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CALCITE DECOMPOSITION IN VACUUM

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August 1982

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Rearrangement of Porous CaO Aggregates During Calcite
Decomposition in Vacuum

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Abstract: High-resolution SEM photographs, N_2 adsorption isotherms, and micrometer measurements have been used to characterize CaO particle shapes and pore size distributions that result when large calcite crystals are decomposed in vacuum at 686°C . Sintering is negligible and the surface area of the CaO reaction product is independent of the extent of reaction for CaO from large calcite crystals. Heatings interrupted by thermal cycling to liquid N_2 temperatures cause surface areas to decrease from $118 \pm 2 \text{ m}^2/\text{g-CaO}$ to $\sim 95 \text{ m}^2/\text{g-CaO}$. In volume elements smaller than $\sim 1 \mu\text{m}$ in cross section, particle shapes and pores size distributions are very similar for CaO from large and small calcite crystals. Collapse of the open structure that results from the 55% difference in molar volume between calcite and CaO brings CaO surfaces into bonded contact, but leaves occasionally irregular pores and cracks with dimensions of the order of 5 to 10 nm and surface ledges which

indicate additional $\sim 0.1 \mu\text{m}$ packing discontinuities in the CaO aggregates. Aggregates from large calcite crystals have additional voids and cracks with cross sections of the order of $\sim 1 \mu\text{m}$ between volume elements of the kind described.

Introduction

When calcite (CaCO_3) crystals of the order of 1 mm cross section are partially decomposed in vacuum, SEM pictures of a surface formed by fracture through the crystal show undecomposed calcite and two distinguishable CaO layers [1,2]. Beruto and Searcy [3] suggested that the intermediate CaO layer transforms to the second CaO layer as a consequence of accumulated strain. A fracture surface of the completely decomposed specimen shows only the outer product layer, CaO in its normal NaCl-type crystal form [4]. TEM observations show that the first product of calcite decomposition, i.e., the intermediate layer, is also NaCl-type CaO formed as needles ~ 10 nm in diameter [5]. The fracture surface of that CaO layer is smooth at magnifications of $\times 10^4$, while the surface of the final CaO layer shows a complex pattern of oriented ridges with cross sections of $\sim 1 \mu\text{m}$. Powell and Searcy [2] suggested that these oriented ridges result because the second layer is formed from the first by a repacking of the CaO needle-shaped particles.

There seems to have been no previous suggestion that powder aggregates of high porosity ($\sim 50\%$ for the CaO in question) may undergo an essentially diffusionless repacking. The principal objective of this research was to seek confirmatory evidence. If repacking occurs, it should result in a change in pore-size distribution and perhaps also in total porosity. Measurements of these quantities are reported and compared with values for CaO from calcite powder. High magnification SEM pictures were obtained from which direct visual comparisons of packing of CaO from large calcite crystals and of CaO from small calcite crystals can be made.

The second objective of this paper was to measure the dependence of surface area and of pore volume on the mole fraction of solid that is converted to CaO. Mikhail et al. [6] recently reported that the specific surface area of CaO made by decomposition of large calcite crystals in vacuum is initially relatively high but decreases as decomposition proceeds--an effect that was attributed to sintering. Their data and conclusions are consistent with data of earlier studies of calcite decomposition in vacuum, but not with recent findings for decomposition of calcite powders [7]. The surface areas of powders vary linearly with the mole fraction of CaO produced, and sintering is negligible at $\sim 650^\circ\text{C}$ in vacuum. It was important to determine if there is the fundamental difference between decomposition of large calcite crystals and powders, as these two sets of recent measurements suggest.

Experimental

Calcite crystals with a spectrographic analysis given in a previous paper [1] were cut along $(10\bar{1}1)$ planes to obtain slices ~ 0.75 mm thick, with areas of $\sim 20\text{ mm}^2$ and ~ 40 mg weight. A sample was placed in an open Pt crucible, which was hung from a quartz wire in one chamber of a symmetrical microbalance in a 2.5 cm diameter quartz furnace. A nonporous quartz specimen of similar dimensions was placed in a Pt crucible in a reference chamber. A chromel-alumel thermocouple was placed 0.5 cm from the bottom of the specimen crucible. Calibration with another thermocouple showed the furnace temperature to be constant within $\pm 1^\circ\text{C}$.

