (s)	700	1	Bastnäsite/monazite (Baotou)	1:0.15:0.04:0.05	10
CaO(s)	800	1	Bastnäsite/monazite (Baotou)	1:0.15	10
Na ₂ CO ₃ (s)	850-900	2	Korean monazite	1:1	14
Charred coal (s)	1400	2	Monazite	2.33:1	15
Al ₂ O ₃ (s)	1800	1	(La,Ce,Nd, or Sm)PO ₄	0.25-2.5	16
SiO ₂ , < 62 μm	No reaction	1	(La,Ce,Nd, or Sm)PO ₄	0.4-4	16

1.1 NaOH Ball Milling and Roasting. Kim and coworkers¹² mixed monazite powder with NaOH and ground the mixture for up to 240 minutes at room temperature. Monazite reacts with NaOH to give sodium phosphate and rare earth hydroxides, which dehydrate above a temperature of ~ 200° C to form rare earth oxides. Good selectivity is obtained for this grinding reaction at ambient temperature, as upon washing of the reaction product the only peaks observed were for rare earth hydroxides or for unreacted monazite. For a milling time of 2 hours at ambient temperature, a phosphate removal from the washed powers in excess of 90% is observed.

NaOH solution roasting has also been carried out at moderate temperatures, typically below 200° C. Solid-state NaOH roasting of RE minerals has also been performed. In one literature study by

Kumari and coworkers,¹⁴ Korean monazite was used as the raw material, with most of the monazite grains ranging in size from 250 to 100 mesh (60-150 microns). The monazite was mixed with NaOH solid and roasted in a muffle furnace for 2 hours at temperatures up to 600° C, with a roasting temperature of 300° C needed to effect 90% phosphate removal within 2 hours. At ambient temperature, virtually no reaction is observed after 2 hours as this effort did not utilize sample grinding to increase reactivity.

1.2. CaO Roasting. Hikichi et al.¹⁶ studied the reactivity of rare earth phosphates with various oxides, instead of corrosives. The oxides chosen for further study were calcium oxide (CaO), aluminum oxide (Al₂O₃), and silicon dioxide (SiO₂). These researchers found that rare earth phosphates react with CaO at temperatures above 700° C, but that a significantly higher temperature of 1800° C was required before RE phosphates would react with Al₂O₃. No reaction was observed between REPO₄ and SiO₂ up to 1700° C. The decomposition of RE phosphates by CaO is very slow and the temperature must be increased to 1300° C for full decomposition to be achieved in the space of 60 minutes.¹⁶ However, it has been shown that the addition of a NaCl-CaCl₂ salt solution to a bastnäsite/monazite mineral mixture enhances the reaction kinetics by formation of a liquid salt phase through which diffusion of the mineral particles occurs more readily. TGA coupled with a heat flow technique such as differential scanning calorimetry (DSC) has previously been used successfully to assess the feasibility of calcination/roasting of RE minerals with CaO^{8,9,10} and CaO-NaCl-CaCl₂. This liquid salt phase enables over 90% decomposition of the rare earth minerals after reaction at 700° C for only 1 hour.¹⁰ This reaction is successfully modeled using the Ginstling-Brundshstein kinetic equation,⁸ which describes the kinetics of solid-solid reaction systems whose rates are limited by the typically slow solid-solid diffusion rates.

1.3 Na₂CO₃ Roasting. Soda ash (Na₂CO₃) roasting of rare earth phosphate has also been studied as a possible means of dephosphorization prior to RE solubilization by acid leaching.¹⁴ A sample laboratory routine for such is given in Figure 1. Na₂CO₃, even in the molten state, is not as corrosive as other molten salts or acid/base. The melting point of soda ash, at 851° C, is considerably lower than that

of CaO (2572° C). Therefore, formation of liquid at moderately high temperatures is feasible and addition of a salt or salt mixture to accelerate kinetics may not be necessary.

However, an experimental Na₂CO₃ roasting of monazite at a 1:1 mass ratio requires the still relatively high minimum temperature of 850-900° C¹⁴ based on a total reaction time of 2 hours, as indicated in Table 1. Such reaction conditions convert 95-100% of the phosphorus in the REPO₄ to Na₃PO₄ so it can be permanently removed from the RE mixture. This temperature range is significantly higher than the 300-400° C required for NaOH roasting at the same 1:1 mass ratio.¹⁴

Going forward, there are two questions:

Can the slow diffusion rates associated with solid-phase Na₂CO₃ roasting of RE minerals be overcome without using molten salt solutions?

Can roasting RE minerals with Na₂CO₃ or another less-corrosive compound be successful in the recovery of RE minerals from coal ash?

In this study, we investigate the feasibility of increasing the kinetics of Na₂CO₃ roasting of RE minerals without the use of corrosive acid/base or molten salt additives. To maintain acceptable reactivity, a possible alternative to the use of corrosives may be to use ball milling not only for improved sample mixing but also to reduce average reactant mixture particle size, therefore increasing the total particle surface area for reaction with the more environmentally friendly Na₂CO₃. Kinetic parameters of solid phase reactions such as the reduction of CuO oxygen carrier materials are frequently expressed as a function of the total surface area for reaction available.¹⁷ Reaction rates may also be enhanced by improved mixing of the solids through a technique such as ball milling. Thus, the focus of this work will be a study of the effect of ball milling on the reaction rate for REPO₄ decomposition.

2. Materials and Methods

2.1 Materials. Lanthanum phosphate monohydrate ($\text{LaPO}_4 \cdot \text{H}_2\text{O}$, 99.99%, CAS 14913-14-5), was obtained from Sigma Aldrich. Sodium carbonate (Na_2CO_3 , 100%, CAS 497-19-8) was obtained from Fisher. Because of the prevalence of lanthanum in monazite, LaPO_4 serves as a convenient proxy for monazite in these studies.

