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**PRODUCTION ENGINEERING FOR GROWTH OF  
SYNTHETIC CALCITE POLARIZER MATERIAL**

**Roger F. Belt, et al**

**Litton Systems, Incorporated**

**Prepared for:**

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PRODUCTION ENGINEERING FOR GROWTH OF  
SYNTHETIC CALCITE POLARIZER MATERIAL

Final Report  
August, 1974

Contract No. DAAB-05-71-C-2636

Prepared by:

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Object of Study: To develop methods  
for the growth of synthetic calcite  
suitable for use in laser polarizers  
and other optical devices.

NOTICES

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This project has been accomplished as part of the U.S.  
Army Manufacturing and Technology Program, which has as its objective  
the timely establishment of manufacturing processes, current or future  
defense programs.

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## ABSTRACT

A preliminary production engineering program was completed for the growth of synthetic calcite for crystal polarizers. Starting materials were powdered high purity  $\text{CaCO}_3$ , natural calcite of uniform composition, or solution recrystallized  $\text{CaCO}_3$ . Both 1.5 and 3.0 inch diameter autoclaves were used to establish most growth variables. Solutions of 6 m  $\text{K}_2\text{CO}_3$  at temperatures of 400 - 450°C and pressures of 20 - 25000 psi were used for mineralizers. At growth gradients of 10 - 20°C, rates of deposition on  $\{10\bar{1}1\}$  cleavage rhomb seeds approached 75  $\mu\text{m}/\text{day}$ . Techniques were perfected for the operation of silver lined autoclaves with 9.0 inch diameter x 9 feet long cavities. Growth conditions were successfully maintained in these large autoclaves to transport 20 lbs of nutrient to calcite seeds. For runs extending up to 60 days, about 3 - 4 mm thick sections of new material were grown on seeds. A number of chemical and physical tests established the high quality reproduction of natural calcite.

## PURPOSE

This production engineering measure was initiated to develop hydrothermal growth procedures for high quality synthetic single crystals of calcite. Calcite is currently the only material available for the construction of many types of polarizers used in conjunction with electro-optically Q-switched crystal lasers. These lasers are required for illuminators, target designators, range finders, display systems, and other military applications. Some immediate uses were contemplated for the TOW, LTDS, LGB, and LIOD programs. The principal problems of the growth program were to enlarge a small laboratory process to pilot production, to strive for maximum yields, and to maintain high quality in all crystals.

## GLOSSARY

- Calcite** - A natural mineral of composition  $\text{CaCO}_3$  which crystallizes in the trigonal system. Its high quality and large optical birefringence are necessary for polarized light applications.
- Polarizer** - A material which transforms natural light into polarized light by virtue of its reflection or transmission properties.
- Autoclave** - A vessel capable of containing a fluid under high temperature and pressure.
- Hydrothermal Growth** - A solution growth technique performed in an autoclave whereby seed crystals are used as substrates for nutrient transport under a thermal gradient.
- Nutrient** - The basic material to be dissolved and transported. It must contain the chemical elements of the crystal to be grown, e.g.  $\text{CaCO}_3$  powder.
- Mineralizer** - A solution used for dissolving and transporting the nutrient. In our system 6 M  $\text{K}_2\text{CO}_3$  was used.
- Seeds** - Single crystals used as substrates for isoeptaxial growth.
- Seed Rack** - Holder for numerous seed crystals.
- Autoclave Liner** - An inert material used to prevent corrosion of the steel autoclave by the mineralizer.
- Baffle** - A simple plate with openings used to control convection and thermal gradient.

## 1.0 INTRODUCTION

Most of the military applications of solid state lasers, such as target designators and range finders, utilize a pulsed Q-switched energy source. A common means of Q-switching is based on the electro-optic Pockels effect. The successful use of this technique requires a highly polarized light beam. Since all crystal lasers emit partially or unpolarized radiation, it is necessary to insert a polarizer in the laser cavity. Normally the polarizer is of the Glan-Thompson type and is inserted between the laser rod and Q-switch. For reproducible results the polarizer material must possess favorable physical properties and have low insertion loss. At the present time calcite is the most widely used polarizer crystal.

In addition to laser systems, single crystals of calcite are required for many other applications of polarized light. Since its study in the late 17th century by Huygens and Bartholinus<sup>1</sup> calcite has remained the primary material because of its high birefringence and excellent quality. In modern times the problems of supply sources, uniform quality, and geological formation have been more intensely studied. Numerous techniques for the preparation of synthetic calcite have been suggested but the natural mineral is currently the only source. There are several disadvantages to a continued reliance on solely the mineral: (1) Large amounts of the highest quality crystal are not on hand or easily discovered (2) The optical properties may change slightly because of impurities or composition (3) The best sources have been located outside of the United States. The technical requirements for good polarizers are expected to increase markedly through military and civilian use of optical devices. Therefore, it is expedient to develop a synthetic method for the growth of calcite.

The single crystal growth of calcite has been investigated by standard and novel procedures. Various solution methods have been described by Ikornikova<sup>2</sup> by Morse and Donnay<sup>3</sup> and lately by Henisch<sup>4</sup>. Reactive precipitation has also been suggested by other authors<sup>5-7</sup>. Gruzensky<sup>8</sup> has grown small crystals by reactive diffusion of  $\text{CaCl}_2$  and  $(\text{NH}_4)_2\text{CO}_3$ . It has also been reported that 200 g crystals have been grown hydrothermally<sup>9</sup>. However such a size probably included a large seed. More modest descriptions of Russian achievements have also been published<sup>10-11</sup>. Growth from a melt appears to be precluded because of decomposition. High pressures may overcome the problem but no preliminary data have been reported. Fluxes have been tried with some success<sup>12</sup>. Growth from a eutectic melt with  $\text{Li}_2\text{CO}_3$  has even yielded cm size crystals<sup>13,14</sup>. The principal difficulties in all techniques have been size and quality. Furthermore, production problems are usually severe because of growth rate, equipment, and cost factors.

While calcite appears in nature in a variety of forms and from many possible growth methods, it is generally agreed that the highest quality calcite, such as the original Iceland spar, is probably formed from hydrothermal solutions. Thus it appears that the most

## Introduction (Continued)

promising procedure for artificial synthesis would be a hydrothermal one. Indeed many preliminary experiments have shown that it is possible to grow optical grade calcite in a manner analogous to that used in the growth of synthetic or "cultured" quartz for piezoelectric applications. During the period 1966-1968, work in the Airtron Laboratory had progressed to the state where hydrothermal growth of several mm of calcite has been obtained on cleavage rhomb seeds. Through optical examination and laser probing, the hydrothermally grown material was found to be free of strain and internal scattering sites. It was generally equivalent to high quality or Schlieren grade natural calcite. Similar results were also reported later using the same hydrothermal solutions<sup>15</sup>. One of the more important features of producing a crystal by synthesis is the control that can be exercised over the purity and uniformity of the end product. This can prove to be of significant importance, particularly in cases where laser applications are concerned. The presence of scattering sites or trace impurities, which would not be critical in the case of ordinary optical applications, may render an optical component unsuitable for use in a laser system.

The growth conditions used for calcite are favorable for large autoclave use. Since preliminary feasibility had been adequately demonstrated in 3 inch diameter systems, the large scale growth resolved itself to developing several new engineering and production procedures for 9 inch diameter systems. The technical approach of these efforts is described in the following sections.

The general objective of the calcite growth program was to prepare high quality single crystals which could subsequently be utilized for laser polarizers. Under the program's scope it was necessary to consider other important production details. Among these were the following: (1) The development of reproducible starting materials such as the  $\text{CaCO}_3$  nutrient. (2) The preliminary evaluation of growth variables in 1.5 - 3.0 inch diameter autoclaves. (3) Seed production in small autoclaves. (4) The design, construction, and operation of nine inch diameter autoclaves with metal liners. (5) Seeded growth runs in large autoclaves. (6) Production runs and quality evaluation based on physical tests. All scheduled deliveries were designated in pounds of material. Basic tests included crystal properties such as light scattering, Twyman-Green interferometer fringe count, polarization performance, and optical absorption. Specific construction of various polarizing configurations was excluded.

## 2.0 RAW MATERIALS PROCESSING

### 2.1 Chemicals and Purity

In any hydrothermal process one must consider the chemical form and purity of the nutrient and the mineralizer. For calcite growth the nutrient is a suitable form of  $\text{CaCO}_3$  while the mineralizer

## Raw Materials Processing (Continued)

is 6 m  $K_2CO_3$  solution. In order to produce optical grade calcite, it is necessary to use high purity reagents. What high purity means or is required for calcite may be gathered from a typical analysis of material as given<sup>16</sup> in Table I. Thus we see that a purity of 99.7% or better is adequate. In the case of quartz growth by hydrothermal technique, the nutrient can be prepared from natural quartz. Ideally this would be attractive for calcite but as Table II illustrates<sup>17</sup>, there is a wide variation in composition for material of different geographical source. Therefore as our starting material we have chosen a reagent grade powdered  $CaCO_3$  having an analysis given in Table III. Except for the element Sr, the powdered  $CaCO_3$  is fully equivalent to natural calcite.  $Sr^{2+}$  is a slightly larger ion than  $Ca^{2+}$  and  $SrCO_3$  has a crystal structure different from calcite. Nevertheless a small amount of Sr can probably be tolerated with no loss in quality.

Since the  $K_2CO_3$  mineralizer is in fairly high concentration within the autoclave, it should be of highest purity and contain no large foreign ions. We have determined from previous experiments that reagent grade  $K_2CO_3$  is entirely satisfactory for our purpose. The analysis of a high grade  $K_2CO_3$  is given in Table IV. For preparation of all solutions it is important to utilize water which is free of ordinary contaminants. Generally a demineralized low conductivity water is essential and may be obtained from many commercial sources. Over the years Airtron has purchased its own equipment for high quality water.

The data in Tables III and IV represent small quantities of starting materials. For actual production runs later in the program, large quantities of both  $CaCO_3$  and  $K_2CO_3$  were purchased in lots of 100 lbs. The analyses of several of these lots are given in Table V. We have found that all of our lot analyses are quite consistent and therefore should give a reproducible end product.

### 2.2 Sintering Experiments on Nutrient

Experience in hydrothermal growth at Airtron has shown that any nutrient is required in pellet form rather than as a powder. Powders have a tendency to settle to the bottom of a reaction vessel and form a sludge. Once this occurs the effective area available for dissolution and nutrient transport is just the top surface of the sludge. The mineralizer solution is then unable to permeate the nutrient thoroughly and percolate from the bottom of the reaction vessel. This greatly diminishes the nutrient/seed area and impedes uniform growth. Consequently, efforts have been directed toward obtaining a  $CaCO_3$  nutrient in sintered form which will remain solid in the hydrothermal environment and allow dissolution to take place throughout the nutrient zone.

It is not possible to obtain sintered  $CaCO_3$  under atomos-

Table I  
Main Impurities in Optical Grade Calcite

<u>Element</u>	<u>Wt %</u>
Al	0.100
Si	0.000
Mn	0.038
Mg	0.015
Fe	0.006
Ni	0.004
Cu	0.002
	<hr/>
Total	0.225

Table II

## Typical Analysis for Calcite Crystals of Various Origin

<u>Component</u>	<u>Calculated</u>	<u>Missouri</u>	<u>Elba</u>	<u>Sweden</u>	<u>New Jersey</u>	<u>Italy</u>	<u>Italy</u>
CaO	56.03	55.74	54.41	48.87	22.15	34.04	55.38
MgO		0.11	0.27		2.72	7.28	0.58
FeO		0.04	0.15		0.29	13.05	
MnO		0.04	0.42	6.21	16.67	1.71	
CO <sub>2</sub>	43.97	43.95	43.55	42.62	42.08	43.84	43.69
Rem.		0.07	1.27	1.59	0.08	0.24	0.30

Table III

## Typical Analysis of Mallinckrodt A. R. Grade Calcium Carbonate

<u>Impurity</u>	<u>Wt %</u>
Alkalinity	To Pass Test
NH <sub>4</sub>	0.003
Ba	0.005
Ce	0.001
Heavy Metals (Pb)	0.001
Insoluble in dilute HCl	0.010
Fe	0.003
Mg	0.020
NH <sub>4</sub> OH ppt	0.010
Oxidizing Substances (NO <sub>3</sub> <sup>-</sup> )	0.005
PO <sub>4</sub>	0.001
K	0.010
Sr	0.100
SO <sub>4</sub>	0.010
<hr/>	
Total	.179

Table IV  
 Impurity Limits for  $K_2CO_3$  Mineralizer  
 Reagent Grade

<u>Impurity</u>	<u>Wt %</u>
Insoluble	0.01
Ce	0.003
SO <sub>4</sub>	0.004
N	0.001
PO <sub>4</sub>	0.001
As	0.0001
Pb	0.0005
Fe	0.0005
Na	0.02
SiO <sub>2</sub>	0.005
Loss at 285°C	1.0

TABLE V

## Spectrographic Analysis of Raw Materials

<u>Element</u>	<u>CaCO<sub>3</sub></u> <u>Lot 4072-Y1</u>	<u>CaCO<sub>3</sub></u> <u>Lot 4072-Y2</u>	<u>K<sub>2</sub>CO<sub>3</sub></u> <u>Lot PX1390-CB603</u>
BARIUM	ND<0.001%	ND<0.001%	ND<0.001%
BERYLLIUM	ND<0.001%	ND<0.001%	ND<0.001%
CALCIUM	High	High	ND<0.003%
LITHIUM	ND<0.001%	ND<0.001%	ND<0.001%
MAGNESIUM	ND<0.001%	0.003%	ND<0.001%
SODIUM	0.004%	0.001%	0.02%
STRONTIUM	0.02%	0.02%	ND<0.001%
POTASSIUM	ND<0.001%	ND<0.001%	High
RUBIDIUM	ND<0.001%	ND<0.001%	0.002%
CESIUM	ND<0.003%	ND<0.003%	ND<0.003%

ND&lt; - Not Detected less than

Note: Other elements not detected

## Raw Materials Processing (Continued)

pheric pressure above 850°C since the reaction  $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$  takes place. Figure 1 shows the equilibrium pressure-temperature<sup>18</sup> data for  $\text{CaCO}_3$ . Curves A and B are from two independent sources. These curves indicate that a  $\text{CO}_2$  pressure in excess of atmospheric pressure must be maintained over  $\text{CaCO}_3$  in order to prevent dissociation. To carry out experiments oriented toward obtaining a suitable nutrient, a sintering vessel was obtained having a continuous use capability of 1200°C temperature and 500 psi pressure. This vessel is illustrated in Figure 2. Our initial goal was to use this small vessel to determine the temperature and pressure conditions required for sintering, and then to obtain a larger scale apparatus for economical production of the nutrient material. Some difficulty was encountered in finding the exact sintering conditions, but the approximate conditions were obtained. Studies have shown that a suitable nutrient can be obtained between 1200 - 1225°C and 450 psi  $\text{CO}_2$  pressure. An example of such a nutrient after sintering is given in Figure 3.

