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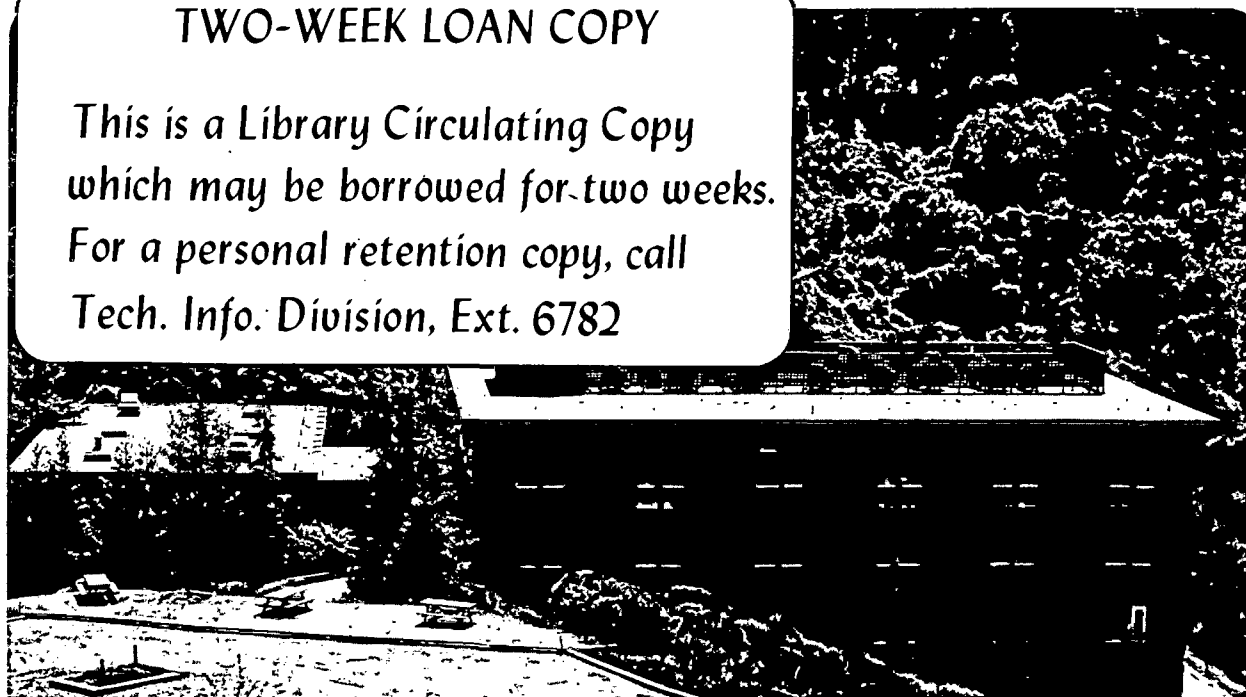
THE KINETICS OF REACTION OF POROUS CaO POWDERS  
WITH WATER VAPOR

Dario Beruto and Alan W. Searcy

July 1979

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## THE KINETICS OF REACTION OF POROUS CaO POWDERS WITH WATER VAPOR

We find that the decomposition of  $\text{Ca(OH)}_2$  in vacuo is similar to the decomposition of  $\text{CaCO}_3$  in vacuo<sup>1</sup> in that both reactions produce porous CaO particles which have the same external dimensions as the original particles of  $\text{CaCO}_3$  or  $\text{Ca(OH)}_2$ . (CaO produced by  $\text{CaCO}_3$  decomposition in vacuo is called sr-CaO.<sup>2</sup> We will call CaO produced by  $\text{Ca(OH)}_2$  decomposition in vacuo h-CaO.) Scanning electron microscope (SEM) observations and BET surface area measurements show that water vapor reacts with either sr-CaO or h-CaO to form  $\text{Ca(OH)}_2$  primarily at interior surfaces of the porous CaO particles. The two reactions initially proceed at similar time-independent rates, but both become slower at later times, and complete reaction of h-CaO requires six times as long as does sr-CaO. The data suggest that the reaction rates at later times are slower, not because a solid state diffusion step becomes rate limiting, but because of decreased access of water vapor to internal particle surfaces.