Weight changes of the samples in vacuum or under N_2 pressures of 1 to 10^5 Pa could be recorded using a single-sided absolute sensor head

placed at the top of the microbalance. The system could be pumped to $\sim 10^{-4}$ Pa at an ion gauge, but pressures at the sample would be somewhat higher.

Weight losses during vacuum decompositions were recorded at 686°C using usually a balance sensitivity of 0.25 mg mm^{-1} . Under these conditions, no weight changes were observed during heating of the sample at 50°C/min to within a few degrees of the decomposition temperature.

The first decomposition was carried out to ~ 10 wt.% of the CO_2 present. Then the sample was cooled in vacuum to room temperature, while the weight was continuously recorded. Liquid N_2 containers were put in place around both quartz tubes, the sensitivity of the microbalance was set at $10^{-3} \text{ mg mm}^{-1}$ without exposure of the specimen to air, and adsorption-desorption isotherms with N_2 were taken at 78K. This cycle was repeated until isotherms had been measured at ~ 10 wt.% intervals to complete decomposition (Table I,B).

To obtain data of higher reliability for low percentage weight losses, four crystal slices of the same dimensions used in the runs described above but with a total mass of 211 mg were arranged to stand on edge in the weight-loss apparatus. The sensitivity of the microbalance was set at 0.025 mg cm^{-1} , and N_2 adsorption measurements were made with the same sample after 5.5%, 10.7% , and 15.9% decomposition (Table I,A).

To test whether the interrupted heatings yielded different final surface areas or porosities from those produced without cooling and reheating steps, three samples were each fully decomposed by isothermal heatings at 686°C (Table I,C).

SEM observations were made on the final oxides after coating them with a ~ 30 nm layer of Au. To minimize hydration, samples were stored under CCl_4 until they were coated for SEM study. To measure the linear shrinkage of specimens after decomposition, slices of the product CaO were placed in a micrometer chamber where dry N_2 was kept flowing. Hydration is slower for the CaO from calcite single crystals than for CaO from calcite powder. The $\sim 3\%$ hydration expected during this operation should not significantly influence these measurements.

Results

Figure 1 shows liquid nitrogen adsorption-desorption isotherms for one sample that was decomposed in a series of interrupted heatings and of a second sample that was decomposed in a single step. The volume of pores that are less than about $0.1 \mu\text{m}$ in cross section is obtained from the volume taken up by a sample of known total volume when the N_2 pressure is $\sim 98\%$ of its saturation value for the liquid N_2 . These mesoporosities are reported in Table I. Total porosity is obtained from the overall dimensions of the CaO aggregates after decomposition, and from the weight of the CaO. The entries under macroporosity (Table I, Column 3) are the calculated differences between the total porosities and the mesoporosities. Some of the differences may actually be a consequence of closed pores (see below). The surface areas of Table I were obtained by the BET method [8].

Table II compares the BET data with data derived by the t-method [9]. The t-method identifies the pressure at which capillary condensation commences as that for which a plot of N_2 volume adsorbed vs the statistical thickness, t , of adsorbed N_2 begins to deviate upward

from a straight line. De Boer and Lippens' reference curve [10] was used. The observation that the pressure for capillary condensation is found by the t-method to be below the pressure at which a hysteresis loop begins in the adsorption isotherms is interpreted to mean that some capillaries have closed ends [11].

Figure 2 shows the variations with mole fraction of CaO of surface area, of total pore volume, and of the volume of those pores small enough ($\leq \sim 0.1 \mu\text{m}$) to cause capillary condensation. These measurements were made in incremental steps with the same sample. Points of this plot were found to be reproducible to approximately $\pm 2\%$ (Table 1,B). The upper dashed curve shows the pore volume predicted from the difference between molar volumes of calcite and of CaO if the initial external dimensions of the single crystal are preserved through the decomposition process. Micrometer measurements show that the final porous CaO aggregates of Table 1,B occupy $96(\pm 2)\%$ of the initial calcite volume. Thus, if overall aggregate shrinkage is a linear function of the extent of reaction, the actual sums of volumes of macropores and closed pores are $\sim 1\%$ lower than values of the Table.