2.2 Experimental Methods. **Sample Prep.** In their Na_2CO_3 roasting of monazite, Kumari et al.¹⁴ used a 1:1 mass ratio of the two reactants as they studied the effect of temperature on the reactivity of the mixture. No particle size reduction technique such as grinding or milling was attempted in the referenced study. Monazite is comprised of ~70 wt % rare earth phosphates. To maintain the ratio of rare earth phosphate to Na_2CO_3 used in this work at a value similar to that employed by Kumari et al., the $\text{LaPO}_4 \cdot \text{H}_2\text{O}:\text{Na}_2\text{CO}_3$ mass ratio of 0.7:1 was used. Two methods were used to prepare samples for the analyses discussed below. Each method first involved the mixing of $\text{LaPO}_4 \cdot \text{H}_2\text{O}$ and Na_2CO_3 at a 0.7:1 ratio or the stoichiometric 1.6:1 ratio by mass. For the first sample prep method, the mixture was hand-mixed (HM) for 30 minutes prior to roasting. The second method consisted of sample mixing/particle size reduction using a reciprocating ball mill (BM) before roasting. Experiments performed in our laboratory indicate that no increase in reactivity is gained if the sample is milled for longer time periods than 30 minutes. Therefore, the milling time was set at 30 minutes.

2.2.1. TGA/DSC. An SDT Q600 instrument (TA Instruments), capable of simultaneously performing both TGA and DSC analyses, was used to analyze the reaction mixtures and pure compounds. Briefly, 10-15 mg of sample were loaded into an alumina sample cup. The sample was heated at a constant temperature ramp rate of 20° C per minute to a maximum temperature no higher than 1000° C under a nitrogen purge of 100 mL per minute.

2.2.2. XRD. X-ray diffraction (XRD) experiments were conducted using a Panalytical X,Pert Pro diffractometer. This instrument was equipped with an Anton Parr HTK 1200 and a copper X-ray tube was

used to collect powder diffraction data for the samples in this work at temperatures from 25 °C to 850 °C. To begin the experiment the powder samples were placed into an alumina sample holder, placed into the HTK 1200, and the sample chamber purged with argon. Diffraction data were collected using copper K α radiation with a wavelength of 1.54 Å from 5° to 50° 2 θ with a step size of 0.167° and a time per step of 100 seconds. All temperature ramps were carried out at a rate of 5 °C/min. Data for each sample was collected at 25 °C before the temperature was ramped to the initial reaction temperature (400 °C for HM and 300 °C for BM). The samples equilibrated for 30 minutes at the initial temperature before data were collected. The temperature was then increased in 25 °C increments until a final temperature of 850 °C was reached. Data were collected at each temperature following a 30-minute hold. The samples were then cooled to 25 °C and a final pattern collected.

2.2.3. Ball Milling Process. A Retsch MM 400 ball mill (25 mL volume) was used in our experiments. This is a dry process. One 12 mm zirconia ball was used in the zirconia-lined milling vessel. Approximately 3 g of reactants were loaded into the vessel, which was then sealed. The milling process commenced at a frequency of 25 s⁻¹ for a time of 30 minutes.

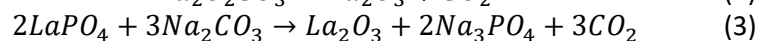
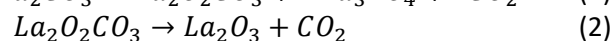
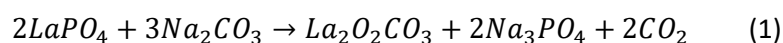
2.2.4. Particle Size Analysis. Particle size analysis was performed using the Mastersizer 3000 with the Hydro MV attachment. The stirrer speed was maintained at 2800 RPM to ensure large and heavy particles were dispersed. Water, with a refractive index of 1.33, was used as the dispersant. The particle refractive index used in the calculation was 1.95. The Dv10, Dv 50, and Dv 90 values, defining the diameter below which 10%, 50%, 90% of the overall particle volume is located, were measured in triplicate.

2.2.5. SEM. An FEI Quanta 450 scanning electron microscope (SEM) with an Oxford Instruments X-MaxN 50 energy dispersive X-ray analyzer was used to investigate the morphology and particle size distribution of the sample after ball milling. The sample was mounted on conductive tape on an aluminum planchet and was not coated prior to analysis. Low vacuum mode was used to compensate

for sample charging. An accelerating voltage of 20 kV and a working distance of about 10 mm were used to examine the sample particles in secondary electron mode.

3. Results and Discussion

3.1. XRD Hot Stage Results. It has been shown that the dephosphorization of $\text{LaPO}_4 \cdot \text{H}_2\text{O}$ does not occur when the compound is heated in the absence of another reactant at temperatures less than 1000°C . However, when it is mixed with Na_2CO_3 and then heated, LaPO_4 breaks down, ultimately forming La_2O_3 in either a two-step (Equations 1 and 2) or an apparently one-step (Equation 3) process.



The XRD hot stage experiments confirm that reaction does indeed occur. For the HM sample, only LaPO_4 peaks are present at 400°C (Figure 2). According to the equilibrium partial CO_2 pressures in Figure 3, at temperatures $\sim 450\text{-}500^\circ\text{C}$ significant formation of $\text{La}_2\text{O}_2\text{CO}_3$ is possible while decomposition of $\text{La}_2\text{O}_2\text{CO}_3$ via Reaction 2 is negligible. However, no reaction was observed for temperatures below 700°C ; La_2O_3 is first detected at 700°C . As $\text{La}_2\text{O}_2\text{CO}_3$ is not detected in the HM sample at 500°C or 600°C , La_2O_3 formation appears to be one-step via Reaction 3. As hot stage temperature is raised above 700°C , the La_2O_3 peaks in the HM sample increase in strength until they dominate at 850°C . However, even at 850°C two very small LaPO_4 peaks remain, indicating that the reaction is not yet complete. From this result, one could conclude that a temperature somewhat higher, such as 900°C , would be necessary to achieve complete reaction in 2-3 hours. Indeed, this result conforms to the work of Kumari et al.,¹⁴ who determined that 900°C was the optimum temperature at which to perform the Na_2CO_3 roasting of Korean monazite.