SEM and x-ray diffraction measurements show that when either sr-CaO or h-CaO reacts with liquid water, the principal reaction path is solution of CaO followed by precipitation of well-crystallized  $\text{Ca(OH)}_2$  from solution (Fig. 1). But water vapor at 4 torr pressure reacts with sr-CaO at 25°C to produce porous, poorly crystalline particles of  $\text{Ca(OH)}_2$  which have nearly the same external dimensions as the initial  $\text{CaCO}_3$  particles (Fig. 2).

The surface area of the  $\text{CaCO}_3$  powder is  $\sim 1 \text{ m}^2/\text{g}$ , of sr-CaO is  $78 \text{ m}^2/\text{g}$ , and of the  $\text{Ca(OH)}_2$  is  $40 \text{ m}^2/\text{g}$ . From the molar volumes of  $\text{CaCO}_3$ , CaO, and  $\text{Ca(OH)}_2$ , the porosities of the sr-CaO and  $\text{Ca(OH)}_2$  particles are calculated to be  $\sim 55\%$  and  $\sim 11\%$ , respectively. The solid portions of the

sr-CaO particles are formed of needle-shaped CaO crystallites of  $\sim 10^{-2}$   $\mu\text{m}$  diameters.<sup>3</sup> The pores must also average about  $\sim 10^{-2}$   $\mu\text{m}$  in cross sections.

Water vapor at 4 torr pressure is not expected to condense at 25°C even in capillaries which are an order of magnitude smaller than those in sr-CaO.<sup>4</sup> Furthermore, the weight change during the reaction of water vapor with sr-CaO is just that required for conversion of the CaO present to  $\text{Ca(OH)}_2$ . If liquid water filled the 11% pore volume when reaction is complete, a larger weight change would be found. We conclude that the path of reaction of water vapor with sr-CaO or with h-CaO, which has a similar initial rate (Fig. 3), does not include a liquid phase transport step.

Conversion of h-CaO to  $\text{Ca(OH)}_2$  by reaction with water vapor causes minor distortions in particle shapes and the development of sets of parallel cracks. The calculated porosities of h-CaO and of the  $\text{Ca(OH)}_2$  produced from it are 49% and 0%, if the cracks and distortions are neglected.

The dimensions of the CaO crystallites that form the framework of h-CaO particles have not been reported. The fact that h-CaO has a higher surface area and greater x-ray diffraction line broadening than sr-CaO (Table I) may be a consequence solely of smaller crystallites in h-CaO or of smaller crystallites coupled with more crystal imperfections. In either event, h-CaO might be expected to react with water vapor more rapidly than sr-CaO does. In fact, however, 99% conversion of h-CaO to  $\text{Ca(OH)}_2$  requires  $1.23 \times 10^4$  sec. compared to  $1.95 \times 10^3$  sec. for sr-CaO.

The time-independence of the initial rates of the reactions (Fig. 3) suggests that a surface or interfacial step is rate limiting for both.

The rather abrupt changes to slower, but again nearly constant, rates when the reactions are partially completed cannot be accounted for by decreases in particle areas, for which the dotted curve of Fig. 3 illustrates the predicted effect.<sup>5</sup>

If diffusion through growing layers of  $\text{Ca(OH)}_2$  were responsible for the decreases in reaction rates, the rates would be expected to vary with the square root of time as the reactions near completion. Instead the rates vary linearly with time. Furthermore, if diffusion through the  $\text{Ca(OH)}_2$  were to become rate limiting, sr-CaO, which has the lower surface area and probably develops thicker layers of  $\text{Ca(OH)}_2$  should react more slowly, not more rapidly, than h-CaO does.