Data measured for 10.5% decomposition are believed to contain systematic errors because of the low total surface area and pore volumes in the small samples used. Data of Table 1,A which were obtained with larger samples and a more sensitive balance setting, are believed to be reliable in indicating that the initial specific surface area and mesoporosity are higher than for samples that had decomposed 20% or more in interrupted heatings.

Three samples that were completely decomposed in one heating at 686°C gave significantly different results from results obtained with

the heatings interrupted by liquid N_2 measurements (Table I,C). Surface areas now were $118(\pm 3)m^2/g$ instead of $\sim 92 m^2/g$, and the pore size distribution was somewhat different. A possible explanation of these differences will be suggested in the discussion section. For the $\sim 118 m^2/g$ CaO, the total volume of an aggregate was $(98 \pm 2)\%$ that of the initial calcite crystal.

An analysis of the N_2 adsorption data by the t-plot method (Table II) showed no evidence for micropores of <1 nm diameter, but showed that capillary condensation occurs in pores >1 nm during adsorption. Pore size distributions calculated on the assumption of either cylindrical cross pores or slit-shaped pores gave good agreement in cumulative surface areas and cumulative volumes to the surface areas measured by the BET method and the directly measured volume of N_2 at the time the saturation pressure was reached.

Table III compares volumes and surface areas of Table II to values calculated by the pore size distribution method on alternate assumptions that pores were slit-shaped or cylindrical. Neither assumption gives an agreement clearly superior to the other; direct observations by SEM (Figs. 3 and 4) show the CaO particles commonly to be rod-shaped, which implies that most pores can be expected to have cylindrical symmetry.

Figure 5 shows pore-size distributions calculated from the isotherms of Fig. 1 on the assumption of cylindrical pore symmetry. It is seen that the most probable diameter for the sample decomposed by interrupted heating is 6.2 nm compared to 5.1 nm for the uninterrupted heating.

As reported by Powell and Searcy [2], at intermediate magnifications SEM photographs of totally decomposed large calcite crystals show regions of the fracture surface with parallel ridges spaced at $\sim 1-2 \mu\text{m}$ apart. Figure 6 shows that the CaO particle shapes and packing in CaO from calcite powder are essentially indistinguishable from those in CaO from large crystals (Fig. 3). The ledge of $\sim 0.1 \mu\text{m}$ height in Fig. 6 is probably of the kind that appear as regularly spaced terraces in the lower-magnification picture (Fig. 2,A) of Ref. 4.

Discussion

Comparison with earlier results. Surface areas measured for CaO prepared by decomposition in one uninterrupted heating at 686°C averaged $118 \pm 3 \text{ m}^2/\text{g}$ compared to $116 \pm 10 \text{ m}^2/\text{g}$ obtained by Powell and Searcy [2] in a completely different apparatus. Interrupted heatings gave significantly lower surface areas, $\sim 92 \text{ m}^2/\text{g}$, at the same temperature. A possible explanation will be suggested in the subsection on the reaction path.

An extrapolation as a function of CO_2 pressure of surface areas measured for CaO powders by Ewing et al. [7] predicts surface areas of $120 \pm 10 \text{ m}^2/\text{g}$ for CaO powders prepared by calcite decomposition in high vacuum at 650°C . The effect of temperature on the surface area of CaO prepared by calcite powder decomposition has not been definitively established but, if that dependence is similar to the dependence for CaO from single crystals [2], then at 686°C the expected surface area would be $\sim 110 \pm 15 \text{ m}^2/\text{g}$ compared to the $118 \pm 3 \text{ m}^2/\text{g}$ found for CaO from large crystals of calcite when fully decomposed in an uninterrupted heating.

Surface areas measured by Beruto, Barco, Searcy, and Spinolo [4], however, for CaO from large crystals of calcite decomposed at 580°C were only 89 m²/g-CaO. That value is not characteristic of vacuum decomposition because the pumping speed at the sample was poor.

The present results of the uninterrupted complete decomposition are in fair agreement with results of the only run of Mikhail et al. that was carried almost to complete (95%) decomposition. They reported a specific surface area at 700°C from this run to be ~115 m²/g, but from the general trend of their data obtained with less completely decomposed samples Mikhail et al. [6] concluded that decomposition at 620°C yields lower surface areas than does decomposition at 700°C. This conclusion appears to be mistaken; for a series of samples from calcite single crystals decomposed at 650°C to 900°C, Powell and Searcy [2] found surface areas to decrease with increased temperatures for decomposition.