The XRD hot stage results for the BM sample are markedly different from those for the HM sample. According to Fig. 2 for the BM sample, the formation of the intermediate species La_2CO_5 begins

when the reaction temperature is raised above 400° C and LaPO_4 has fully disappeared by 500° C. At this temperature, no La_2O_3 is detected. According to Figure 3, the equilibrium CO_2 concentration associated with the $\text{La}_2\text{O}_2\text{CO}_3$ -forming Reaction 1 is nearly an order of magnitude greater than that associated with the La_2O_3 -forming Reaction 3. Strong peaks for La_2O_3 are observed by 600° C and the presence of only La_2O_3 and Na_3PO_4 peaks at 775° C indicate that the reaction is complete at this temperature.

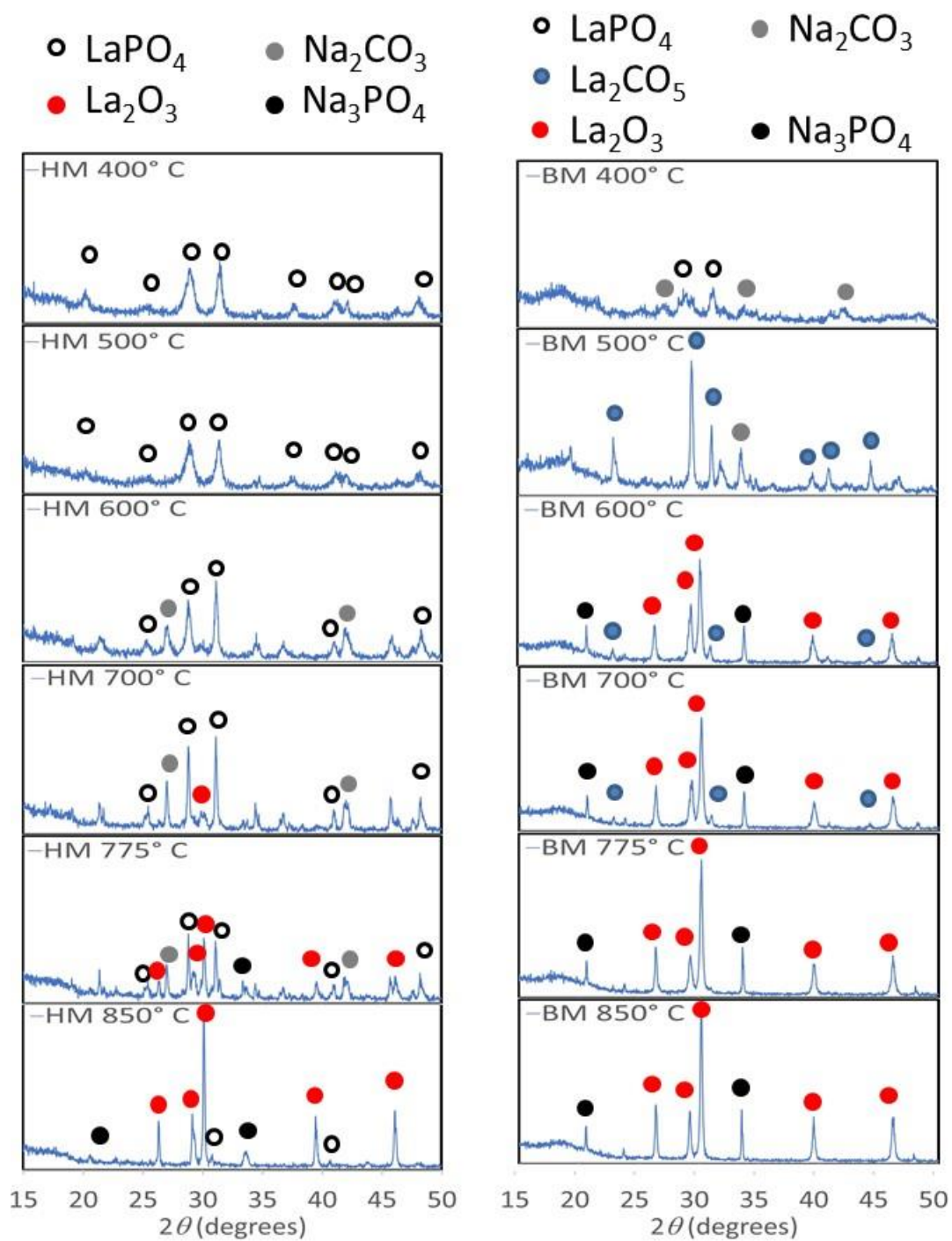


Figure 2. XRD patterns for the HM and BM samples at various temperatures throughout the reaction indicate that the BM sample is much more reactive than the HM sample. The formation of the $\text{La}_2\text{O}_2\text{CO}_3$ intermediate appears to facilitate the formation of La_2O_3 and Na_3PO_4 in the case of the BM sample.

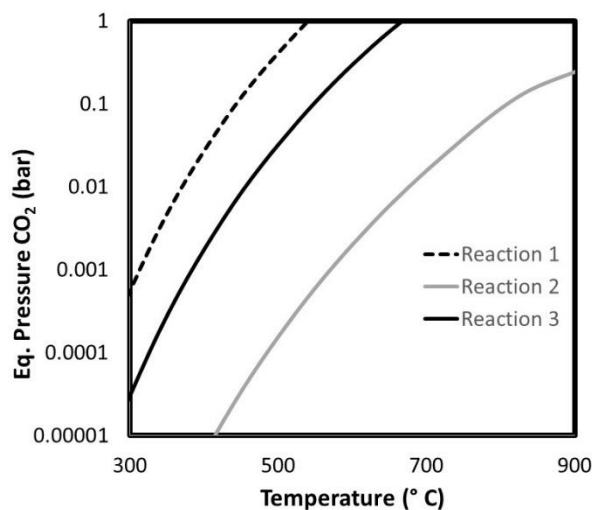


Figure 3. Equilibrium partial CO₂ pressure associated with Reactions 1-3. Thermodynamic Gibbs energy data used to calculate these curves are given in References 18 and 19.