$\text{Ca(OH)}_2$  probably influences the reaction rates by reducing the access of water vapor to the interior particle surfaces. If the reaction proceeds by conversion of close packed layers of  $\text{O}^{2-}$  ions in CaO crystallites to the pairs of  $\text{OH}^{-1}$  layers which are characteristic of the  $\text{Ca(OH)}_2$  structure,<sup>5</sup> little change will occur in ion distances in the planes of close packing, but marked expansion will occur in the direction normal to the close packed layers. The cracks and shape distortions produced when h-CaO is converted to  $\text{Ca(OH)}_2$  are evidence that the  $\text{Ca(OH)}_2$  does grow anisotropically. The  $\text{Ca(OH)}_2$  that grows in the h-CaO apparently does not neatly refill the pores, but blocks some pores long before reaction is complete. Cracks developed by the growth process provide some access of water to the particle interiors. Because of the cracks, the surface area of the final  $\text{Ca(OH)}_2$  is increased over that of the initial  $\text{Ca(OH)}_2$  (Table I). Even though the complete conversion of sr-CaO particles to  $\text{Ca(OH)}_2$  leaves ~11% internal porosity, anisotropic growth of

$\text{Ca(OH)}_2$  could close or greatly constrict some sections of the pores with, as observed, an effect on the reaction time which is similar to, but smaller than, that of  $\text{Ca(OH)}_2$  growth in h-CaO.

If porous CaO powders which will react completely with water vapor or other gaseous oxides in the minimum possible time are sought, emphasis should be placed on seeking reactions that yield CaO with surface areas as high as those found for h-CaO and sr-CaO, but with higher porosities. Candidate reactions are those in which the ratio of the molar volume of reactant,  $M_R$ , to the molar volume of CaO,  $M_{\text{CaO}}$  is higher than  $M_{\text{CaCO}_3}/M_{\text{CaO}}$ .

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Table I. Surface Areas and Crystallinities of CaO and Ca(OH)<sub>2</sub>