The problems encountered in early experiments were related to furnace lifetime. This was reduced considerably due to operation under a  $\text{CO}_2$  atmosphere and the resistance windings have repeatedly broken from corrosion. Originally, the furnace consisted of a nichrome clam-shell type heating element, but this was replaced with Kanthal A-1 resistance wire due to malfunction. This second element also malfunctioned and it was later determined that the maximum element temperature allowed for Kanthal A-1 under a  $\text{CO}_2$  atmosphere is 1100°C. Consequently, the heating element in the large sintering apparatus had to be platinum wound.

Results of sintering experiments in the small vessel are summarized in Table VI. These studies have shown that the dissociation of  $\text{CaCO}_3$  follows curve A rather than curve B of Figure 1. In addition, our studies have shown that between 1100°C and 1200°C the dissociation curve is shifted to the right of curve A, indicating that even at 1200°C a suitable pressure can be obtained within the limits of the apparatus.

Though our goal was to obtain a nutrient consisting of 100%  $\text{CaCO}_3$ , two successful tests occurred with material which exhibited a weight loss, indicating a possible conversion to  $\text{CaO}$ . However, the furnace elements broke during these runs so it was not clear whether the weight loss, if from  $\text{CaCO}_3$  dissociation, occurred during the runs or after malfunction of the furnace. In any case, the presence of small amounts of  $\text{CaO}$  has not had a deleterious effect on the nutrient. The weight loss also could have been attributed to an unknown amount of water which was purposely pressed into the nutrient prior to the runs. Data in the literature have indicated that the presence of water has a beneficial effect on the conversion of  $\text{CaO}$  to  $\text{CaCO}_3$ <sup>19</sup>. Other references in the literature<sup>20-21</sup> have pointed out that the presence of  $\text{CaO}$  with  $\text{CaCO}_3$  promotes melting at lower temperatures than we have experienced. Since the temperature limit of the smaller

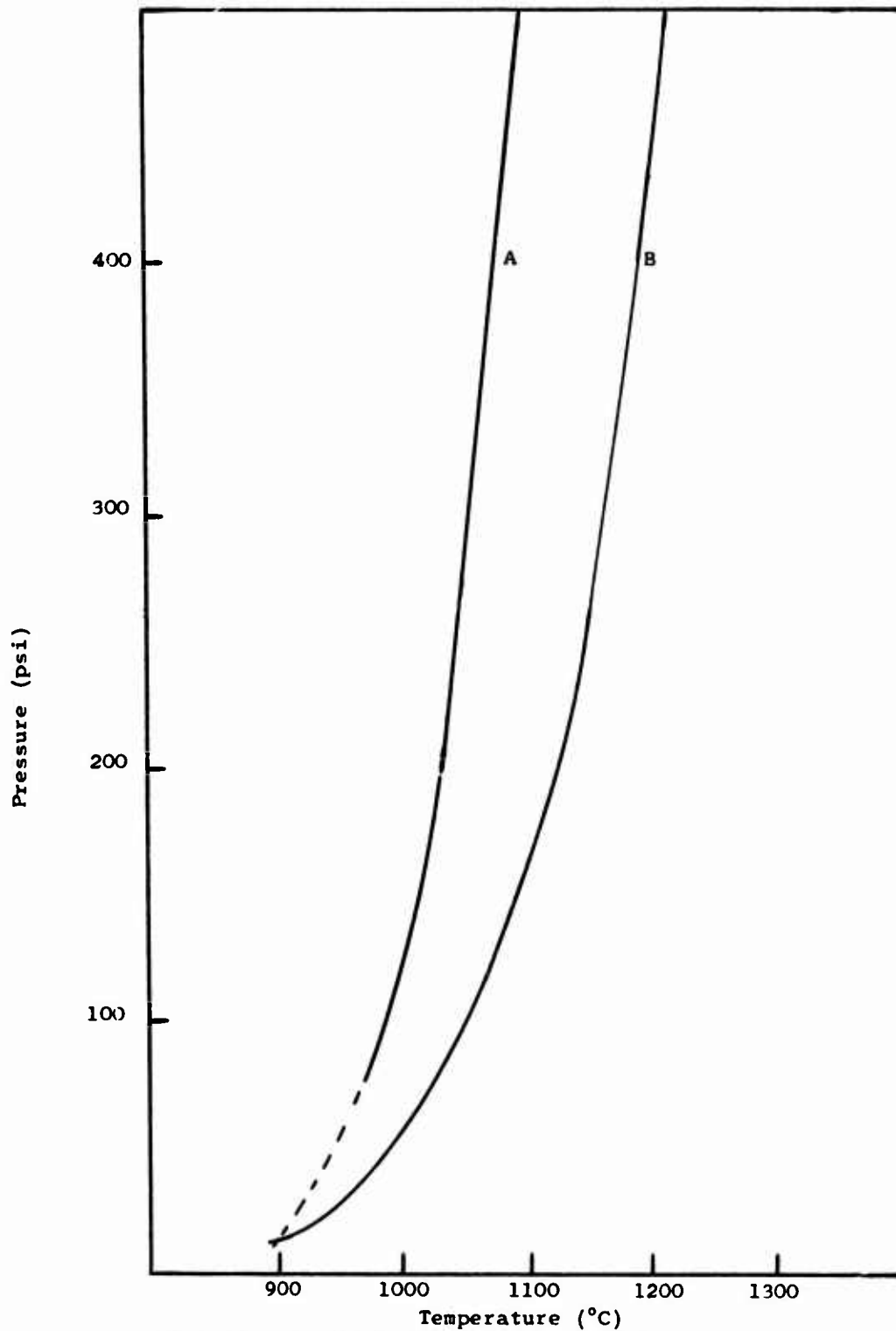


Figure No. 1 Equilibrium Data for  $\text{CaCO}_3$



Figure No. 2 Pressure Sintering Furnace for Preparation of Nutrient



Figure 3      Sintered Nutrient of  $\text{CaCO}_3$

Table VI

Results of  $\text{CaCO}_3$  Sintering Experiments  
in Small Vessel

Sinter Run No.	Total Run Time (Hrs)+	Average Temp. ( $^{\circ}\text{C}$ )	Average Pressure (Psi)	Nutrient Composition	Weight Loss (%)++	Comments
CaS-1	8	908	112	100% $\text{CaCO}_3$	0.09	Inside not as sintered as outside. Fell apart in hydrothermal environment.
CaS-2	8	1011	161	100% $\text{CaCO}_3$	0.07	Outside surface did not powder when rubbed. Fell apart in hydrothermal environment.
CaS-3	48	1057	368	100% $\text{CaCO}_3$	15.63	Solid pellets. Nutrient fell apart in hydrothermal environment.
CaS-4	26	1110	248	100% $\text{CaCO}_3$	17.59	Solid pellets. Nutrient held together in hydrothermal environment.
CaS-5	23	1032	266	.95 $\text{CaCO}_3$ .05 $\text{K}_2\text{CO}_3$	0.42	Pellets showed evidence of melting. Nutrient appeared granular. Fell apart in hydrothermal environment.
CaS-6	21	1038	275	.98 $\text{CaCO}_3$ .02 $\text{K}_2\text{CO}_3$	0.95	Pellets glassy outside, granular and glassy inside. Held together in boiling water but crushed under finger pressure.

Table VI (Continued)

Results of CaCO<sub>3</sub> Sintering Experiments

Sinter Run No.	Total Run Time (Hrs)+	Average Temp. (°C)	Average Pressure (Psi)	Nutrient Composition	Weight Loss (%)++	Comments
CaS-7	22	1083	412	a).99 CaCO <sub>3</sub> - .01 K <sub>2</sub> CO <sub>3</sub> b).995 CaCO <sub>3</sub> .005 K <sub>2</sub> CO <sub>3</sub>	0.62	Pellets glassy outside, granular inside. Fell apart in hydrothermal environment.
CaS-8	7.5	1091	417	a) 100% CaCO <sub>3</sub> b) .98 CaCO <sub>3</sub> - .02 K <sub>2</sub> CO <sub>3</sub> c) .995 CaCO <sub>3</sub> - .005K <sub>2</sub> CO <sub>3</sub> d) .999 CaCO <sub>3</sub> - .001 K <sub>2</sub> CO <sub>3</sub>	1.14	Run was aborted because of pressure leak. All fell apart in hydrothermal environment.
CaS-9	24	1128	427	100% CaCO <sub>3</sub>	0.07	Pellets glassy outside, fine grain structure inside. Fell apart in hydrothermal environment.
CaS-10	24	1150	415	a) 100% CaCO <sub>3</sub> b) 100% CaCO <sub>3</sub> W/H <sub>2</sub> O	---	Pellet with H <sub>2</sub> O seemed to be less solid. Both nutrients fell apart in hydrothermal environment.
CaS-11	24	1181	414	a) 100% CaCO <sub>3</sub> b) 100% CaCO <sub>3</sub>	0.33	Pellets glassy outside, grainy inside. Pellet W/O H <sub>2</sub> O seemed to have larger grain structure. Fell apart in Tem-Pres test.
CaS-12	24	>1200	>360	a) 100% CaCO <sub>3</sub> b) 100% CaCO <sub>3</sub>	27.16	Conditions vague due to power failure. Pellets extremely hard and glassy. Pellet w/o H <sub>2</sub> O held together in Tem-Pres.

+ Total run time includes time required to reach operating conditions

++ Very small weight losses are probably due to weighing errors.

TABLE VI (Continued)

Results of  $\text{CaCO}_3$  Sintering Experiments

Sinter Run No.	Total Run Time (Hrs) +	Average Temp. ( $^{\circ}\text{C}$ )	Average Pressure (psi)	Nutrient Composition	Weight Loss (%) ++	Comments
CaS-13	22	1215	440	a) 100% $\text{CaCO}_3$	32	a) Pellet was sandy outside, solid and glassy inside.
				b) 100% $\text{CaCO}_3$ w/ $\text{H}_2\text{O}$		b) Sandy outside and glassy inside.
				c) 99% $\text{CaCO}_3$ 1% $\text{CaO}$		c) Glassy outside, melted at one end. All fell apart in hydrothermal environment.
CaS-14	8.5	800	500	.44 $\text{CaCO}_3$	8.7 (gain in weight)	Conversion to $\text{CaCO}_3$ . Nutrient fell apart in hydrothermal environment.
				.56 $\text{Ca}(\text{OH})_2$		
CaS-15	46	1030	225	a) .90 $\text{CaCO}_3$	1.2	Nutrient was not tested since it was extremely crumbly.
				.10 $\text{CaO}$ b) .80 $\text{CaCO}_3$ .20 $\text{CaO}$ w/ $\text{H}_2\text{O}$		
CaS-16	24	650	399	70% $\text{CaCO}_3$	9.3 (gain in weight)	Net weight gain signifies conversion. Pellet very hard. Nutrient fell apart in hydrothermal environment.
				30% $\text{Ca}(\text{OH})_2$		
CaS-17	46	900	400	70% $\text{CaCO}_3$	3.3	Nutrient appeared very solid - melting and grain growth evident. Nutrient held together in hydrothermal environment.
				30% $\text{Ca}(\text{OH})_2$		
CaS-18	42.5	900	397	70% $\text{CaO}$	9.4 (gain in weight)	90% conversion to $\text{CaCO}_3$ . Nutrient fell apart in hydrothermal environment.
				30% $\text{Ca}(\text{OH})_2$		
CaS-19	42.5	905	403	70% $\text{CaCO}_3$ 30% $\text{Ca}(\text{OH})_2$	9.5 (gain in weight)	Nutrient fell apart in hydrothermal environment.

TABLE VI (Continued)  
Results of CaCO<sub>3</sub> Sintering Experiments

<u>Sinter Run No.</u>	<u>Total Run Time (hrs.)</u>	<u>Average Sample Temp. (°C)</u>	<u>Average* Pressure (psi)</u>	<u>Compact Composition (%CaCO<sub>3</sub>/ %CaO)</u>	<u>Weight Loss During Sintering</u>	<u>Comments</u>
CaS-20	25	1195	550	100/0	Yes	75% conversion to CaO, melting occurred.
CaS-21	24	1175	550	100/0	Yes	Copious melting observed.
CaS-22	23	1150	540	100/0	Negligible	Pellets displayed glassy exterior, but crumbly interior.
CaS-23	52	1150	550	100/0	Yes	46% conversion to CaO. Melting observed. Fused & solidified material crumbly, i.e. not useful.
CaS-24	21	1150	560	100/0	-	36% CaO conversion.
CaS-25	26	1130	560	100/0	-	11.7 CaO conversion.
CaS-26	72	1100	550	100/0	-	Material not suitable for further evaluation.

\* - Carbon Dioxide Atmosphere

## Raw Materials Processing (Continued)

sintering vessel is about 1100°C due to the CO<sub>2</sub> atmosphere, efforts were continued in this direction. It was felt that the temperature for sintering 100% CaCO<sub>3</sub> had for the most part been isolated and the larger vessel was designed with this goal in mind.

The tests used to evaluate the suitability of the sintered nutrient had been of two types. The first consists of a heating in boiling water and the second is to run some of it under hydrothermal conditions in Airtron's 1/4 inch Tem-Pres unit. For the latter some of the material is sealed in a 1-1/2 inch platinum capsule with a 6 m K<sub>2</sub>CO<sub>3</sub> mineralizer solution and run under nearly isothermal conditions at 450°C and 25000 psi. If the nutrient fails to remain solid in this environment, it would likewise fall apart in larger hydrothermal runs under similar conditions. It would, therefore, be unsuitable for use as a nutrient material. It is interesting to note that an early sintering run which exhibited a weight loss did hold together in a Tem-Pres test. The presence of some CaO may, therefore, be desirable.