In order to obtain a measure of the amount by which the Na₂CO₃ roasting temperature of LaPO₄ can be reduced, the 2-hour La₂O₃ decomposition ratio, or yield, was studied. For a reaction temperature to be feasible, more than 90% decomposition of LaPO₄*H₂O to La₂O₃ should be obtained at that temperature within a time span of 2 hours. The decomposition ratios obtained in various studies are plotted in Figure 4. For the HM sample, yields in excess of 70% are observed at 810° C but fall drastically as temperature is lowered. At 700° C, the decomposition ratio (0.15) obtained for the hand-mixed (HM) sample is very similar to the decomposition ratio (0.13) obtained by Kumari et al.¹⁴ for the reaction of Na₂CO₃ with monazite at the same temperature. Monazite is a mixture of different rare earth phosphates (most notably La/Ce/Nd), but also includes impurities such as thorium and uranium. Even though LaPO₄*H₂O represents only one compound present in monazite, the results in Figure 4 indicate that its reactivity during Na₂CO₃ roasting is similar to that of monazite. Such behavior suggests that this compound is a good proxy for monazite. Indeed, when subjected to CaO roast at temperatures from

600-1300° C, LaPO_4 also exhibits reactivity similar to that of phosphates of Ce, Nd, Sm, Y, Er, and Yb.¹⁶ Even if excess Na_2CO_3 is used (the stoichiometric ratio is approximately 1:1.4 Na_2CO_3 : $\text{LaPO}_4 \cdot \text{H}_2\text{O}$ by mass), the decomposition ratio is not enhanced considerably. However, application of the ball milling technique prior to roasting results in a yield of 90% at 625° C after 2 hr! This improves even on the promising research of Bian et al.,⁸ who observed that CaO roasting of mixed rare earth minerals could be sped up if the reaction mixture was doped with NaCl and CaCl_2 salts. In that instance, approximately 90% conversion was obtained at 700° C after a reaction time of 1 hr.

It is apparent that the ball milling process significantly improved the reactivity of $\text{LaPO}_4 \cdot \text{H}_2\text{O}$ with Na_2CO_3 . Reactive grinding can be ruled out as a cause for the increased reactivity of the BM sample as the XRD hot stage results in Figure 2 indicate that the reactants are unchanged even after the BM sample has been heated up to 400° C. However, as shown in Figure 5, a wet particle size analysis indicates that the ball milling process shifts the $\text{LaPO}_4 \cdot \text{H}_2\text{O}$ particle size distribution of the BM sample in the direction of smaller particle sizes relative to the as-received $\text{LaPO}_4 \cdot \text{H}_2\text{O}$. The Na_2CO_3 particles dissolve in the dispersant water used in the wet particle size analysis and therefore their size is not determined. In addition, SEM results (Figure 6) confirm that the small particles are compacted by the ball milling process, compacting the particles and maximizing the surface area over which unlike particles can come into contact. The effect of the particle size reduction, enhanced mixing from ball milling, and particle aggregation is to increase the rate of reaction, particularly so at lower temperatures.

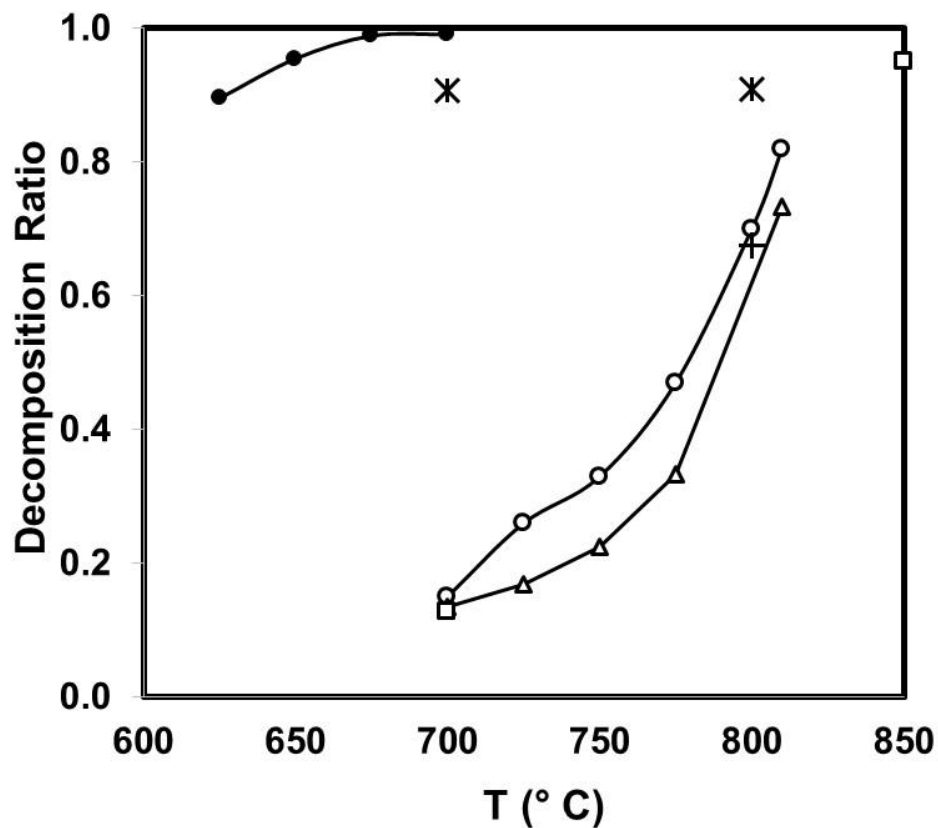


Figure 4. Variation of decomposition ratio with respect to temperature for samples prepared both by mortar and pestle (MP) and by hand-mixing (HM).