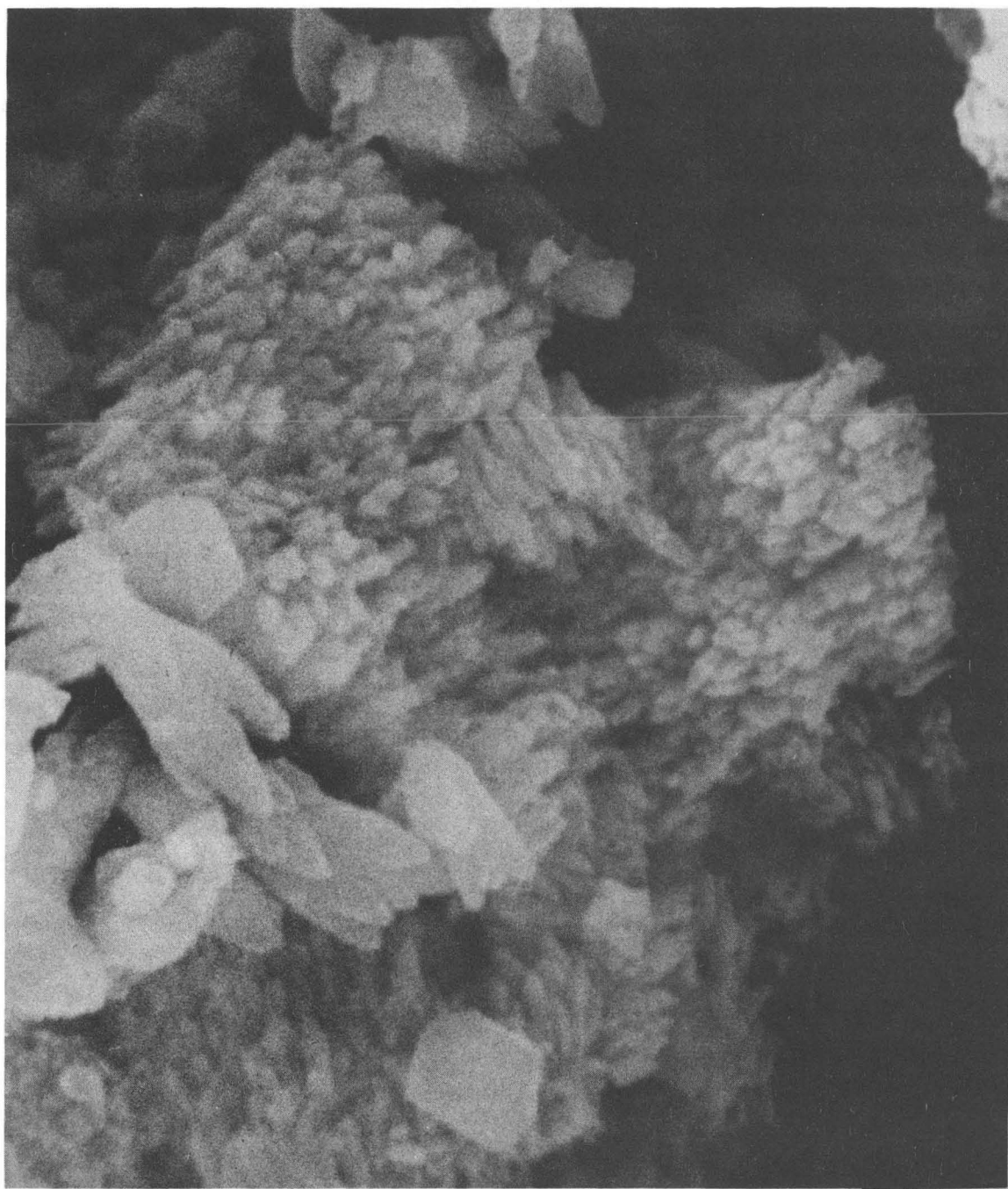
| Material            | Source of Material                                                                 | Surface Area (m <sup>2</sup> /g) | Integral Breadth of Major x-ray Diffraction Peak† (radius X 10 <sup>3</sup> ) |
|---------------------|------------------------------------------------------------------------------------|----------------------------------|-------------------------------------------------------------------------------|
| CaO                 | Decomposition Ca(OH) <sub>2</sub><br>1-10 μm powder, Dry N <sub>2</sub> ,<br>400°C | 2-3                              | 5.5                                                                           |
| h-CaO               | Decomposition same<br>Ca(OH) <sub>2</sub> powder <u>in vacuo</u> ,<br>350°C        | 133                              | 13.1                                                                          |
| sr-CaO              | Decomposition CaCO <sub>3</sub><br>1-10 μm powder <u>in vacuo</u><br>500°C         | 78                               | 9.8*                                                                          |
| Ca(OH) <sub>2</sub> | Commercial powder                                                                  | 7                                | 4.3                                                                           |
| Ca(OH) <sub>2</sub> | H <sub>2</sub> O(g) + h-CaO                                                        | 16                               | 23.4                                                                          |
| Ca(OH) <sub>2</sub> | H <sub>2</sub> O(g) + sr-CaO                                                       | 40                               | 22.9                                                                          |

† Integral breadths are the ratios of the area under the (200) reflection of CaO or (101) hexagonal reflection of Ca(OH)<sub>2</sub> to the peak height.

\* The lower crystallinity for sr-CaO implied by Fig. 4 of Ref. 1 was a consequence of hydrolysis. The present measurements were made on samples decomposed in vacuo in the x-ray chamber.