In most runs we succeeded in producing material which remained intact in tests approximating conditions under which we will be operating in the 9-inch system. However, in a few crystal growth runs an experimental batch of pellets disintegrated. Two possible reasons were immediately considered (1) A general microscopic observation revealed fine particle size (2) weight determinations showed the composition to be 90% CaCO<sub>3</sub>: 10% CaO. Because of temperature limitations using base-metal resistance heaters, these pellets were reacted at the lower end of the temperature range. Higher temperatures were known to be more effective for producing a well-sintered product. Therefore the base metal heating elements were replaced with platinum and we were able to sinter at higher temperatures. With this extended capability and appropriate high carbon dioxide pressure we were able to attain larger grain growth and conversion to 100% calcium carbonate.

The data and results from all CaCO<sub>3</sub> sintering experiments in the small vessel are presented in Table VI. Most of the experiments resulted in weight losses when using CaCO<sub>3</sub> and weight gains in the cases where the mixture of CaCO<sub>3</sub> and Ca(OH)<sub>2</sub> was used. In all cases, except run No. CaS-17, the nutrient disintegrated in the hydrothermal environment. In run CaS-17 a nutrient mixture of 70% CaCO<sub>3</sub>, 30% Ca(OH)<sub>2</sub> resulted in a 3.3 weight % loss. The nutrient in this case, however, appeared very solid and held together in the hydrothermal environment.

Our best practice consisted of isostatically pressing the starting powder into 3-inch diameter compacts that are circumferentially notched to enable them to be broken into 1-inch long pieces. A typical compact is shown in Figure 4. These were then sintered at high temperature under an atmosphere of CO<sub>2</sub> which is required to suppress dissociation of the carbonate.

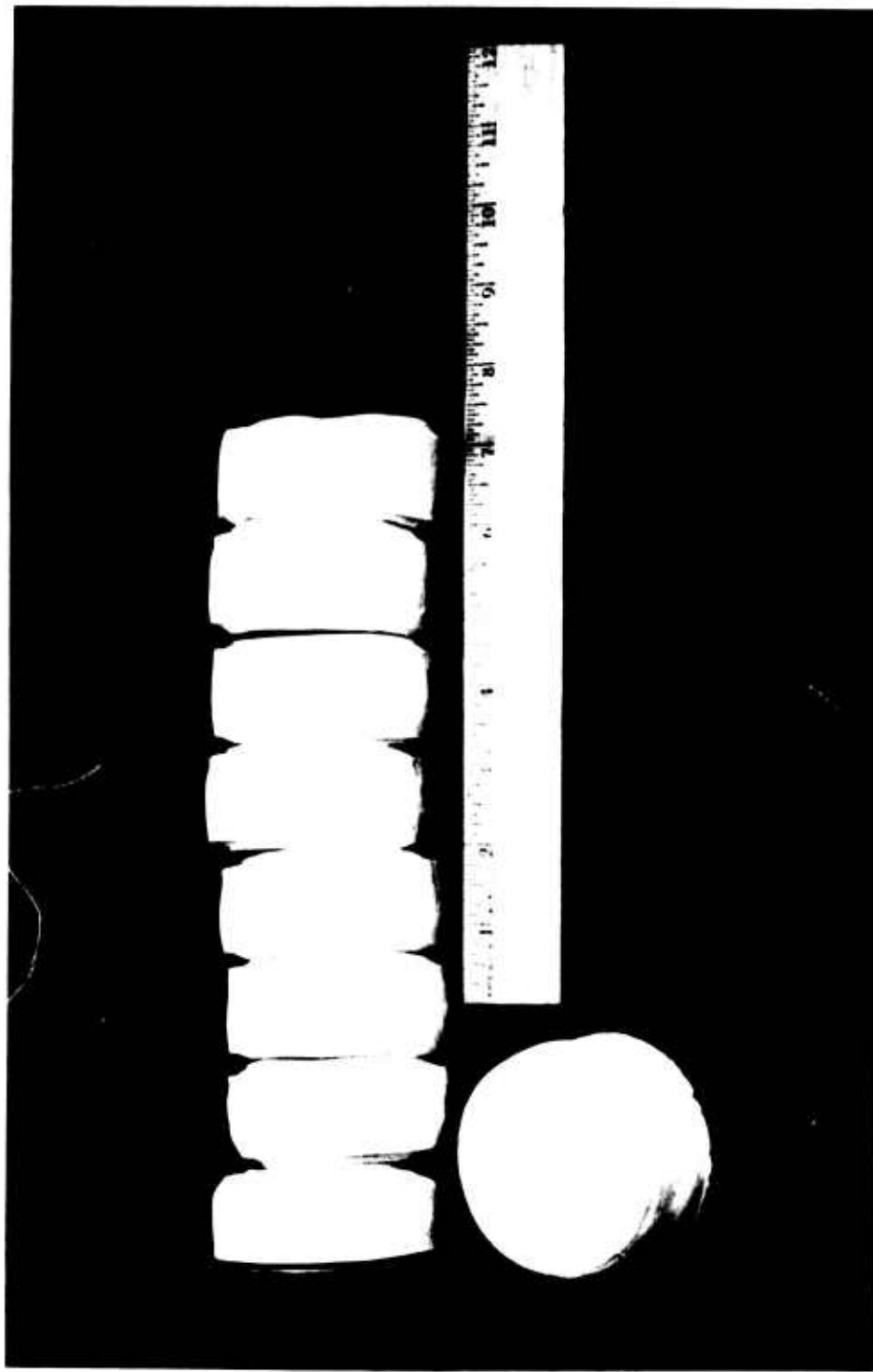


Figure 4 Isostatically compacted  $\text{CaCO}_3$  prior to sintering. Notches cause controlled fracturing on release of pressure soak.

## Raw Materials Processsing (Continued)

Our initial sintering experiments were conducted in the small prototype vessel and completed during the early months of this contract. Work in this vessel was limited to pressures of 500 psi and, consequently, carbonate temperatures of approximately 1120°C. Most results did not lead to the definition of satisfactory sintering conditions. We, therefore, undertook a series of sintering tests in our production-scale sintering vessel (Fig. 5) where pressures of 1400 psi and temperatures up to 1200°C for this CO<sub>2</sub> activity could be obtained. Our runs in this equipment, which was brought on line during the third quarter, are summarized in Table VII. These results showed that our effort to produce a sintered nutrient proceeded with ideal conditions not yet defined. Higher sintering temperatures were indicated for future efforts in this phase of the work.

For most materials, diffusion controlled sintering proceeds rapidly at homologous temperatures<sup>†</sup> of .75 to .85. Thus, sintering temperatures over 900°C are to be expected for CaCO<sub>3</sub>. Unfortunately, the dissociation of this material via the reaction  $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$  requires the presence of high carbon dioxide overpressures. The experimental difficulties associated with producing these temperatures in the presence of high pressure gas that readily transports heat to pressure chamber walls have proved to be substantial. Therefore the high pressure sintering furnace was further modified over the original design. Ceramic sealed power feed throughs were first installed. These proved to be necessary because the teflon seals previously used degraded when exposed to heated CO<sub>2</sub>. In addition the silica wool insulation used since the furnace was first started was replaced by insulating firebrick to confirm the choice of material. Test runs quickly proved the silica wool to be superior. Two experimental sintering runs were performed in the midst of these equipment modifications and made at 1100°C-700 psi CO<sub>2</sub> and 1150°C -600 psi CO<sub>2</sub>. No weight loss was observed in either sample but each was reduced to fine powder when placed in boiling water. The second material was decidedly superior to the former. Other modifications which doubled the power:volume ratio in the hot zone were made. Unfortunately at high pressures the increased thermal conductivity of the compressed gas became dominant and the rate of heat transfer through the insulation increased drastically. This resulted in a situation where the heater resistance wire was easily overloaded unless sufficient material was incorporated in the windings.

After suffering a few furnace failures, the length of the heated tube was reduced from 24 to 18 inches. The wire that was in the eliminated length was then wound back on the outside of the new element and the two concentric windings connected in parallel to eliminate large voltage drops across the layer of refractory cement. This configuration worked well for several experimental runs, but failures occurred again.

<sup>†</sup>The homologous temperature of a material is defined as the ratio of its absolute temperature to its absolute melting point.

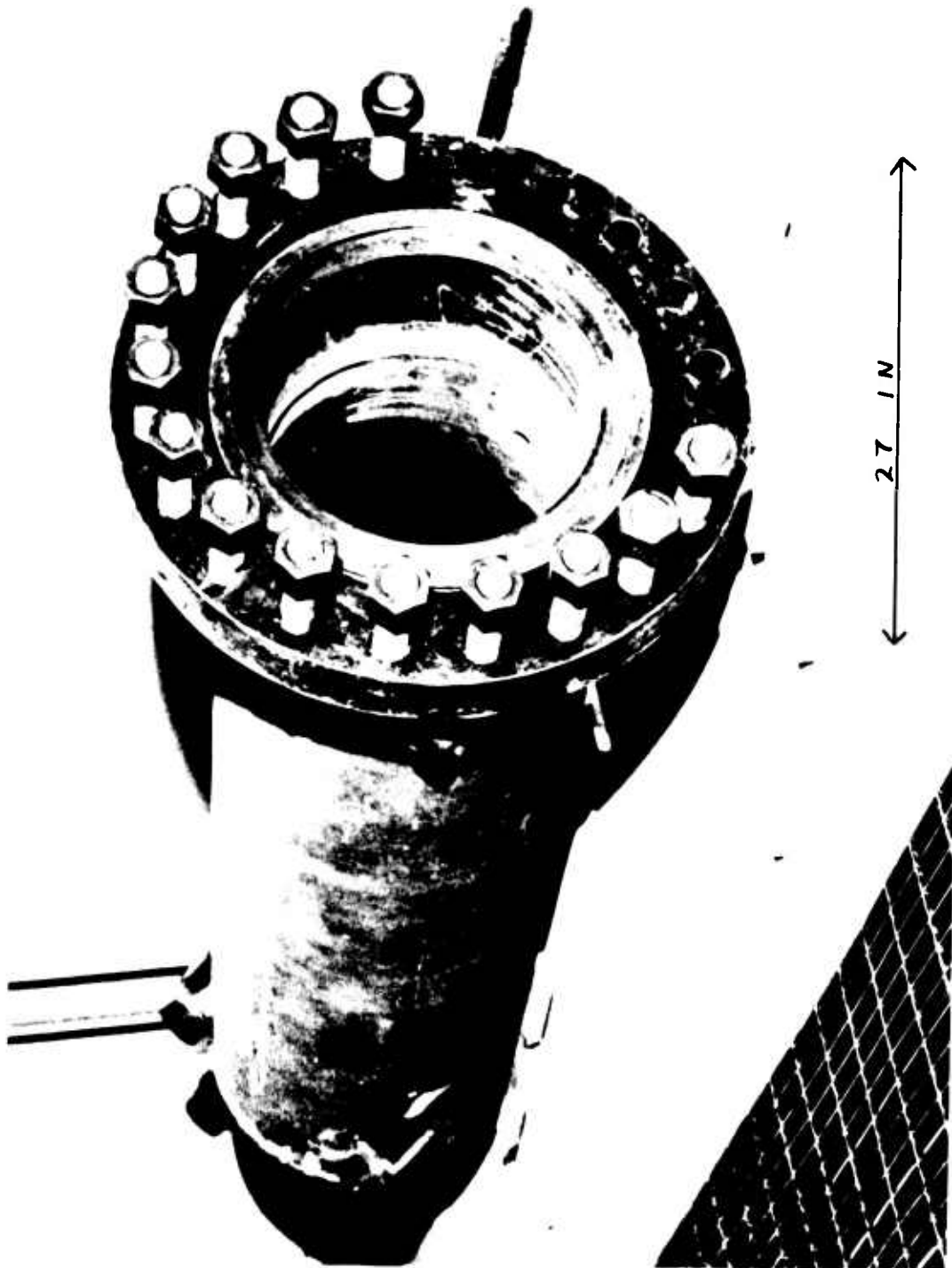


Figure 5 Large Furnace for Sintering Nutrient

TABLE VII  
Results of CaCO<sub>3</sub> Sintering Experiments  
in  
Large Sintering Vessel

<u>Sinter Run No.</u>	<u>Total Run Time (hrs.)</u>	<u>Average Sample Temp. (°C)</u>	<u>Average* Pressure (psi)</u>	<u>Compact Composition (%CaCO<sub>3</sub>/ %CaO)</u>	<u>Weight Loss During Sintering</u>	<u>Comments</u>
LS-1	24	1190	660	100/0	-	Material survived boiling water, but failed in Autoclave Test.
ES-2	15	1185	705	100/0	-	"
LS-3	96	1185	710			Some material from this run passed boiling water test, but soundness did not justify Autoclave testing.

\* - Carbon Dioxide Atmosphere

## Raw Materials Processing (Continued)

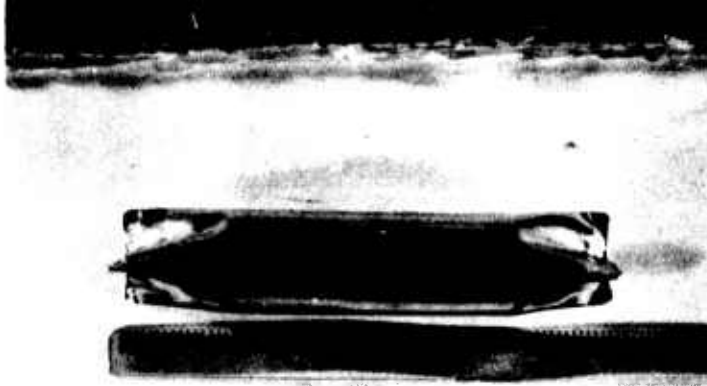
We verified that two modes of failure have been operating. The first is thermal overloading of the resistance element itself. This was encountered, recognized, and eliminated through a succession of increases in the diameter and length of the heating wire. Our furnace had a length of 18 inches and two concentric windings of reclaimed 16 gauge platinum wire. While it easily achieved reactive sintering temperatures in  $\text{CO}_2$ , it failed unexpectedly after only a few heats. A second furnace element was constructed of virgin materials following the same scheme, but it also failed after demonstrating that it could easily achieve temperature. It was clear that the mode of failure of these latter units was quite different from that observed earlier.