● 30 min BM, $\text{LaPO}_4 \cdot \text{H}_2\text{O} : \text{Na}_2\text{CO}_3$ 0.7:1, reaction time 2 hr

○ 30 min HM, $\text{LaPO}_4 \cdot \text{H}_2\text{O} : \text{Na}_2\text{CO}_3$ 0.7:1, reaction time 2 hr

Δ 30 min HM, $\text{LaPO}_4 \cdot \text{H}_2\text{O} : \text{Na}_2\text{CO}_3$ 1.6:1, reaction time 2 hr

□ Monazite: Na_2CO_3 1:1¹⁴, reaction time 2 hr

+ CaO and Mixed rare earth minerals, 0.15:1, reaction time 1 hr¹⁰

* CaO, NaCl, CaCl₂ and Mixed rare earth minerals, 0.15:0.04:0.06:1, reaction time 1 hr¹⁰

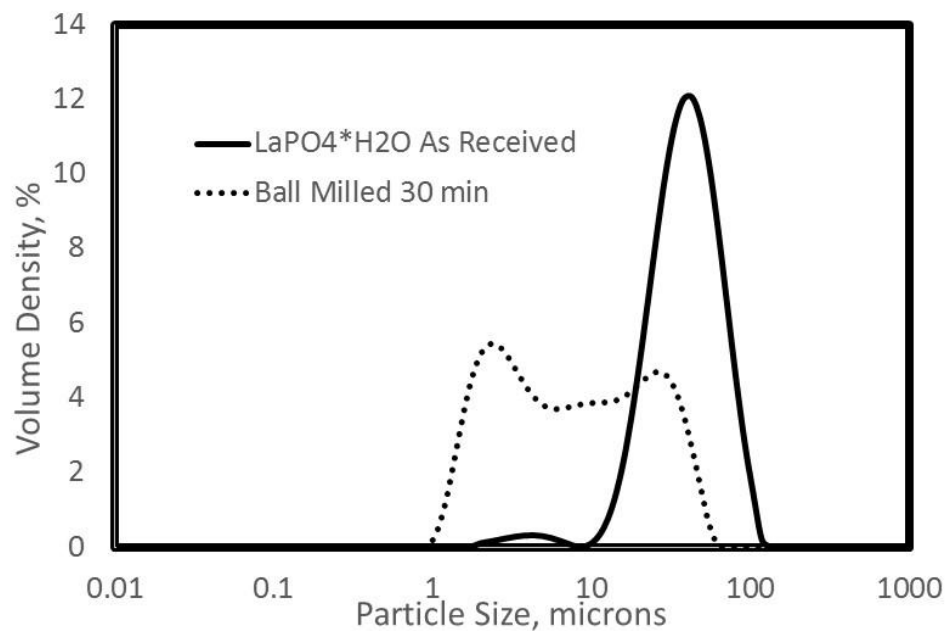


Figure 5. The effect of ball milling the $\text{LaPO}_4 \cdot \text{H}_2\text{O} + \text{Na}_2\text{CO}_3$ mixture for 30 minutes prior to reaction is the shift the volume-averaged size distribution of the reacting particles significantly in the direction of smaller particle size.

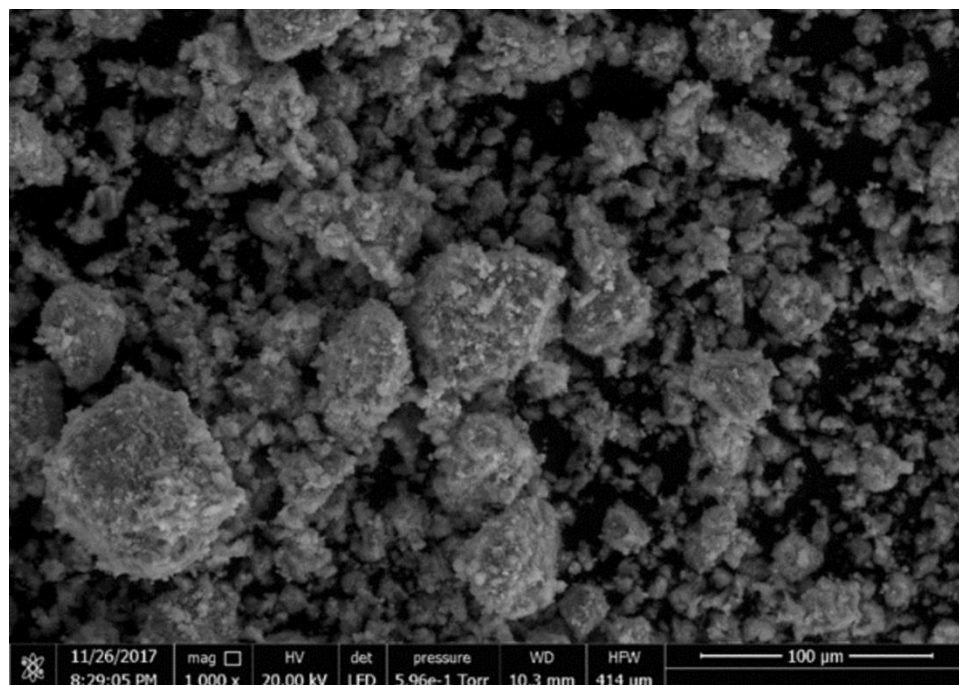
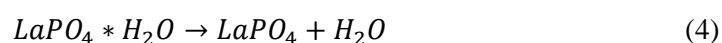


Figure 6. SEM results confirm that the small micron-sized particles formed during the ball milling process are compacted into aggregates.