Experience of the present study demonstrates that systematic error is high in measurements of the surface area of the CaO samples that have been less than 20% decomposed. The measurements reported in Table I,A with conditions optimized for the study of early phases of decomposition yield calculated initial surface areas of ~115 m²/g-CaO instead of 80 m²/g-CaO, which was found when weights close to the limit of the balance scale setting were measured. It may be that the very high initial specific surface areas observed by Mikhail et al., 160 m²/g-CaO, for low percentages of decomposition also reflect systematic error.

Evidence for a complex pore structure. Pore-size distribution curves (Fig. 5) show pores of the order of 5 nm cross sections to be

present. Comparison of the total porosity, which is calculated from the micrometer measurements of total volume and from the mass of CaO, to the mesoporosity, which is determined from the volume of liquid nitrogen condensed in the CaO aggregates when the N_2 gas pressure reaches its saturation value, provided unambiguous evidence of pores in at least two size ranges in these aggregates.

Powell and Searcy [2] suggested that the ridges spaced $\sim 1 \mu m$ apart in fracture surface reflect the presence of macropores of $\sim 1 \mu m$ cross sections. Figure 3, which is a high-resolution micrograph of an outer surface, shows that regular arrays of CaO particles are indeed separated by $\sim 1 \mu m$ cracks. As noted by Roberts, Jacobson, and Searcy [12], the gas-phase permeability measured in CaO aggregates from calcite crystal slices can be reconciled with their high surface areas if the pores have a size distribution of the kind for which evidence is reported here.

The probable path of particle repacking. If sintering were important during the time of decomposition, fully decomposed samples would be expected to have lower surface areas, and perhaps also different pore size distributions, than partly decomposed samples. But as long as the decomposition is not interrupted, the specific surface areas and porosities are the same at $\sim 5\%$ and at 100% decomposition (Table I,A,C). Additional evidence that sintering is negligible in vacuum is provided by the observation that the surface areas of fully decomposed samples were not significantly different when the time of heating was extended beyond the normal decomposition time, 10-12 hours, by an additional 8-10 hours. It can be shown that the observed packing

of CaO particles must be produced from an initially more open and uniform arrangement by a diffusionless process.

Towes [5] demonstrated, by means of TEM, that the CaO from calcite decomposition in vacuum at an unknown temperature forms as "needles" of diameters of the order of 10 nm. The SEM observations of Figs. 3, 4 and 6 confirm this finding, but under the conditions of this study the particles can more appropriately be called rod-shaped. These SEM observations provide the information necessary to deduce salient features of the positions and orientations of the CaO relative to the advancing reaction interface.

The roughly hemispherical features of Figs. 3 and 6 are the tips of CaO rods that grow along the rod axis as decomposition proceeds. The rods are of roughly the same cross sections and tend toward local close packing. Rods can only have approximately uniform cross sections if they are initially formed with approximately uniform spacing along the reaction interface; each rod must form by collecting Ca^{++} and O^- ions from a calcite volume element that is proportional to the rod volume.

Unless CaO particle rearrangement occurs, the porosity of the CaO aggregate is fixed at 55%--the difference in CaCO_3 and CaO molar volumes--regardless of the CaO particle dimensions. Ewing et al. noted that CO_2 pressures below 10^{-2} times the equilibrium decomposition pressure influence the CaO surface area (and presumably the rod dimensions) even though CO_2 does not significantly catalyze sintering at such low pressures. Increased CO_2 pressure in this range probably increases the spacing between CaO particle nuclei on the calcite surface.

Figure 7 is a schematic drawing of the initial arrangement of CaO particles relative to the calcite surface. Figure 7,A depicts a cross section drawn normal to the axes of a parallel bundle of rods when porosity is 55% and the rods are arranged in an assumed close-packed array. Figure 7,B is a cross section drawn normal to the advancing interface in a close-packed line of rods. The rods are drawn in two sets because x-ray studies [13] and ridge patterns in fracture surfaces [2] indicate that the CaO rods grow in more than one alignment with the Ca^{++} and $\text{CO}_3^{=}$ ion planes of the calcite surface [13].