Examination of the furnace showed that the ceramic core adjacent to the resistor wire had fused at the top of the core near the rear of the furnace. Calcium oxide attack on the windings followed and caused the subsequent failure. This mode of failure had not been observed earlier because previous furnaces could not be heated sufficiently to produce it. Once enough power was delivered to the furnace core to achieve the needed sample temperature, the new failure mode began to operate. We believe that this is a result of chemical interaction between the carbon dioxide atmosphere and trace impurities in the alumina furnace core and resistor embedding cement. Carbonate formers such as magnesium, iron and calcium are present in commercial alumina. The presence of even small amounts of reactive oxides rapidly progressed to degeneration of the surrounding ceramic. To correct this situation the furnace was reconstructed with a new configuration. The sintered sample and its carbon dioxide atmosphere were enclosed in a thin walled tube of platinum. The pressure vessel that encloses the furnace was then pressurized with nitrogen. The conditions of these runs are given in Table VIII. The results of the second are of particular note. When the sample was removed from the sintering vessel, it was observed that the platinum envelope had deformed and pinched at one point and a small hole had developed. When the foil was opened, the partially melted sample shown in Figure 6 was seen. X-ray diffractometry showed partial (ca. 10%) decomposition to calcium oxide in the frozen melt, but no decomposition in the other material. A nugget of transparent solid calcite was also found. Apparently calcite can form under these conditions either through liquid phase sintering or as the first solid to form at the liquidus.

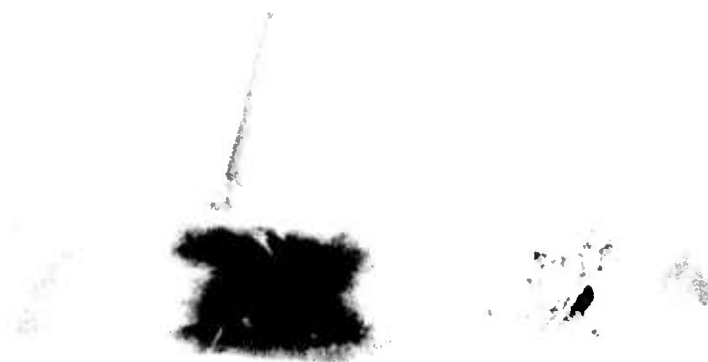
In addition to sintering in a pressurized atmosphere, two runs were made in which powdered calcium carbonate was hot pressed in a graphite die at 4000 psi and temperatures to 550 and 950°C respectively. Samples cut from other pressings easily resisted boiling water, yet they disintegrated completely under hydrothermal conditions. While these runs did not yield suitable nutrient material, they did provide preliminary data on the hot strength of calcite, a property directly related to powder consolidation at high temperature. The procedure used in the hot pressing was to place the powder into the

Table VIII  
Nutrient Sintering Experiments  
Platinum Enclosed

<u>Run No.</u>	<u>Temp.</u> <u>(°C)</u>	<u>Run Conditions</u> <u>Pressure</u> <u>(psi)</u>	<u>Duration</u> <u>(hours)</u>	<u>Remarks</u>
Ca S-73-1	900	1000	96	Density increased but compact failed in cold water.
Ca S-73-2	900	1150	96	Some melting and decomposition -Calcite nugget formed in melt area. All material except nugget failed in autoclave test.
Ca S-73-3	900	1300	24	Little sintering accomplished. Material fell apart in cold water.



(a)



(b)

Figure 6 Calcium carbonate sintering.  
(a) platinum enclosed sample prior to sintering,  
(b) carbonate after sintering. Note melted region  
at left.

## Raw Materials Processing (Continued)

die at room temperature, apply the ram pressure, and then raise the temperature of the die and piston ends. Ram movement was monitored by a differential transformer and indicated powder densification when it was corrected for the effects of thermal expansion in the ram. During heating from room temperature, little densification took place below ca. 775°C. As the temperature rose above that point the carbonate powder yielded continuously until the sample reached 800°C. No appreciable ram movement was detected between that point and 950°C. These observations indicate that shear induced flow, which is the central advantage of this method, takes place in calcite at temperatures significantly below those estimated as adequate for success in the high pressure sintering equipment. Densification was not sufficient to meet nutrient requirements but was observed in sintered samples. Therefore, we have observed in calcite both the mechanical and transport phenomena that are usually regarded as necessary for consolidation in sintering.

From all of the sintering experiments conducted during this program, it can be seen that an entirely satisfactory procedure has yet to be achieved. Some standard ceramic processes appear to be useless when applied to  $\text{CaCO}_3$ . Other were not attempted because of a lack of time and equipment. Obviously there has been little fundamental work on consolidation of decomposable compounds by sintering. Therefore our engineering pursuits appeared to have limited theoretical verification. Also there have been few studies on mechanical properties of soft compounds such as calcite. Generally initial packing is related to deformation mechanisms while most heat induced sintering takes place via a first step diffusion.

### 2.3 Nutrient Preparation by Hydrothermal Recrystallization

Throughout nature there are many forms of consolidated  $\text{CaCO}_3$  such as limestone, marine life, and stalactites. Most of these are known to be formed from dilute carbonate solutions by recrystallization. While all of these forms are too impure to be used as our nutrient source, the method of production was amenable to our equipment. Thus  $\text{CaCO}_3$  powder can be dissolved in  $\text{K}_2\text{CO}_3$  solutions under hydrothermal conditions and transported to a more compact form in an autoclave. The end product need not be a good quality single crystal but small crystallites of mm size would suffice. Furthermore the process is potentially rapid under a high thermal gradient. Some initial experiments were performed to check the feasibility of such an approach. All work was done with our standard  $\text{CaCO}_3$  and  $\text{K}_2\text{CO}_3$  reagents.

Calcium carbonate powder was introduced first into the nutrient zone of a small autoclave and then transported across a temperature difference of 45 degrees in a 6 molar solution of potassium carbonate. The average autoclave temperature was 475°C. A

## Raw Materials Processing (Continued)

comparison of the input powder and the resulting coarsened calcite is given in Fig. 7. The results of this experiment were sufficiently encouraging that trial runs were next made in the production autoclaves. Following successful completion of these runs, the recrystallized material can be used directly as nutrient in a production run.

A typical nutrient transport run was conducted in one of Airtron's twenty-two centimeter diameter autoclaves as follows. Thirty-six kilograms of chemically pure  $\text{CaCO}_3$  powder, which had been isostatically pressed into 125-150  $\text{cm}^3$  pellets, were charged into the bottom of a silver growth can. The can was then filled with a  $\text{K}_2\text{CO}_3$  transport solution and inserted into the autoclave. After a week of transport across a  $50^\circ\text{C}$  temperature difference, with the lower half of the autoclave at  $430^\circ\text{C}$ , ten kilograms of recrystallized material were obtained. Improvements in this transport rate were realized in subsequent runs when silver trays were placed on the sixteen levels of the seed rack. In addition, the transport rate should increase over the duration of a run because the area of deposition increases with growth. Through this technique we hoped to synthesize 25-50 kg of recrystallized  $\text{CaCO}_3$  nutrient which would be sufficient for about two growth runs. Table IX lists some of the runs attempted in the production autoclaves. While overall results were satisfactory, it appears that a higher transport rate is required to make the process economical.

### 2.4 Seed Crystal Preparation

Seed crystal blanks have been cut from natural calcite on a continuing basis for the small seed crystal growth program. Natural calcite seed blanks also were prepared for the initial 9-inch autoclave runs. Eventually, as work progressed with the 9-inch systems and the process became regenerative, we switched over to exclusive use of seed blanks cut from the synthetic crystals. This is always preferable to minimize the possibility of introduction of undesirable impurities. The natural calcite from which seeds have been cut was obtained from a commercial source<sup>22</sup> which was designated as their "optical reject" grade calcite. In addition some of this natural calcite has been used for nutrient in the absence of a suitable sintered form of  $\text{CaCO}_3$ . Material for this use has also been obtained from an alternate source<sup>23</sup>.

Our present method of seed preparation is to cut blanks with due regard for crystal orientation using a rotary diamond saw. Following this the blanks are carefully cleaned in methanol to remove all traces of the cementing material used to fix the parent crystals to the cutting pedestal. The blanks are then lapped using 240 and 600 grit silicon carbide. To remove possible surface damage, the blanks are finished by treatment in 50 per cent acetic acid for one hour.

To accelerate the preparation of seed stock for production

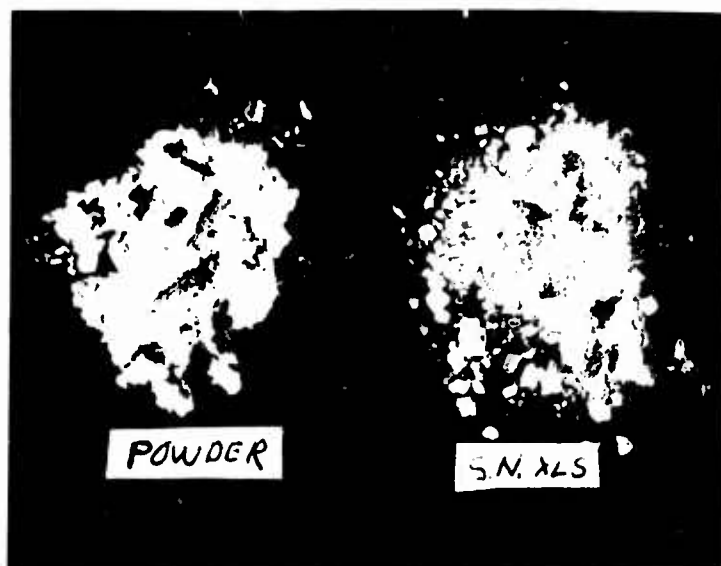


Figure 7      Calcite nutrient preparation via hydrothermal recrystallization. Calcite powder (left) is coarsened into material (right) suitable for use in single crystal growth.

Table IX

## Nutrient Transport Runs in Production Autoclaves

Run No.	Internal Fill Fraction	Bottom Temp. (°C)	Middle Temp. (°C)	Top Temp (°C)	Pressure (kbar/ksi)	Days of Run	Wt. (kg)	CaCO <sub>3</sub> Transported (kg)
Ca 9-16*	.855	430	415	415	1.7/25	2	36	-
Ca 9/17	.855	430	415	415	1.7/25	36	36	2
Ca 9-18	.855	445	367	323	1.7/22.6	30+	80	10 - 15

\*Run aborted near temperature to correct internal fill

## Raw Materials Processing (Continued)

runs of 100-150 seeds, we have used a gauged-blade "bread-slicer" type saw. This saw is capable of cutting up to 20-30 seeds in one operation. Furthermore, the surfaces are relatively free from major damage. This saw is illustrated in Figure 8.

### 3.0 SMALL AUTOCLAVE EXPERIMENTS

#### 3.1 Survey of Work

The production engineering schedule for the construction, installation, and growth in the 9.0 inch diameter autoclaves called for implementation nearly a year after contract start. During this interval preliminary runs were to be made in smaller autoclaves to refine growth conditions such as temperature, pressure, solubility, morphology, seed production, evaluation of nutrients, temperature gradient, baffle opening, and other minor operating procedures. All of the equipment needed for these small runs was already in operating condition and only modifications were required. Basically three sizes of autoclaves were available, i.e. 0.25, 1.5, and 3.0 inch diameter systems all of which we have designated as small in contrast to the 9.0 inch diameter autoclaves. The description of the small autoclaves and the data obtained are given in the following sections.

#### 3.2 Research Unit Description

The precise definition of temperature, pressure, and phase relations has to be achieved in a known manner. Most of this work took place before the contract began and suitable growth conditions were determined by means of a four station Tem-Pres Research<sup>24</sup> Hydrothermal Unit Model HR-1B-4 which is illustrated in Figure 9. Each station consists of a furnace with independent temperature controls, an autoclave manufactured from Stellite which was 0.375 inch I.D. x 7 inches long and a pressure gauge equipped with bourdon tubing suitable for use with water. An air-operated pressure generator having 60000 psi capability at room temperature is mounted in the shielded cabinet.