3.2. TGA/DSC to Determine Decomposition Ratio with Respect to Time. TGA/DSC can be used to obtain activation energy and kinetic data. A single run nets sufficient information for calculating the reaction rate constant k at a given temperature. The relevant kinetic data, including apparent activation energy E_a and Arrhenius prefactor k_0 , can be determined from the results of as little as three isothermal TGA runs. While this approach doesn't account for the possibility of multiple simultaneous reactions, it does allow the researcher to optimize the overall rate of decomposition with respect to temperature.²⁰

Next, an illustration of how TGA was used to study the kinetics of the Na_2CO_3 roasting of LaPO_4 is given. First, a mixture comprised of 0.7 parts $\text{LaPO}_4 \cdot \text{H}_2\text{O}$ to 1 part Na_2CO_3 on a mass basis is prepared (this mass ratio represents about twice the minimum amount of Na_2CO_3 needed to ensure that the reaction goes to completion). We chose to conduct our kinetic analyses with excess Na_2CO_3 to ensure that the reaction went to completion. Kinetic analyses were then carried out for the BM mixture.

The methodology used to determine extent of reaction data for the BM sample is illustrated in Figure 7 and Equations 5 and 6. Based on the XRD hot stage results presented in Figure 2, the TGA ramp rate was set to $20^\circ \text{C}/\text{min}$ and ramped to a temperature between $450\text{-}500^\circ \text{C}$. As this ramp is occurring, $\sim 11\%$ of the initial sample mass is lost in the form of water desorption and from the dehydration of $\text{LaPO}_4 \cdot \text{H}_2\text{O}$. With the help of XRD,²¹ it can be established that the following dehydration reaction occurs near 200°C :



If the Na_2CO_3 has picked up any hydration, a similar reaction occurs with $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ as it undergoes dehydration around 100°C . Between $450\text{--}500^\circ\text{C}$, Reaction 1 proceeds as LaPO_4 and Na_2CO_3 react while Reaction 2 does not. Since no La_2O_3 is detected at 500°C , it can be assumed that Reaction 2 does not proceed at this temperature. As indicated in Figure 7, the temperature inside the TGA is held constant (in this case, at 500°C) until Reaction 1 goes to completion. Even though conversion of $\sim 75\%$ is observed within ~ 3 hr, the time for Reaction 1 was set to 30 hr to ensure that Reaction 1 does in fact go to completion.

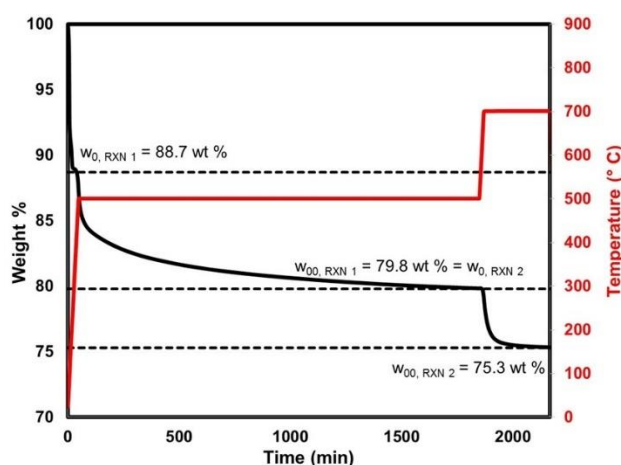


Figure 7. Isothermal TGA conducted on $\text{LaPO}_4 + \text{Na}_2\text{CO}_3$ by ramping to 500°C at $20^\circ\text{C}/\text{min}$ and holding for 1800 min to complete Reaction 1, then ramping to 700°C at $20^\circ\text{C}/\text{min}$ and holding for 300 min to complete Reaction 2.

From the TGA plot in Figure 7, the extent X_1 of Reaction 1 and X_2 of Reaction 2 can be determined as a function of the TGA weight % $w(t)$ at time t , the sample weight percent $w_{0, RXN1}$ and $w_{\infty, RXN1}$ present before Reactions 1 and 2 begin, and the weight percent $w_{\infty, RXN1}$ and $w_{\infty, RXN2}$ present at the end of Reactions 1 and 2.

$$X_1 = \frac{w_{0,RXN1} - w(t)}{w_{0,RXN1} - w_{\infty,RXN1}}, w_{0,RXN1} > w(t) > w_{\infty,RXN1} \quad (5)$$

$$X_2 = \frac{w_{0,RXN2} - w(t)}{w_{0,RXN2} - w_{\infty,RXN2}}, w_{0,RXN2} > w(t) > w_{\infty,RXN2} \quad (6)$$

3.3 Determination of Reaction Kinetics. Once X_1 and X_2 are determined as a function of reaction time, it is possible to define kinetic models that govern the respective rates of Reactions 1 and 2.

Reaction rate is given as:

$$\frac{dX}{dt} = k(T)f(X) \quad (7)$$

In Equation 7, X is the conversion, t is reaction time, T is reaction temperature, and $f(X)$ is the kinetic relationship. Rate constant $k(T)$ is a function of the kinetic parameters of activation energy E_a and Arrhenius pre-factor k_0 . At isothermal reaction conditions, the value of $k(T)$ can be determined by integrating Equation 7.

$$g(X) = \int_0^X \frac{dX}{f(X)} = k(T)t \quad (8)$$

The choice of a kinetic model is an important one. The kinetic model takes into consideration factors such as particle shape and diffusion limitations that can affect reaction kinetics. Several common models useful for solid-phase reactions are summarized in Table 2 below.

Reaction 1 between LaPO_4 and Na_2CO_3 is a solid-solid phase reaction. It has been shown that an ash diffusion-limited kinetic model describes solid phase RE mineral decomposition reactions.²² The ash diffusion-limited model requires a plot of $(1 - 2/3X - (1 - X)^{2/3})$ vs. t , with the slope of this plot being equal to the apparent rate constant $k(T)$ at that temperature. Indeed, of the models in Table 2, the ash diffusion model gives the most linear fit to the experimental TGA data obtained for X_1 . The results for the fit of the ash diffusion model to the kinetic data are given in Figure 8a. Equations 9-11 each fail to describe the experimental data. Because of the requirement of an adjustable parameter N , the nucleation and growth model was not considered as a kinetic model for Reaction 1.