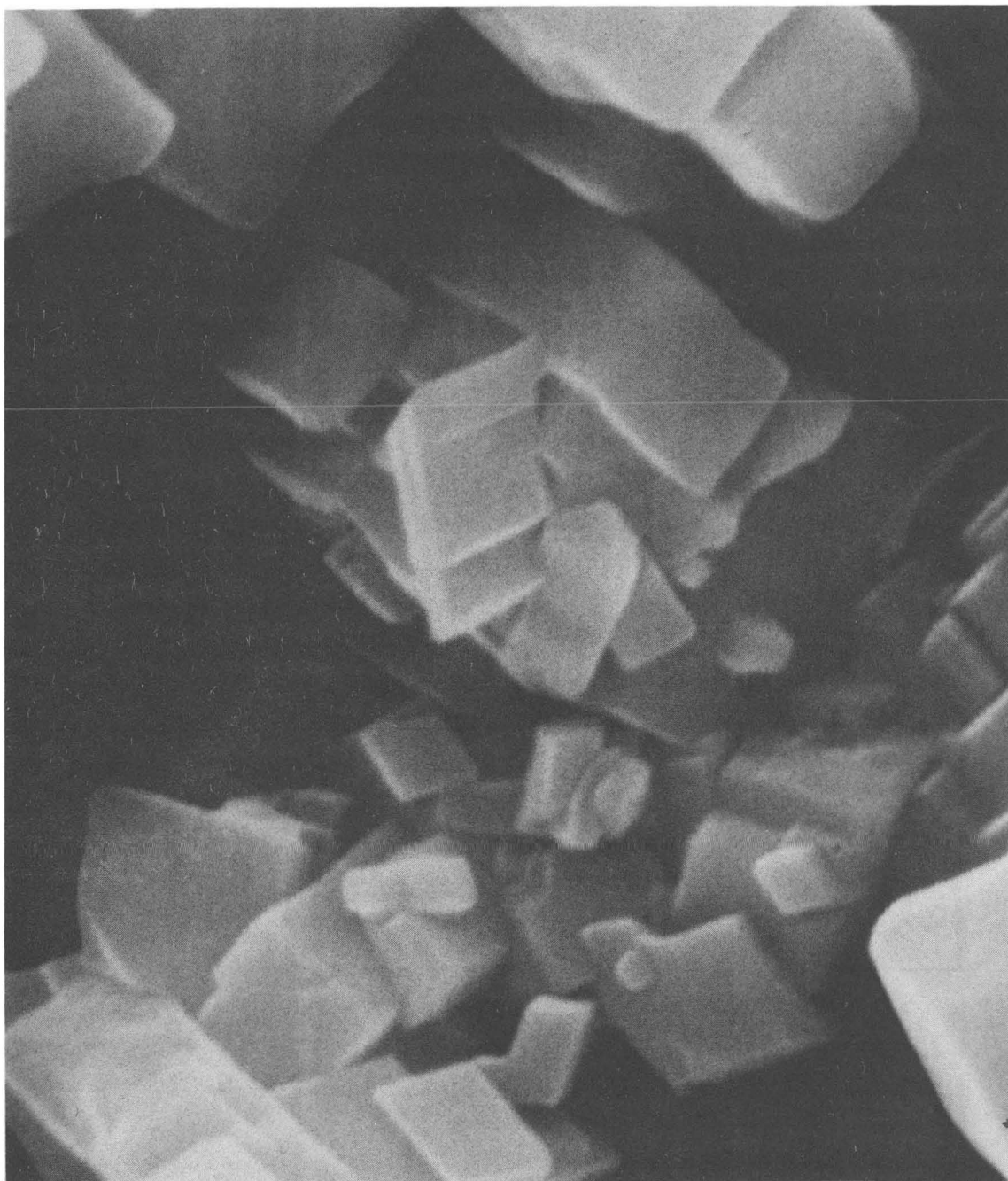
FIGURE CAPTIONS

1. SEM photograph (20,000X) of  $\text{Ca(OH)}_2$  produced by reaction of liquid water with CaO from decomposition of  $\text{CaCO}_3$  in vacuo. Shapes are characteristic of crystalline  $\text{Ca(OH)}_2$ .
2. SEM photograph (20,000X) of  $\text{Ca(OH)}_2$  produced by reaction of water vapor (Pressure, 4 torr; temperature 25°C) with CaO from decomposition of  $\text{CaCO}_3$  in vacuo. Shapes are essentially those of the original rhombohedral  $\text{CaCO}_3$  particles.
3. Rates of reaction with water vapor of CaO from decomposition in vacuo of  $\text{CaCO}_3$  (solid line) and  $\text{Ca(OH)}_2$  (dashed line). Both CaO samples weighed about 27 mg. Dotted line is the curve that would be followed if rates were determined by decreasing spherical surface areas.<sup>5</sup>