Platinum reaction capsules illustrated in Figure 10 are constructed from 0.25 inch O.D. x 0.005 inch wall tubing. They contain the seed, nutrient, and mineralizer to a predetermined degree of fill. When these capsules are placed in the autoclaves, temperatures are monitored by Chromel-Alumel thermocouples strapped onto the autoclave in such a way as to correspond to the top and bottom end of the capsule. The bottom couple is the indicating thermocouple once the system achieves an initial thermal steady-state, while control is by means of a couple located at the furnace heating element during the heating period. By means of the Tem-Pres system it was determined that 6 m  $K_2CO_3$  mineralizer produced acceptable growth conditions at a nominal temperature of 400°C and a pressure of 25000 psi. The solubility data of calcite in this mineralizer at 25000 psi

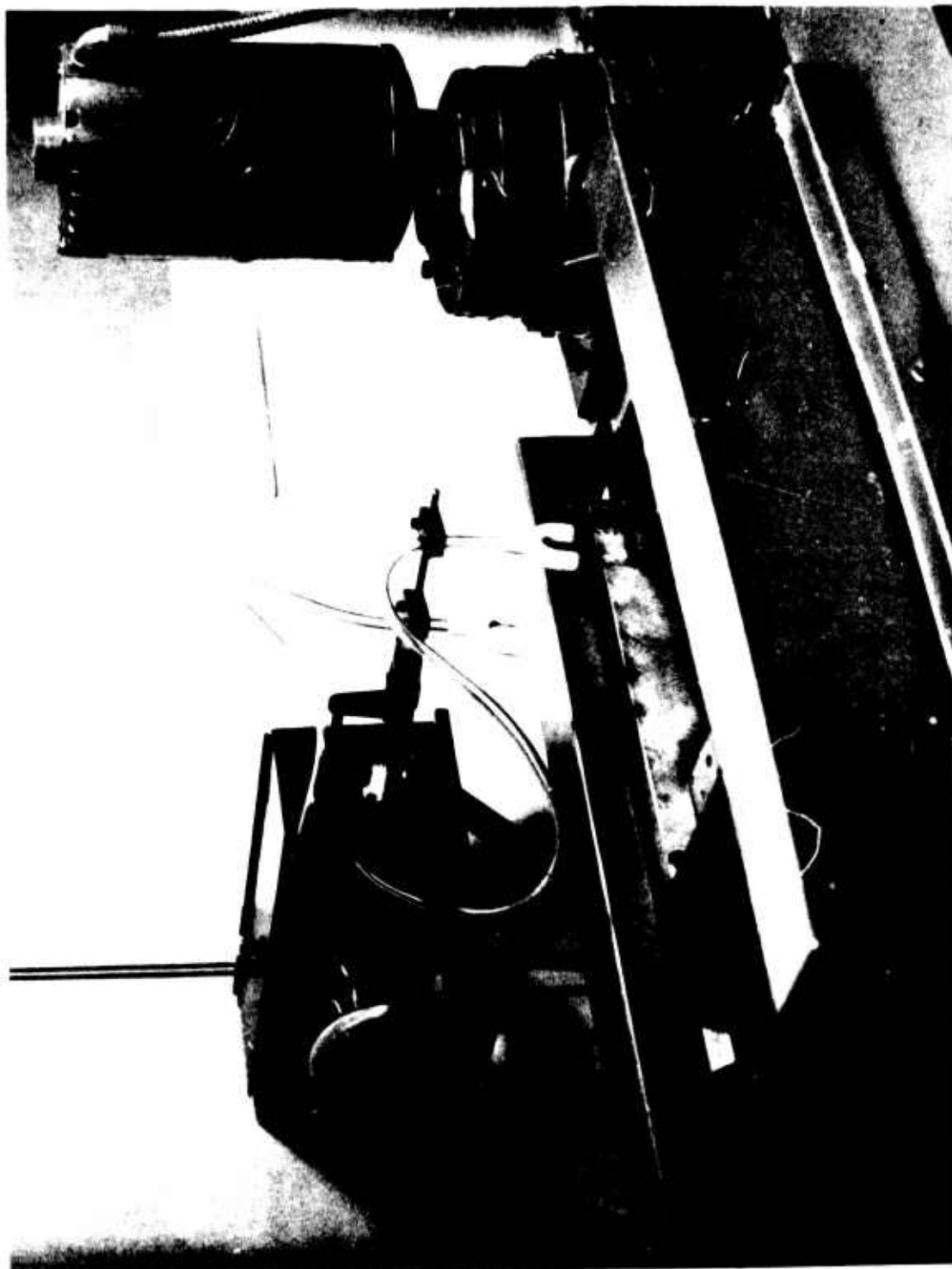


Figure 8 Multiple Blade Saw for Seed Cutting

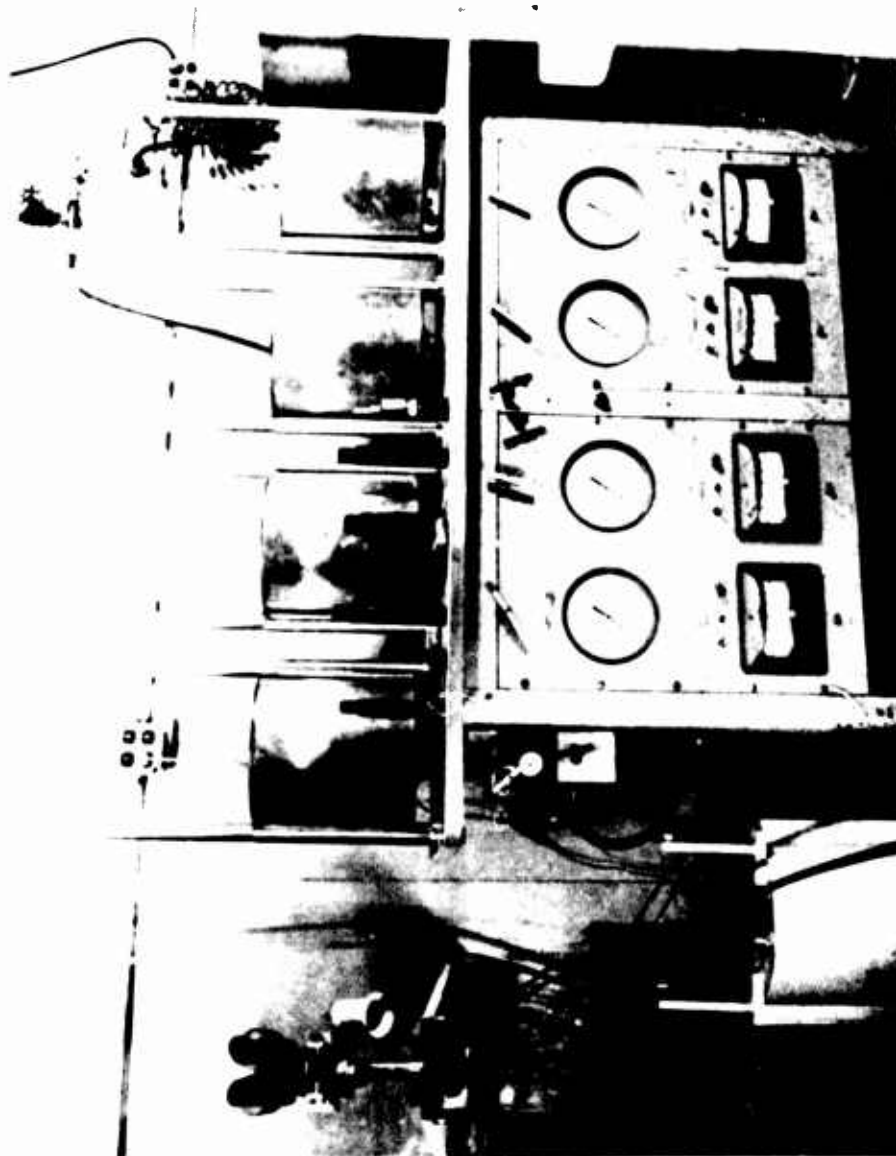


Figure 9 Tem Pres Unit for Preliminary Hydrothermal Growth

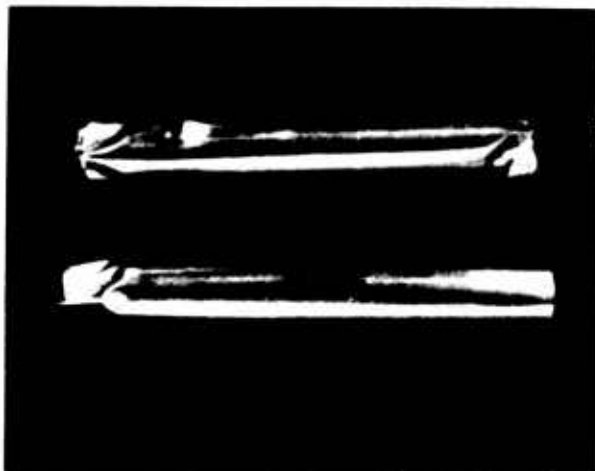


Figure 10     Platinum Capsules for Tem Pres Autoclave Use

### Small Autoclave Experiments (Continued)

for various temperatures are given in Figure 11. Data were obtained by means of the weight loss method using natural calcite seeds. Similar data were obtained later in the program with larger autoclaves.

#### 3.3 Description of Principal Autoclaves

One objective in the calcite hydrothermal growth program was to determine the growth conditions in smaller hydrothermal vessels and then to scale these conditions up for growth in the 9 inch I.D. vessels. A secondary objective was the growth of seeds in the smaller vessels for eventual use in the larger system. From previous results it was known that material cut from these seeds would be more suitable for use in the larger system than would be seeds cut from natural calcite. Two sizes of autoclaves were available to accomplish these goals. The first was a vessel measuring 1.5 inches I.D. x 3 inches O.D. x 21 inches long, while the second was a vessel measuring 3 inches I.D. x 6 inches O.D. x 42.75 inches long. The vessels were constructed from A-286 steel alloy as well as the covers, seal rings, and main nuts.

In order to prevent contact of the steel autoclave body with the  $K_2CO_3$  mineralizer and subsequent corrosive attack of the autoclave, a silver can or liner was used to contain the nutrient, seeds and mineralizer solution. Construction of the cans was of pure silver tubing, and flat welded circles of silver were used to close the opposite ends of the tube. The baffle and seed rack were also of pure silver and their design is shown in Figure 12 and 13. The two sizes of cans used in the above autoclaves are 1.44 inches O.D. x 14.5 inches long and 2.94 inches O.D. x 35.0 inches long. A visual description of the entire hydrothermal system is given in Figure 14.

Heat was supplied to the hydrothermal system by two methods with the aim of eventually switching to the second method. In the first system a furnace such as that described in Figure 15 supplied heat by means of clam-shell type heaters. These furnaces were originally designed and built by a local supplier<sup>26</sup> of such equipment. The heater sections were constructed of Nichrome resistance wire cemented in a grooved ceramic, insulating ceramic wool materials, and outer metal shells. The bottom section of the autoclave must be the hotter section so the main heat is supplied by means of a hot plate on which the autoclaves rest. Desired gradients are then obtained by "trimming" with the clam-shell heater elements. The second system provided heat by means of band heaters<sup>27</sup> which are strapped to the autoclave body. In this case the main heat is again provided by a hot plate. A metal shield is placed around the autoclave so that insulation can be provided by a fill of vermiculite. It was felt that this was the better method of applying heat since a more intimate contact is provided for heat transfer and the band heater positions can be easily changed to adjust thermal gradients.

The power to the heating system was controlled by a

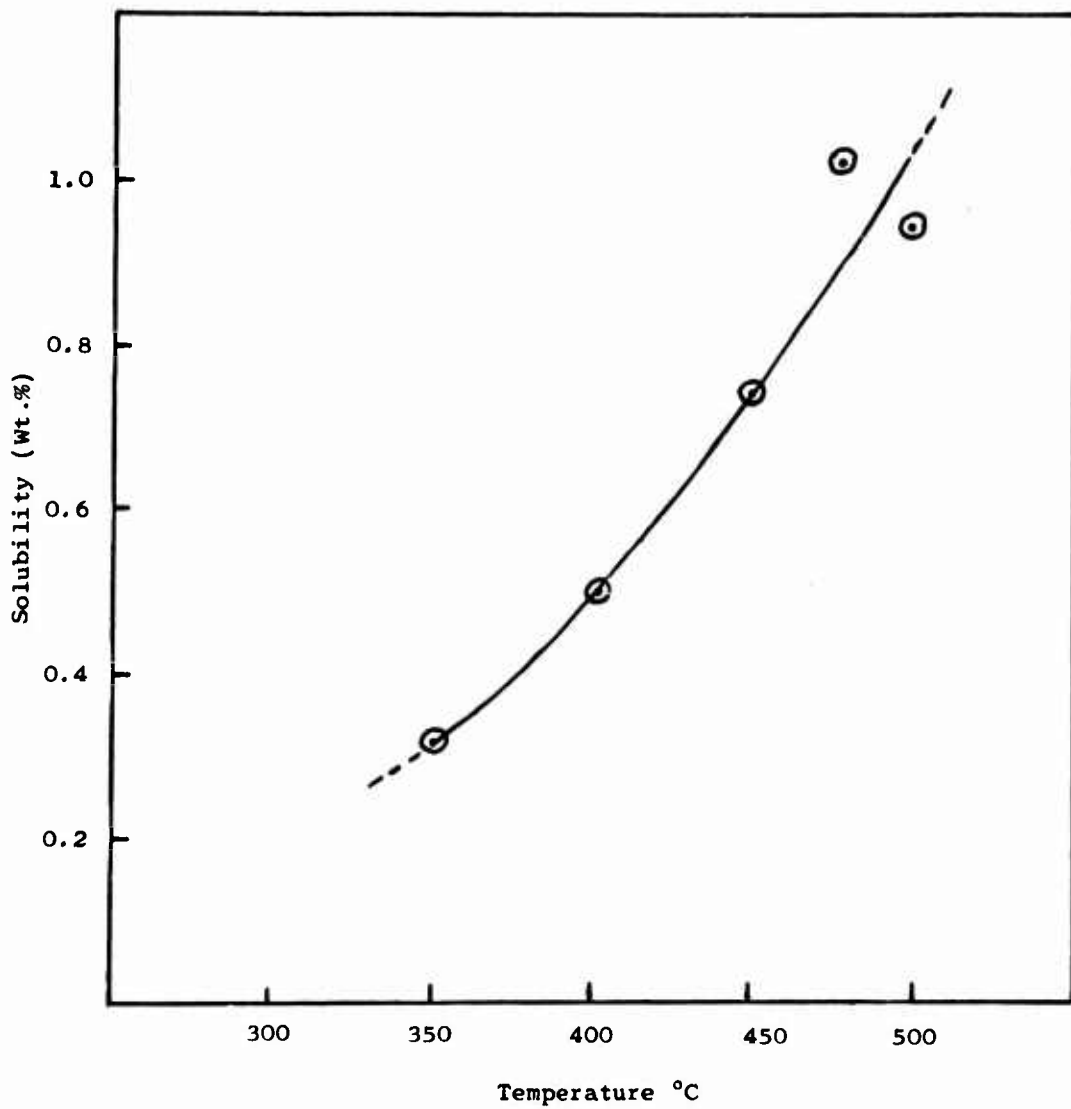


Figure 11 Solubility of  $\text{CaCO}_3$  at 25,000 psi in 6 m  $\text{K}_2\text{CO}_3$