Table 2. Summary of kinetic models tested in this work.

Kinetic model description	$f(X)$	$g(X)$	
Film diffusion-limited by rate of CO ₂ diffusion from film at particle surface into purge gas)	1	X	(9)
Contracting Cylindrical particles, reaction rate-limited (2-D)	$2(1 - X)^{1/2}$	$1 - (1 - X)^{1/2}$	(10)
Contracting Spherical particles, reaction rate-limited (3-D)	$3(1 - X)^{2/3}$	$1 - (1 - X)^{1/3}$	(11)
Spherical particles, ash diffusion-limited by rate of CO ₂ diffusion back out of particle interior)	$\frac{(1 - X)^{1/3}}{2[1 - (1 - X)^{1/3}]}$	$3 - 2X - 3(1 - X)^{2/3}$	(12)
Nucleation and growth	$N^{-1}(1 - X)[- \ln(1 - X)]^{1-N}$	$[- \ln(1 - X)]^N$	(13)

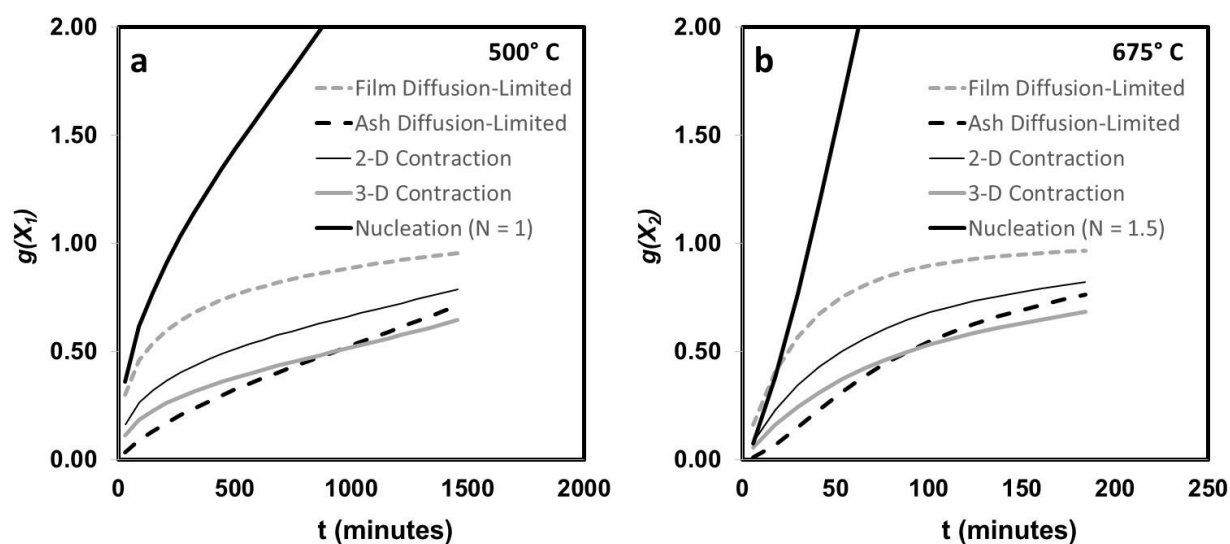


Figure 8. The best models to fit the kinetic data are the ash diffusion model for Reaction 1 (a) and the nucleation-and-growth model for Reaction 2 (b). Sample was ball milled for 30 minutes prior to reaction.

The loss of CO₂ from La₂CO₅ in Reaction 2, on the other hand, is not a solid-solid phase reaction. Rather in Reaction 2, the CO₂ gas is lost from a solid particle. The nucleation and growth model has

previously been used successfully to model the kinetics of the reduction of hematite.²³ During this process, CO₂ and H₂O gases are evolved as hematite is reduced in the presence of CH₄. Therefore, this model was used to describe the kinetics of Reaction 2.

When the value of k has been calculated for a number of temperatures, the activation energy E_a can be determined from Equation 14 by plotting $\ln k$ vs inverse temperature $1/T$ according to the Arrhenius relationship given in Equation 14. As deduced from Figure 9, apparent activation energy $E_a = 25.58$ kJ/mol and the Arrhenius prefactor $k_0 = 0.153$ min⁻¹ for Reaction 1. For Reaction 2, apparent activation energy $E_a = 46.52$ kJ/mol and the Arrhenius prefactor $k_0 = 12.5$ min⁻¹.

$$\ln k = \ln k_0 - \frac{E_a}{RT} \quad (14)$$

In Equation 15, the reaction rate constant k is defined as a function of the activation energy E_a and the reaction order n , and the rate prefactor constant A .