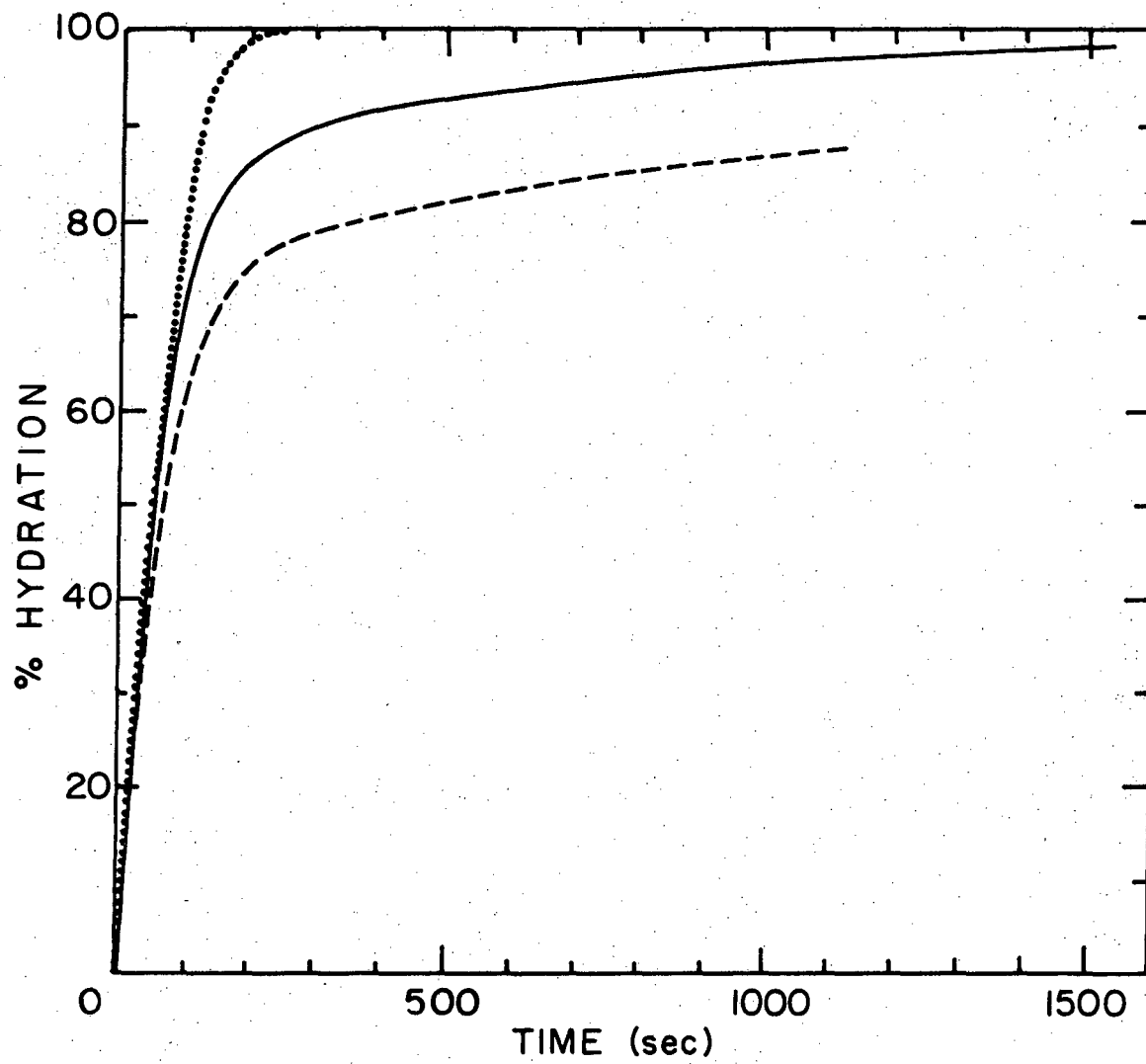
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Fig. 1



XBB796-8299

Fig. 2



XBL 797-6507

Fig. 3

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