Seam Welded  
Silver Disk  
Bottom

Seamless Silver Tube  
0.060 inch wall

Lid to be  
welded to top

Figure No.12 Sketch of Silver Liner for Autoclave

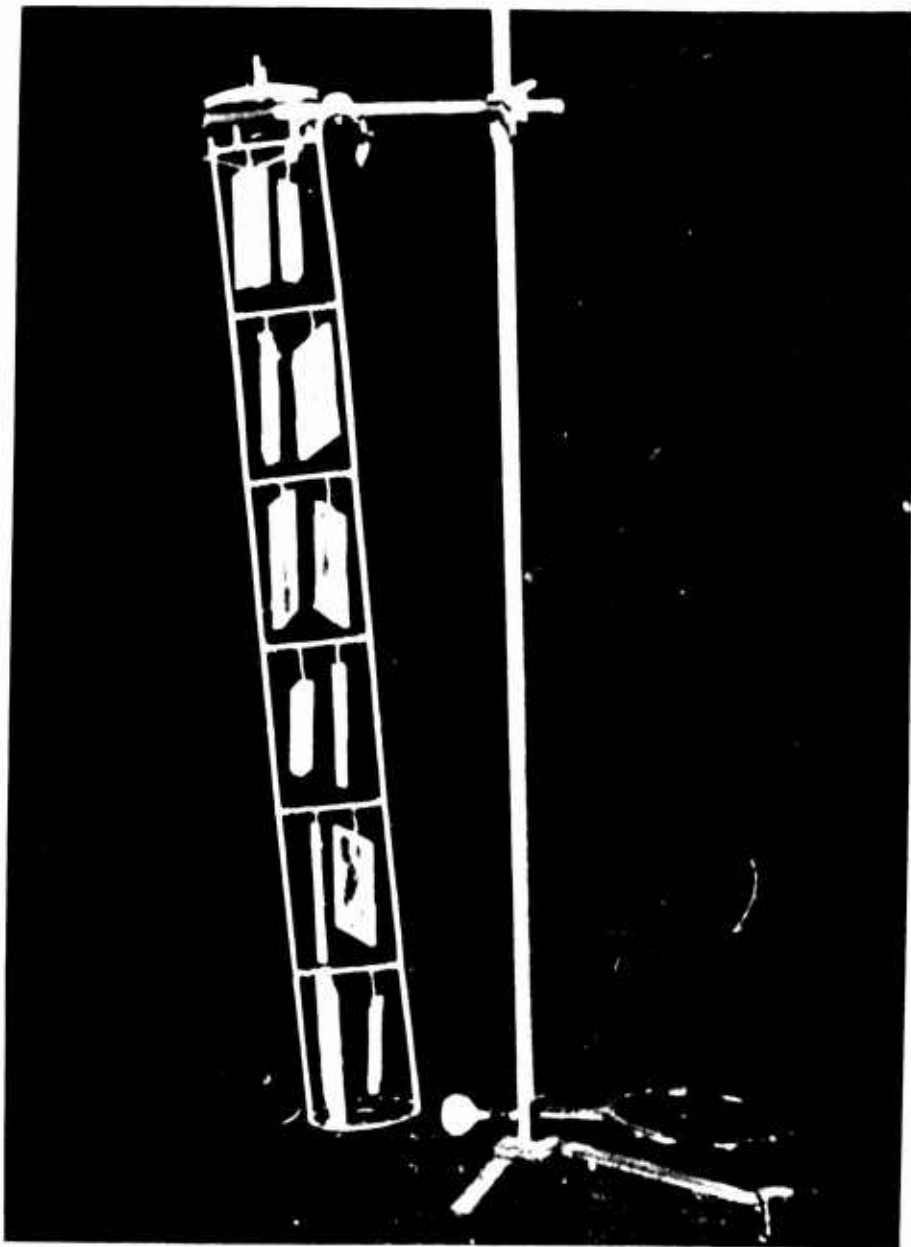


Figure 13 Seed Rack for Small Autoclave Use

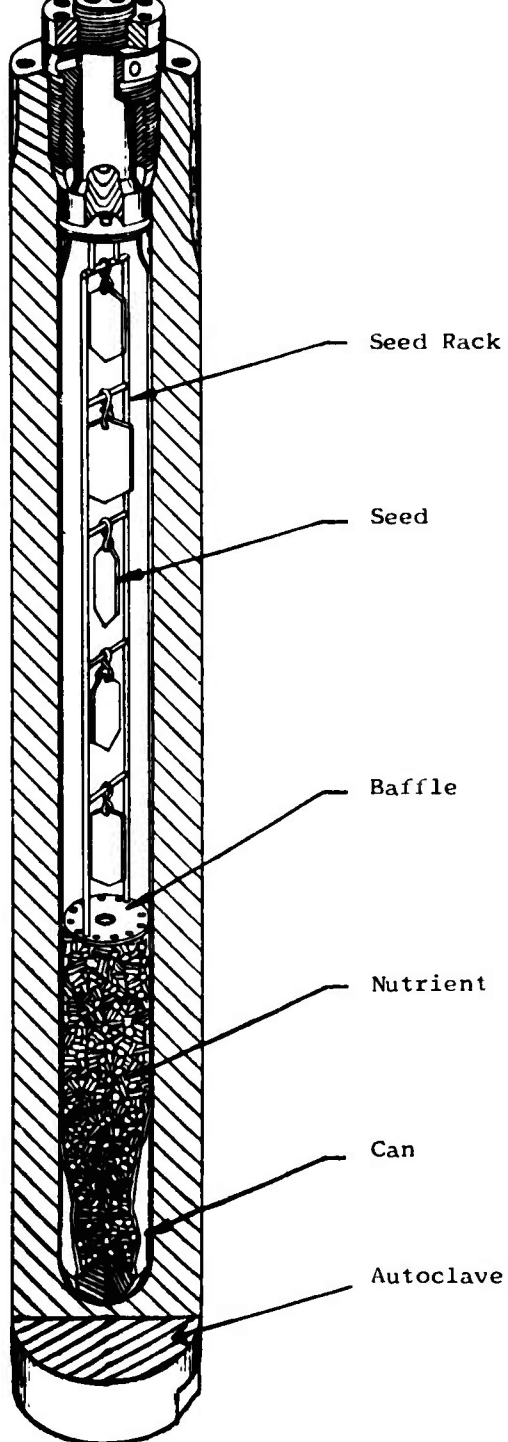


Figure 14 Complete Hydrothermal System

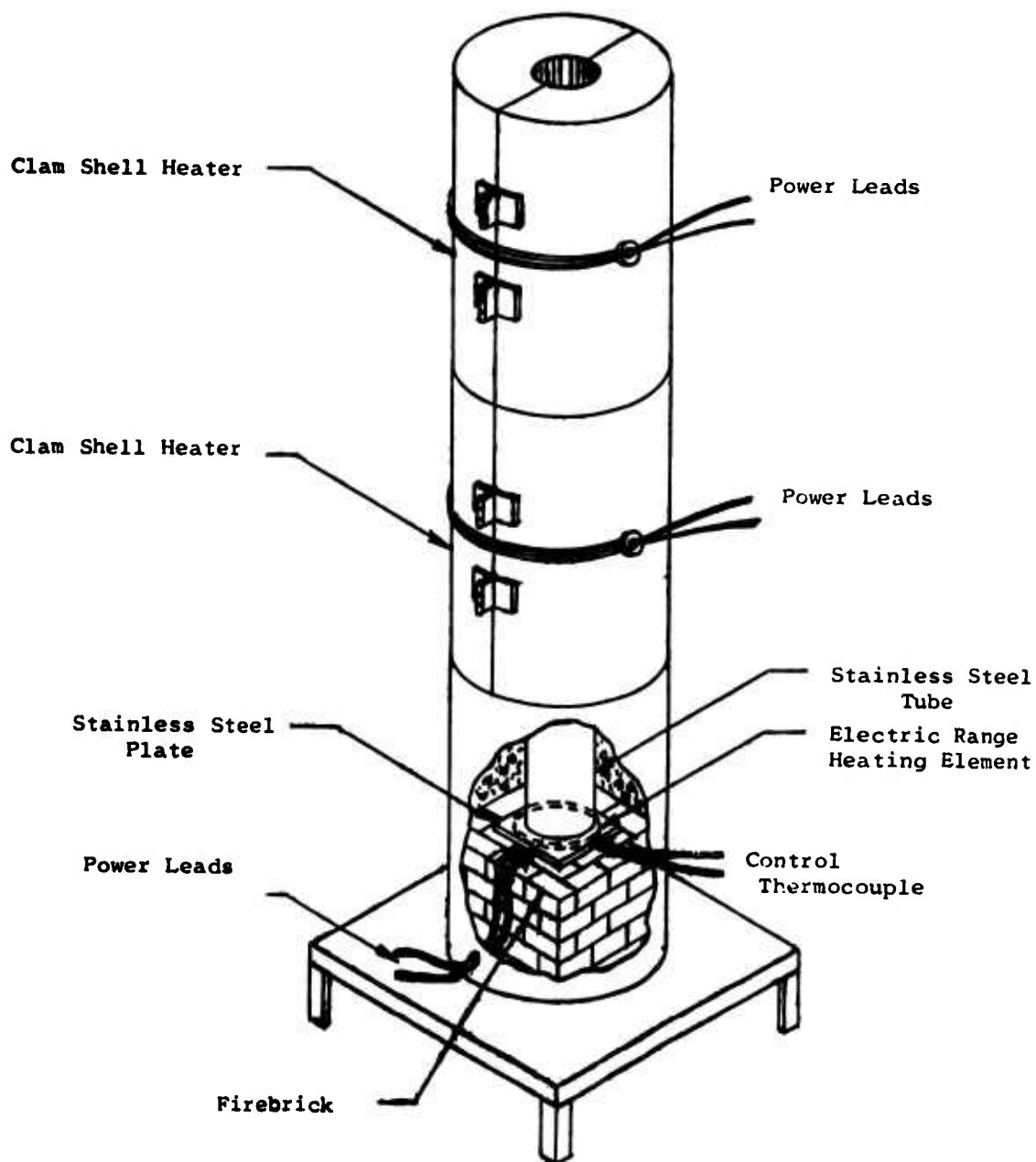


Figure 15 Hydrothermal Furnace for Small Autoclaves

### Small Autoclave Experiments (Continued)

saturable core reactor through a West Programmer Controller<sup>28</sup>. The control couple was cemented to the firebrick immediately below the hot plate element. The clam-shell heaters or band heaters were also controlled by the West instrument by means of a manually set ratio for power distribution to each element. This distribution of power was accomplished by the S-92 option of the West JS BG-3R Program Controller, which allows the output from one temperature to drive up to three saturable reactors. In our case only two reactors were used.

A schematic of the control system is shown in Figure 16. The control couple as shown in Figure 15 supplies the input signal for the operation of the controller and driver. Reactor R1 as shown in Figure 16 is used to power the hot plate while Reactor R2 is used to power the heaters. The ratio control of the two heaters allows more latitude in temperature profile adjustment than would be possible with a single heater by varying thermal insulation conditions. Other operating temperatures are obtained by means of thermocouples attached with metal straps at various positions along the autoclave's length. It has been shown that these externally measured temperatures correspond closely to the internal temperatures. We have defined an "average operating temperature" as the numerical average of these measured temperatures.

Pressure in the system is measured by direct reading of Bourdon type gauges connected directly to the internal cavity of the autoclave. The pliable silver cans are deformed under only slight pressure so the gauge pressure is an accurate measure of the internal pressure of the can. It should be remembered that the internal can pressure is obtained by initially adjusting the internal fill of the can and the external fill of the autoclave to predetermine values. Ashcroft Maxisafe<sup>29</sup> gauges using Monel Bourdon tubes connected to the autoclaves by F250-C fittings are used.

### 3.4 General Discussion of Hydrothermal Technique

The literature<sup>30-32</sup> contains several detailed descriptions of standard hydrothermal technique and its application to the growth of many crystals. The procedures and small autoclave equipment for the growth of calcite are presented here since several departures from previous literature have been initiated. The autoclaves used by Airtron for experimental growth of large crystals were described in Section 3.3. All of these utilize a modified Bridgman seal. Details of the autoclave and closure are shown in Figure 14. Since the solvents normally used for hydrothermal crystal growth are corrosive at the elevated crystal growth temperatures and pressures, noble metal liners or cans are used to contain the hydrothermal fluid. Airtron personnel have developed a technique whereby the delicate problem of pressure balance is simplified by the use of a large can. Since the can nearly occupies the entire autoclave cavity, the vessel approaches that of a lined vessel.