$$k = Ae^{-\frac{E_a}{RT}} \quad (15)$$

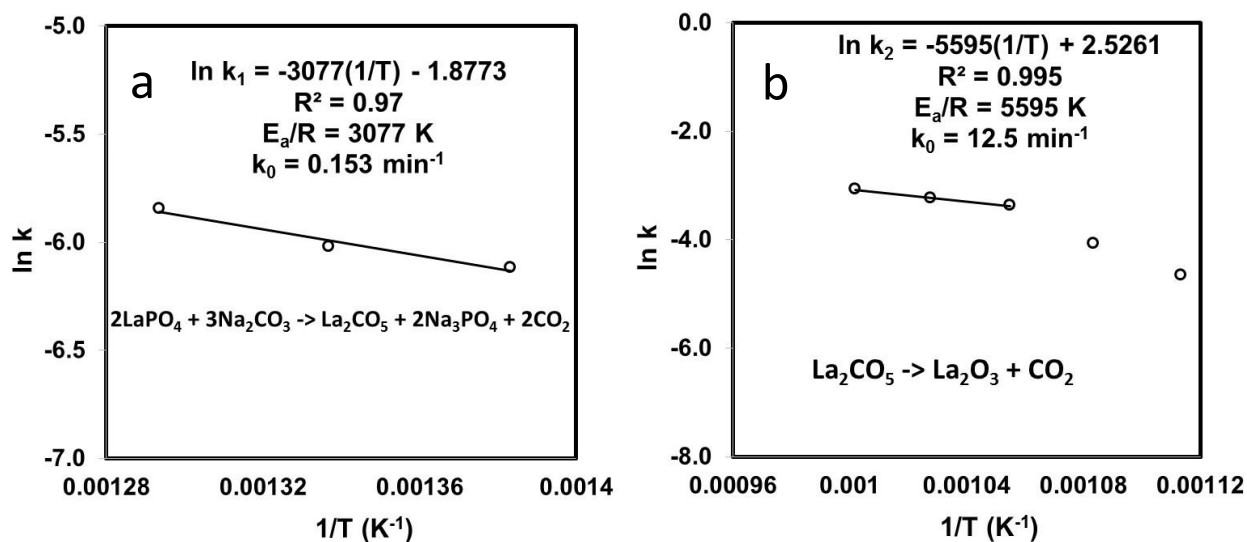


Figure 9. Plots to determine Arrhenius prefactor k_0 and activation energy E_a are determined for (a) Reaction 1 and (b) Reaction 2. Sample was ball milled for 30 minutes prior to reaction.

The plot of $\ln k_2$ vs $1/T$ is especially noteworthy. Over the temperature range of 625-725° C ($1/T = 0.00112$ to 0.00100) the plot of $\ln k_2$ vs $1/T$ is not linear as expected. Rather, the plot of $\ln k_2$ vs $1/T$ in this region can be divided into two regions. In the first region, from 625-675° C, the value of $\ln k_2$ grows relatively quickly. In the second region, from 675-725° C, the growth of $\ln k_2$ levels off greatly. We postulate that at temperatures below 675° C, the reaction is thermodynamically limited by the low value of the equilibrium CO_2 pressure for Reaction 2. This value grows from 0.0036 bar (0.36 mol % at 1 bar total pressure) at 625° C and grows to approximately 0.006 bar (0.6 mol %) at 675° C, while considerably larger at 0.025 bar (2.5 mol %) at 725° C. We hypothesize that above 675° C, the rate of reaction is no longer thermodynamically limited but rather kinetically limited. It is likely that the TGA purge gas is able to remove CO_2 generated from the TGA chamber such that the CO_2 concentration within is maintained below the thermodynamically limiting value. Therefore, in determining E_a and k_0 for Reaction 2, only the reaction data for the temperature range 675-725° C were considered. Notably, it is reported that higher calcination temperatures of 800° C are necessary to cause the loss of CO_2 from La_2CO_5 within a time of less than 2 hours.²⁴

4. Conclusions

Previous experiments by Kumari et al.¹⁴ suggest that it is necessary to heat an equimass mixture of LaPO_4 and phosphate-rich monazite to at least the boiling point of pure Na_2CO_3 , 851° C, to achieve decomposition ratios of 0.9 to 1.0 after 2 hours. In this work, comparable results were obtained for mixtures of the model monazite compound $\text{LaPO}_4 \cdot \text{H}_2\text{O}$ and Na_2CO_3 as decomposition ratios of 0.7-0.8 were obtained at the slightly lower temperature of 810° C. After milling the reactants in a reciprocating ball mill for 30 minutes prior to reaction, XRD hot stage experiments and 2-hour decomposition ratio data confirm that the minimum reaction temperature for La_2O_3 production was reduced to as low as 625° C and the lanthanum oxycarbonate intermediate $\text{La}_2\text{O}_2\text{CO}_3$ can be produced at temperatures of

approximately 500° C! To date, this temperature is the lowest suggested for La₂O₃ production by the Na₂CO₃ roasting of LaPO₄. This increase in reactivity happens without the addition of corrosive salts to the reaction mixture. There appear to be several factors causing the increased reactivity of the BM sample. First, the ball milling process mixes the reactants much more efficiently than can be accomplished manually. Wet particle size analysis indicates that the average particle size is reduced by almost an order of magnitude. SEM results indicate that the small particles are then compacted by the ball milling process, forming aggregates. The overall effect is that the total surface area of unlike particles in contact is significantly increased relative to the HM sample.

XRD hot stage experiments confirm that the Na₂CO₃ roasting of LaPO₄*H₂O occurs via a two-reaction mechanism, with La₂O₂CO₃ and La₂O₃ the rare earth products of the respective reactions. TGA experiments were used to obtain values for the reaction rate constants k_1 and k_2 at each reaction temperature of interest. From these values the kinetic parameters were determined for each reaction. The apparent activation energy and Arrhenius pre-factor were 25.58 kJ/mol and 0.153 min⁻¹ for Reaction 1 and 46.52 kJ/mol and 12.5 min⁻¹ for Reaction 2. We believe that the reaction kinetics would be accelerated if this reaction were conducted in a fluidized bed reactor, to purge out CO₂ so that the low equilibrium constants do not limit the rate of either reaction.

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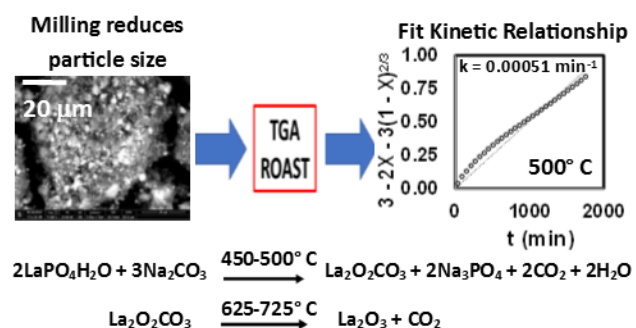
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“For Table of Contents Only”



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