The CaO intermediate layer observed during decomposition of large calcite crystals shows no resolvable features with dimensions of the order of $1\text{ }\mu\text{m}$ when exposed by fracture. This observation is consistent with the interpretation that the intermediate layer has an open structure described in terms of Fig. 7. The transformation to the final CaO aggregate occurs probably not because of internal strains, as initially hypothesized, but because the array of separated rods collapses to bring the rod surfaces in contact. Because sintering is too slow to cause significant changes in surface areas, collapse of the separated rods might be expected to produce a mass of essentially unbonded particles; evidently, however, for these very small particles, the forces of surface interaction are strong enough to cause strong interfacial bonding.

Towes [5] reported that the CaO particles grow to lengths of $0.1\text{ }\mu\text{m}$ or more. Towes' TEM studies were necessarily made with thin sections; in large calcite crystals, the maximum lengths of the CaO needles may be considerably greater. For calcite particles of the order of 1-10 mm in cross section, needle growth is likely to be terminated

when the tips of a collection of needles growing with common orientation intercepts the tips of another collection of needles growing with a different orientation relative to the reaction surface. For calcite powders, collapse of the initially open array of needles can occur toward the center of the CaO aggregate formed from each calcite powder particle. Small cracks or voids, like the ~ 10 nm irregularities of Fig. 8, are produced but macrocracks or voids do not form. For large crystals subvolumes have rod packing like that of the powder (compare Figs. 3 and 4 to Fig. 6 and compare microporosities), but the overall aggregate volume, when decomposition of a large calcite crystal is carried out in a single uninterrupted heating, is only $(2 \pm 2)\%$ less than the volume of the initial crystal. The total volume of these large aggregates can only be conserved by the creation of macropores or cracks between more closely packed subvolumes. The $1 \mu\text{m}$ crack in Fig. 3 is formed between two such subvolume elements.

Stress at particle-particle contact would play only a secondary role in the processes so far described. Decreases in surface area and in mesoporosities that result from thermal cycling in the course of the decomposition reaction (Table I,B) must, however, reflect the breaking of interparticle contacts and repacking of particles as a result of thermally induced stresses. After two or three thermal cycles, the effect of thermal stress-induced repacking on surface areas and mesopore volumes remains directly proportional to the quantity of CaO formed (Fig. 2). The measurable mesoporosities and total aggregate volumes are little different from those of samples not subjected to cycling (Fig. 5; Table I,C), but the surface areas are some $25 \text{ m}^2/\text{g-CaO}$ less. This difference suggests that the cycling produces closed pores

for which the surfaces are inaccessible to N_2 gas. This possibility could be tested by comparing the macroporosities calculated in Table I to macroporosities measured by mercury porosimetry. A porosimeter was not readily available at the time of this study.

Summary

High-resolution SEM photographs, N_2 adsorption isotherms, and micrometer measurements have been used to characterize CaO particle shapes and pore size distributions that result when large calcite crystals are decomposed in vacuum below 700°C . Sintering is negligible and the surface area of the CaO reaction product is independent of the extent of reaction for CaO from large calcite crystals, just as was reported for CaO from calcite powder decomposition. In volume elements smaller than $\sim 1\ \mu\text{m}$ in cross section, particle shapes and pore size distributions are very similar for CaO from large and small calcite crystals. Collapse of the open structure that results from the 55% difference in molar volume between calcite and CaO brings CaO surfaces into bonded contact, but leaves occasionally irregular pores and cracks with dimensions of the order of 5 to 10 nm and surface ledges which indicate additional $\sim 0.1\ \mu\text{m}$ packing discontinuities in the CaO aggregates. Aggregates from large calcite crystals have additional voids and cracks with cross sections of the order of $\sim 1\ \mu\text{m}$, between volume elements of the kind described.

It is evident that the pore structure of the larger aggregates would make them poor starting materials for formation of dense sintered CaO bodies; because of the small CaO particle sizes, sintering might occur at relatively low temperatures, but $\sim 1\ \mu\text{m}$ voids would remain

between sintered masses. The complex pore structure, however, might be useful if the CaO were to be used as a catalyst; the permeability of the aggregates is comparable with theoretical expectations for a solid with uniform pores $\geq 0.2 \mu\text{m}$ [12], while the surface areas are much greater than would be found for a sample with pores of $0.2 \mu\text{m}$ or larger dimensions.