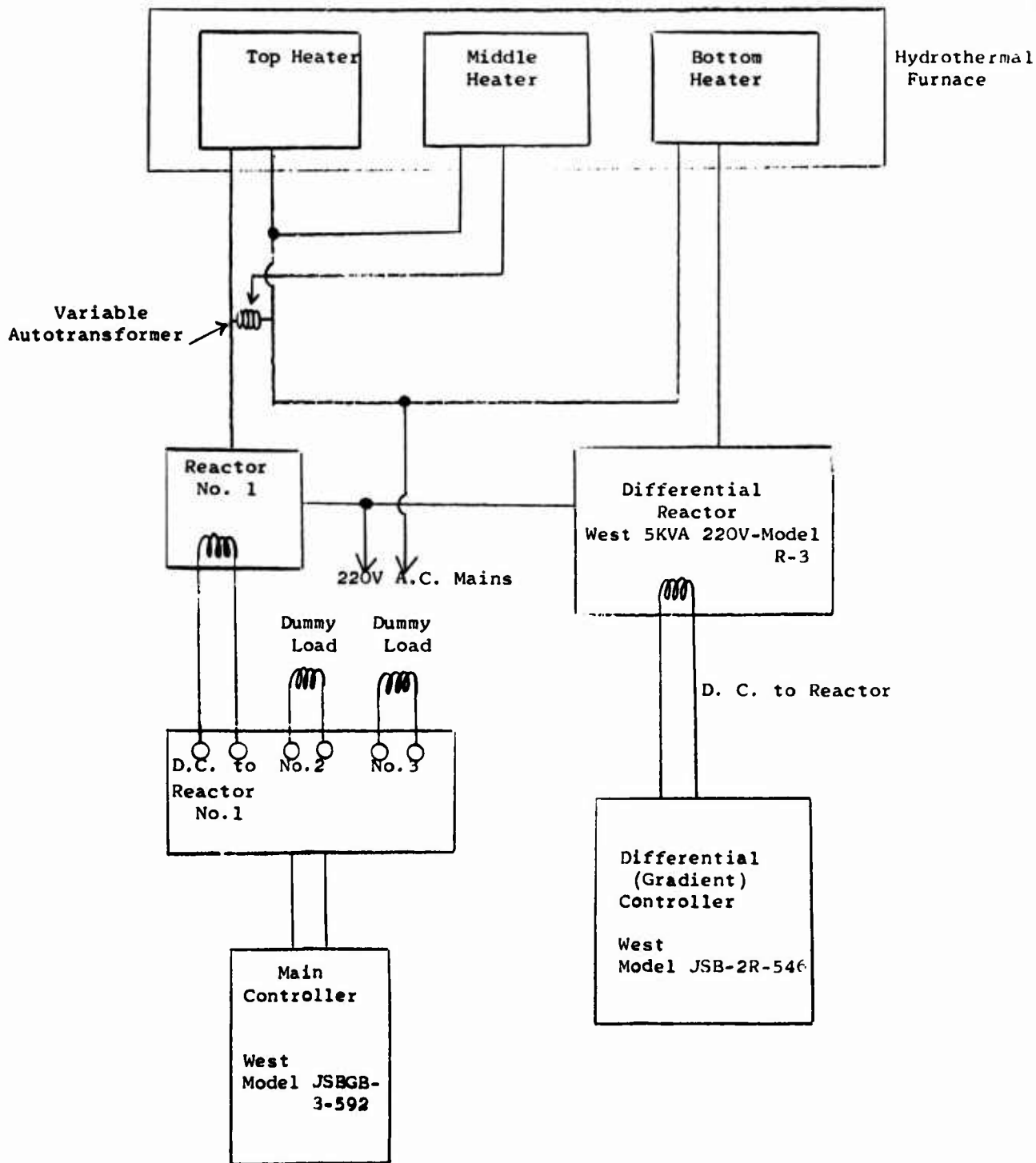


Figure 16 Schematic of Heater Control System for Small Autoclaves

### Small Autoclave Experiments (Continued)

In practice the can, seed ladder, baffle pieces, tubing, and wire are constructed of the same metal. Silver has been found to be the most satisfactory metal because it is relatively inexpensive and is normally not attacked by hydrothermal solvents. The can is charged to about one third full with nutrient material of the compound to be grown. The form of this material can be crystalline or sintered and ideally is of one quarter to one half inch in particle size. The ladder with the attached baffle plate and suspended seeds are then put in place in the can. The top is then welded in an inert atmosphere. The requisite internal fill of solvent to generate the desired pressure at the working temperature is added through a fill pipe. The pipe is then crimped and welded so that the contents of the can are now enclosed in a sealed container. The solvent used in most hydrothermal systems is water to which a compound is added to increase the solubility of the desired compound. Our experience has been that hydroxides and carbonates (particularly potassium carbonate) are excellent mineralizers. For calcite growth a 6 m  $K_2CO_3$  solution was always used.

The can is placed in the autoclave and an external fill of water calculated from Kennedy's<sup>33</sup> tables is added and the vessel sealed. The autoclave is then placed in a furnace constructed such that various temperatures and temperature gradients can be achieved by controlling the amount and area where power is introduced. Thermocouples strapped along the exterior surfaces of the vessel provide a means of measuring the temperature gradients and monitoring the temperature by control equipment. The thermocouples are usually placed at the bottom, middle, and top of the autoclaves.

When the temperature in the can rises, the liquid first fills the can, and as the critical point is reached, the solvent becomes a fluid behaving as a gas but having the density of a light liquid. The vessel is heated so that the bottom is hottest. The fluid in the nutrient region dissolves the nutrient and the fluid becomes saturated at the high temperature. The top of the vessel is heated but is kept 10-50°C cooler than the bottom. Because of this temperature gradient, convection currents within the can are established which transport the saturated solution from the nutrient chamber to seed chamber. Since the temperature in the latter region is lower than the nutrient the fluid cools and becomes supersaturated. Crystallization on the seeds then commences. The process described above provides a working description of the system which is obviously a steady state process.

The baffle in the system serves to restrict the flow of the fluid within the system. Normally the hole space in the baffle is 5 - 15% of the total area of the plate which is nearly the internal diameter of the can. The restriction of flow between the two chambers is intended to provide as nearly as possible for isothermal conditions within each chamber, and thus to insure saturation of the fluid in the nutrient chamber and complete solute depletion by crystallization in

### Small Autoclave Experiments (Continued)

the growth chamber.

Before the can is placed in the autoclave, it is checked for leaks at the welded seams. If all welds are leaktight, the can is inserted in the autoclave, the external fill is made, and the entire autoclave sealed. One of the most frequent difficulties in the use of autoclaves is the attainment of a satisfactory pressure seal. We have utilized a technique developed over the years to give trouble-free operation. Our procedure consists of lapping the seal area in the vessel with a special tool fitted for that vessel. The seal is then polished with very fine abrasive paper. After each run is made, all removable seal parts are examined and machined where necessary.

When the autoclave is being brought to operating temperature, checks are constantly made on temperature and pressure. The latter is monitored constantly to assure that sealing took place. Generally if the pressure remains fixed for a couple of days, the autoclave is operating correctly. Final small adjustments are then made on the bottom, middle, and top sections of the autoclave. For extended runs of one week to two months, the temperatures and pressure are recorded daily to verify correct conditions. At the end of a run, the autoclave is cooled to room temperature, carefully opened, and the contents are examined. For each run all operating conditions are recorded, the seed crystals are weighed before and after the run, their thicknesses are measured between the major growth faces, and a nominal growth rate is then calculated. Further adjustments are then made in future operating variables.

#### 3.5 Examples of Test Runs

In order to illustrate the data obtained from our small autoclaves, three runs were made early in the program. The main purpose was to examine the temperature growth gradient  $\Delta T$  which directly affects quality, rate of growth, and solution concentration gradient.

Run X114 was made in a 3 inch autoclave using a 6 m  $K_2CO_3$  mineralizer solution and a 7.5% baffle area. The temperature of the nutrient zone was  $395^\circ C$  while there was a temperature differential between the nutrient and growth zones of  $21^\circ C$ . The top of the autoclave was kept hotter to minimize spontaneous nucleation at the top of the growth chamber. Two types of seeds were used, spontaneous nucleated (S.N.) seeds from past runs and seeds cleaved from natural calcite rhombs. It had been our experience that growth on the S.N. seeds is usually superior. This run, however, produced spurious growth on the S.N. seeds while growth on the cleaved seeds was cloudy with spontaneous nucleation covering the seeds' surfaces. There was also a large amount of spontaneous nucleation in the run which could have resulted from recorded temperature fluctuations

### Small Autoclave Experiments (Continued)

early in the run. The pressure was also too low and required fill adjustment in future runs. In addition, the use of a larger baffle area was suggested since it appeared that the nutrient was not reaching the seeds at a fast enough rate. The growth was poor as evidenced by the crystals in Figure 17. The data for the run are recorded in Table X.

Run X117 was made in a 1.5 inch autoclave using a 6 m  $K_2CO_3$  mineralizer and a 10% baffle area. The temperature of the nutrient zone was  $353^\circ C$  while the temperature differential between the nutrient and growth zones was  $10^\circ C$ . S.N. as well as cleaved seeds were used. Once again the growth on the S.N. seeds was poor while hopper growth was apparent on the cleaved seeds. There was some spontaneous nucleation on the seeds as well but clean, transparent areas were visible in later stages of growth. There was a trace of brown impurity in the seeds, probably arising from iron present in the natural calcite nutrient used. The quality of growth which took place in this run can be observed in Figure 18. Data are given in Table XI.

The purpose of Run X118 was to study the effect of a higher temperature with a smaller baffle area. The run was made in a 1.5 inch autoclave using a 6 m  $K_2CO_3$  solution and a 5% baffle area. The mean temperature of the nutrient zone was  $376^\circ C$  while the temperature differential between the nutrient and growth zones was  $12^\circ C$ . Once again cleaved and S.N. seeds were used. Though growth on the cleaved seeds was apparent, the S.N. seeds had dissolved and dissolution was likewise apparent on the cleaved seeds. Since there was a fair amount of spontaneous nucleation in the run the problem was most likely due to the small baffle area used. The nutrient had been depleted only slightly and nearly all of this was accounted for in the spontaneous nucleation. The bottom surface of the baffle may have also been plugged although this was not obvious when the silver liner was opened. If this had happened then nutrient would have been prevented from transporting and transport would have been limited to the growth zone. Data for the run are given in Table XII.

### 3.6 Preliminary Study of Seed Orientation

During the initial contract phase, small runs were made using clear, transparent, spontaneously nucleated, rhombohedral crystals from previous growth runs as a nutrient and seed wafers were cut from "optical reject grade" natural calcite. Seeds of different orientations were tried to determine the effect of orientation on quality and rate of growth. In general, natural seeds cut parallel to the rhombohedral cleavage direction and synthetic calcite seeds consistently exhibited solid overgrowth of new material having high optical clarity. Seeds cut normal to the optic or C - crystallographic axis with [0001] orientation showed spectacular growth parallel to the rhombohedral cleavage directions ( $10\bar{1}1$ ), ( $01\bar{1}1$ ), and ( $1101$ ). However, all the crystals have tended to resemble large

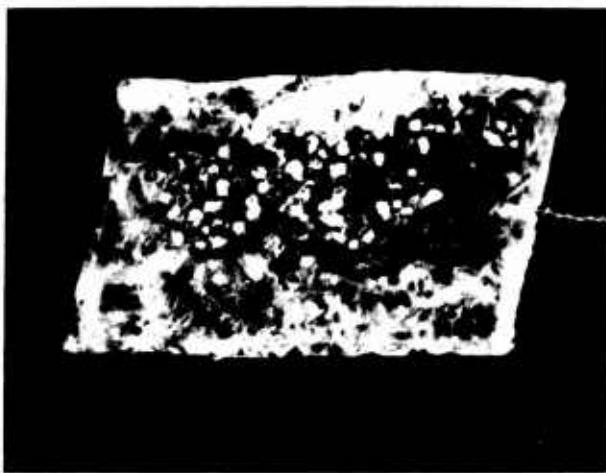


Figure 17      Crystals from Run X-114

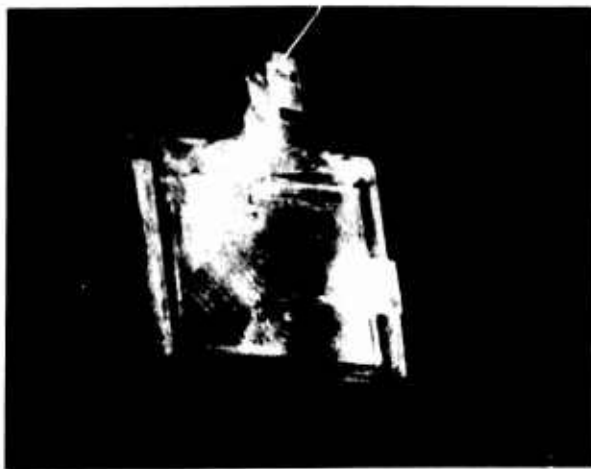


Figure 18      Crystals from Run X-117

Table X

## Results of 3 Inch Hydrothermal Calcite Run X-114

Seed No.	Orientation	Seed Weight Before	Seed Weight After	Seed Weight Gain (%)	Seed Thickness Before	Seed Thickness (In.) After	Growth Rate Mil/day
1A	Cleavage Plane	23.994	49.197	205	0.160	0.267	1.6
1B	S.N.*	0.192	0.969	505	0.080	0.238	2.3
1C	S.N.	0.222	1.290	581	0.111	0.267	2.3
2A	S.N.	0.188	0.879	468	0.108	0.259	2.2
2B	S.N.	0.176	0.754	429	0.069	0.213	3.6
2C	Cleavage Plane	25.057	53.748	214	0.128	0.217	1.3
3A	Cleavage Plane	30.436	60.309	198	0.148	0.225	1.1
3B	S.N.	0.181	1.007	567	0.090	0.204	1.7
3C	S.N.	0.307	0.926	302	0.176	0.270	1.4
4A	S.N.	0.243	1.010	415	0.102	0.251	2.2
4B	S.N.	0.200	1.509	754	0.085	0.208	3.3
4C	Cleavage Plane	21.553	43.792	198	0.150	0.299	2.2

\*Spontaneously nucleated seed

Test Conditions

Test Duration - 838 Hours

Mean Temperature of Top Zone - 382°C

Mean Temperature of Growth Zone - 374°C

Mean Temperature of Nutrient Zone - 395°C

Mean Gradient - 21°C

Mean Pressure - 20,900 psi

External Fill - 82% Internal Fill - 89%

Weight of Nutrient - 125 gms

Table XI

Results of 1.5 Inch Hydrothermal Calcite Run X-117

Seed No.	Orientation	Weight Before After		Weight Gain (%)	Thickness (In.) Before After		Growth Rate Mil./day
1A	Cleavage Plane	3.85	9.28	241	0.125	0.297	2.3
1B	S.N.*	0.133	---**	---**	0.055	---**	---**
2A	S.N.	0.180	---	---	0.093	---	---
2B	S.N.	0.164	---	---	0.085	---	---
2C	Cleavage Plane	2.79	9.96	357	0.098	0.238	1.9
3A	Cleavage Plane	3.55	9.61	271	0.149	0.301	2.0
3B	Cleavage Plane	1.90	5.97	314	0.120	0.296	2.4

\*Spontaneous Nucleated Seed

\*\*Not determined due to spontaneous nucleation on seed wire

Test Conditions

Test Duration - 911 Hours

Mean Gradient - 10°C

Mean Temperature of Top Zone - 346°C

Mean Pressure - 25,300 psi

Mean Temperature of Growth Zone - 343°C

Internal Fill - 94%

Mean Temperature of Nutrient Zone - 353°C

External Fill - 92%

Weight of Nutrient - 215 gms

Table XII

## Results of 1.5 Inch Hydrothermal Calcite Run X-118

Seed No.	Orientation	Weight (g)		Weight Gain (%)	Thickness (In.)		Growth Rate Mil/day
		Before	After		Before	After	
1A	Cleavage Plane	2.777	0.617	---	0.109	0.124	0.2
1B	S.N.*	0.185	0.233	12.6	0.106	0.134	---
1C	S.N.	0.166	---	---	0.107	---	---
2A	S.N.	0.201	---	---	0.117	---	---
2B	S.N.	0.194	---	---	0.113	---	---
2C	Cleavage Plane	3.984	4.114	10.4	0.133	0.139	0.1
3A	Cleavage Plane	3.563	2.928	---	0.145	0.124	---
3B	S.N.	0.225	---	---	0.107	---	---
3C	S.N.	0.244	---	---	0.114	---	---

\*Spontaneously nucleated seed

\*\*Seed dissolved

Test Conditions

Test Duration - 768 Hours

Mean Gradient - 12°C

Mean Temperature of Top Zone - 369°C

Mean Pressure - 24,200 psi

Mean Temperature of Growth Zone - 364°C

Internal Fill - 93%

Mean Temperature of Nutrient Zone - 376°C

Weight of Nutrient - 215 gms

### Small Autoclave Experiments (Continued)

rhombohedral "boxes" due to rapid sheet-like growth in the cleavage directions, with a slower growth rate in the C - direction. We attempted further refinement in the established optimum growth conditions; these included type of nutrient, mineralizer composition, temperature gradient, and rate of transport. Ultimately we hoped that advantage could be taken of this dynamic growth potential since growth rates are often a limiting factor in hydrothermal systems. During the first quarter thirteen hydrothermal calcite runs were made using the 1.5 inch and 3 inch hydrothermal units. The experimental data and results for these runs are presented in Table XIII.