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Table I. Influence of Extent of Decomposition in Porosity and Surface Area.

	Fraction decomposed (%) (error equal to $\pm 5\%$ of the given value)	Mesoporosity (%)	Macroporosity (%)	Surface area ($\text{m}^2/\text{g-CaO}$)
A	5.5	43.5	11.5	115
	10.7	42	13	114
	15.5	40	15	108
B*	10.5	28 , 30	27 , 25	78 , 80
	21	34 , 35	21 , 20	95 , 97
	32	36.5 , 36.5	18.5 , 18.5	99 , 98
	42.5	36 , 36.5	19 , 18.5	101 , 103
	53	36 , 35.5	19 , 19.5	96 , 97
	59.5	34.5 , 35	20.5 , 20	91 , 93
	70	36.5 , 36.5	18.5 , 18.5	94 , 92
	80	36.5 , 36.5	18.5 , 18.5	92 , 94
	90	36.5 , 36.5	18.5 , 18.5	94 , 94
	100	36 , 35.5	19 , 19.5	94 , 92
C**	100	42	12	120
	100	41.5	12.5	117
	100	41.5	12.5	118

* These data were calculated assuming that no shrinkage was occurring during the partial decomposition. The 100% decomposed sample showed a shrinkage of 4%; this makes the final mesoporosity equal to 37%.

** These data were based on an observed 2% total shrinkage.

Table II. t-plot Results

Fraction decomposition (wt.%)	Specific surface areas of CaO		P/P ₀ onset of capillary condensation	
	S _{BET} (m ² /g-CaO)	S _t (m ² /g-CaO)	from hysteresis loop	from t-plot
21	96	92	.43	-
32	98.5	-	-	-
42.5	102	101	.43	.31
53	96.5	-	-	-
59.5	92	89.5	.55	.30
70	93	-	-	-
80	93	92	.55	.33
90	94	-	-	-
100	93	94	.50	.36

Table III. Pore Size Distribution Calculations.

Fraction decomposed (%) (m ² /g-CaO)	Volume of mesopores (NTP cm ³ /g-CaO)	Area (m ² /g)	Cumulative vol. (NTP cm ³ /g-CaO)	Slit model*		Ave.pore diameter (nm)	Open cylindrically shaped pores**	
				Cumulative area (m ² /g-CaO)	Cumulative area (m ² /g-CaO)		Cum.vol (NTP cm ³ /g-CaO)	Cum.area
21	149.3	95	-	-	-	-	-	-
42.5	152.4	102	153.6	108.7	4.8	146.6	105.3	
59.5	146.5	92	145.3	91.3	5.3	140.7	90.5	
80	133.6	93	151.1	90	6.0	147	93	
100	149.9	93	144	83	5.9	142	88	

* Desorption isotherm data

** Adsorption isotherm data

Figure Captions

- Fig.1 Adsorption-desorption isotherms for CaO from calcite single crystals totally decomposed without cooling and for CaO from calcite decomposition interrupted by cooling to liquid N₂ temperatures (triangles).
- Fig.2 Fraction of submicron pore volume (α_v) and total surface (S) vs fraction of calcite decomposed (α_w).
- Fig.3 SEM picture of outer surface of CaO aggregate formed by decomposing a large calcite crystal in vacuum at 686°C.
- Fig.4 SEM picture of a surface of easy fracture through a CaO aggregate formed by decomposing a large calcite crystal in vacuum at 686°C.
- Fig.5 Pore size distribution for the samples of Fig. 1.
- Fig.6 SEM picture of surface of CaO aggregate formed by decomposing CaO powder in vacuum at 610°C.
- Fig.7 Schematic drawings of arrangement of CaO rods formed by calcite decomposition in vacuum before any rearrangement. (a) Cross section through a bundle of rods assumed close-packed and equal in diameter; (b) Cross section through a line of CaO rods arranged in two different orientations.
- Fig.8 Higher magnification SEM photograph of the CaO aggregate shown in Fig. 6.

XBL827-6081

Figure 1

XBL827-6082

Figure 2

0.1 μm

XBB 825-4481B

Figure 3

0.1 μm

XBB 825-4484A

Figure 4

Figure 5

0.1 μm

XBB 825-4481C

Figure 6

XBL 829-9635

Figure 7

0.1 μm

XBB 825-4480C

Figure 8

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