Run CA-2 utilized natural calcite as the nutrient but there was no clear crystal growth evident. However, in run CA-3 where marble was used as the nutrient there was mostly clear growth occurring on the seeds, especially the rhombohedral cleavage orientation. Growth on C-plane seeds was in the form of large skeletal rhombs with box-like growth as in Figure 19. Surfaces of the seed crystal displayed considerable rhomb-stepped (hopper) growth. Marble as the nutrient appeared to have improved overall growth. Growth rates for this run were as high as 5 mils/day. In runs CA-5 and CA-6, a lower growth temperature of 320 - 330°C appeared to improve the quality of growth despite lower growth rates. Also, in these runs less spontaneous nucleation was observed in relation to previous runs. Larger baffle openings at 15 and 20% used in runs CA-7 and CA-8 respectively, did not appear to improve the quality of calcite growth. Mostly hopper growth was seen in CA-7 while in CA-8 the rhomb cleavage seeds showed the largest growth rates as well as the best quality growth of those orientations evaluated. A higher temperature run (CA-11) was conducted at 410°C and resulted in growth on the seeds followed by dissolution.

Three hydrothermal calcite runs were conducted with the 3-inch hydrothermal units and a 7.5% baffle. Natural calcite was used as nutrient in runs CA-1 and CA-4 at growth temperatures of 325 and 360°C respectively. The best growth in CA-1 occurred on rhomb cleavage seeds as in Figure 20. Some transparent growth was evident but hopper growth was again present. C-plane seeds tended to grow very rapidly along cleavage directions, but growth in the C direction was markedly diminished. In the case of run CA-4, seeds on the bottom were dissolving while 85% of the nutrient went to form spontaneous nucleated crystals which covered all seeds. A mixture of 62% marble and 38% natural calcite was used as the nutrient in run CA-9 at a temperature of 320°C. Poor growth resulted from this combination and was probably a direct result of impurities in the marble.

#### 3.7 Temperature of Nutrient

A series of 1.5 inch autoclave experiments (CA-15, 16, 19, 20 and 26 of Table XIII) was run to determine the effect of nutrient temperature on the process. These growth attempts were intended

Table XIII

## Small Autoclave Runs

Run No.	Size (Inch)	Internal/External Fill (%)		Baffle (%)	Temperature (°C)			Pressure (10 <sup>3</sup> psi)	Time (days)	Nutrient	Growth Rate (Mils/day)
		Internal	External		Top	Middle	Bottom				
CA-1	3.0	93	87	7.5	322	325	355	32.0	40	NC	2.2 - 4.3
2	1.5	94	90	10	362	358	368	22.8	19	NC	0.6 - 4.7
3	1.5	94	90	10	360	356	366	26.7	19	M	3.0 - 5.1
4	3.0	90	88	7.5	367	360	389	24.2	35	NC	0.2 - 2.4
5	1.5	95	91	10	333	331	344	26.0	17	NC	1.5 - 2.9
6	1.5	94	90	10	321	322	334	27.0	25	M	2.2 - 3.9
7	1.5	94	90	15	322	327	338	20.0	24	M	1.5 - 4.8
8	1.5	95	91	20	321	323	342	25.0	33	M	0.4 - 1.9
9	3.0	92	86	7.5	336	320	348	23.5	34	M-NC	1.0 - 3.3
10	1.5	94	90	10	346	347	360	25.5	6	SC	0 - 4.0
11	1.5	90	85	10	409	404	412	20.5	20	NC	0.6 - 1.5
12	1.5	90	85	15	416	412	417	15.9	4	M	4 - 4.4
13	1.5	92	88	10	389	389	394	30.6	21	SC	0.4 - 1.9
14	3.0	90	92	7.5	Aborted Run			18.5	23	NC	
15	3.0	89	84	20	430	426	434	18.3	24	SC	Seeds Dissolved
16	1.5	90	85	10	415	417	420	29.0	30	SC	Seeds Dissolved

Table XIII (Continued)

## Small Autoclave Runs

Run No.	Size (Inch)	Internal/External Fill (%)		Baffle (%)	Temperature (°C)			Pressure (10 <sup>3</sup> psi)	Time (days)	Nutrient	Growth Rate (Mils/day)
		Internal	External		Top	Middle	Bottom				
CA-17	3.0	92	94	7.5	380	382	400	16.0	1	NC	Aborted Run
18	3.0	92	86	7.5	330	323	353	21.4	21	M	3.0 - 5.7
19	1.5	95	91	10	320	325	340	24	29	NC	1.0 - 1.4
20	1.5	94	89	10	375	370	380	26	18	NC	0.9 - 3.0
21	1.5	91	86	10	Aborted Run					NC	
22	1.5	95	91	10	297	302	318	27	11	NC	0.4 - 0.8
23	3.0	95	97	7.5	273	277	308	29	11	NC	1.6 - 2.45
24	3.0	90	84	7.5	348	342	373	19.8	14	M	1.5 - 2.5
25		N E V E R     R U N									
26	1.5	94	90	5	338	338	353	29.6	17	NC	0.6 - 1.2
27	1.5	92	88	5	398	392	407	24.4	13	NC	1.9
28	3	90	84	7.5	348	350	405	20.0	14	NC	2.2
30	3	90	84	7.5	353	344	374	20.0	14	NC	3.1
31	1.5	94	90	10	358	353	360	29.0	14	NC	2.9
32	3.0	86	82	7.5	460	450	460	26.5	8	NC	4 - 8
33	3.0	86	82	7.5	455	450	455	23.1	8	NC	3 - 5

Table XIII (Continued)

## Small Autoclave Runs

Run No.	Size (Inch)	Internal/External Fill (%)	Baffle (%)	Temperature (°C)		Pressure (10 <sup>3</sup> psi)	Time (days)	Nutrient	Growth Rate (Mils/day)
				Top	Middle Bottom				
CA-34	3.0	87	7.5	445	450	455	25.0	NC	2 - 4
35	3.0	87	7.5	445	450	455	25.0	NC	2 - 4
36	3.0	87	7.5	445	450	455	25.0	NC	2 - 4
37	3.0	87	7.5	443	443	450	21.8	NC	6.0
38	3.0	87	7.5	435	440	450	24.3	NC	--
39	3.0	89	7.5	435	440	450	25.0	NC	3.0
40	1.5	89	10	435	440	450	24.3	P	1.0
41	1.5	89	10	435	440	450	21.8	SN	2 - 4
42	1.5	56	10	656	668	678	20.8	SN	--
43	3.0	88	7.5	412	415	425	25.0	NC	1 - 2
44	1.5	91.5	7.5	420	430	450	23.5	P	.1 - 1.42
45	1.5	86	7.5	417	455	500	22.0	P	--
46	1.5	90	7.5	430	425	450	21.5	NC	3 - 6
47	1.5	89	7.5	432	437	450	21.2	NC	1.0



Figure 19      Hopper Type Growth Along  
Cleavage Planes, Run CA-1



Figure 20      Good Growth of Calcite on  
Seed, Run CA-1

### Small Autoclave Experiments (Continued)

to be run with pressure, nutrient temperature differential, and mineralizer composition held constant. The bottom or nutrient temperature ranged from 340 to 435°C at an average  $\Delta T$  of about 10°C between the nutrient and seeds. Growth rates were measured on the cleavage faces and were generally found to increase with the higher nutrient temperature even though two of the runs at the high temperature were troubled with seal problems. Runs CA-27 to CA-31 were made at nutrient temperatures of 350 - 400°C. These showed that nominal growth rates of 50 - 75  $\mu\text{m}/\text{day}$  could be attained on cleavage faces. Two more hydrothermal growth experiments designated CA-32 and CA-33 were run at temperatures higher than those used before. Growth was carried out in 3.0 inch autoclaves with the seed section of the autoclave held at 450°C and the nutrient section maintained at 10 and 5°C higher, respectively. The data obtained from these runs are given in Table XIII. The rapid growth rates of run CA-32 are of note. Unfortunately, this achievement in rate appeared to be at the expense of growth quality.

The morphology of the growth on the major faces of cleavage {1101} rhomb seeds was also of interest. As shown in Figure 21 growth ledges on these surfaces were parallel to the other cleavage planes and the steps without exception faced away from the adjacent trigonal coigns of the rhomb. The effect was that of scales that felt rough when one's finger was moved diagonally across the face toward the trigonal coign and smooth when moved in the opposite direction. The basal planes {0001} undoubtedly played a central role in the growth process. This situation is to be expected because of the strong electrostatic field that is present at {0001} surfaces resulting from the alternate stacking of cation and anion layers in this direction. (This should not be confused with the electric effects observed in materials having non-centro symmetric or polar structures.)

An attempt was made in Run CA-33 to find a growth surface that would compromise the stability of the r form<sup>34</sup> (as evidenced by its growth from spontaneous nucleation) and the activity of the basal plane. Four seeds having e-faces were placed on different rungs of the seed ladder in the three-inch autoclave. As shown in Figure 22 (a) growth on these surfaces was not smooth under these conditions; corrugated facets developed parallel to the adjacent r-planes. Reference to the stereogram of Figure 22 (b) showed that this is a natural consequence of symmetry and the stability of the r-form. It follows from symmetry that the appearance of each of the r-faces is equally probable on c-plane surfaces. This has indeed been observed in earlier runs, as illustrated in Figure 23.

Figure 24 indicates the type of growth observed on other seeds having e-form major faces. The crystal shown was grown from a seed plate which had major faces of the e-form and minor faces of r-form. While the e-surface became faceted, as described above, rapid edgewise growth parallel to the complementary r-plane occurred at the intersection of these two planes. Had the run been of longer

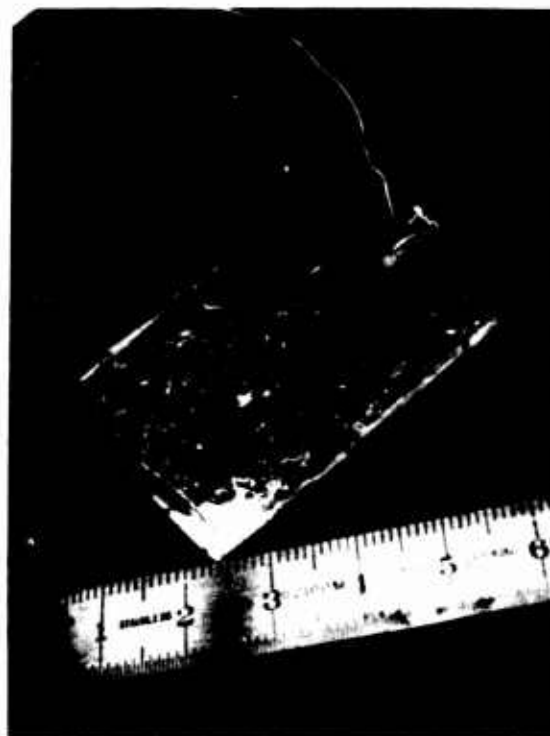
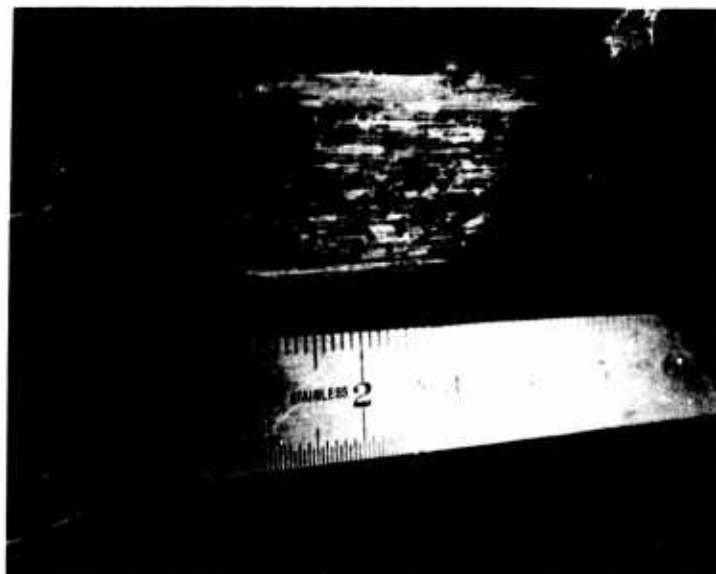
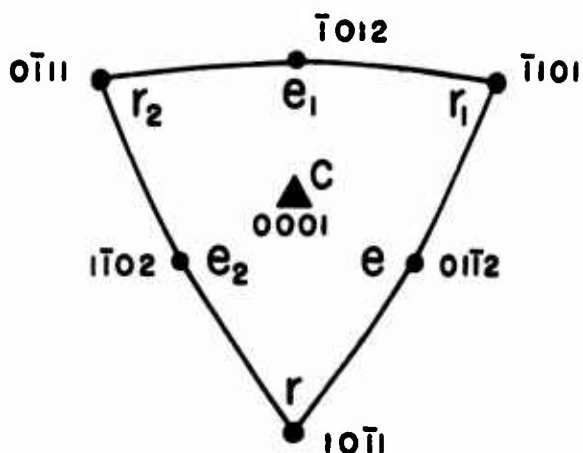


Figure 21      Growth on cleavage rhomb (r-form) seed  
showing ledges oriented with respect to  
the triad. The trigonal coign is upper-  
most.



(a)



(b)

Figure 22 (a) Growth on  $e_1$  faces bounded by  $r$ 's. Note symmetry of corrugations. Ledges are parallel to  $r_1$  and  $r_2$ . Note also the edgewise growth of  $r$ , the complementary cleavage face.

(b) Stereographic projection of the calcite lattice near the triad.

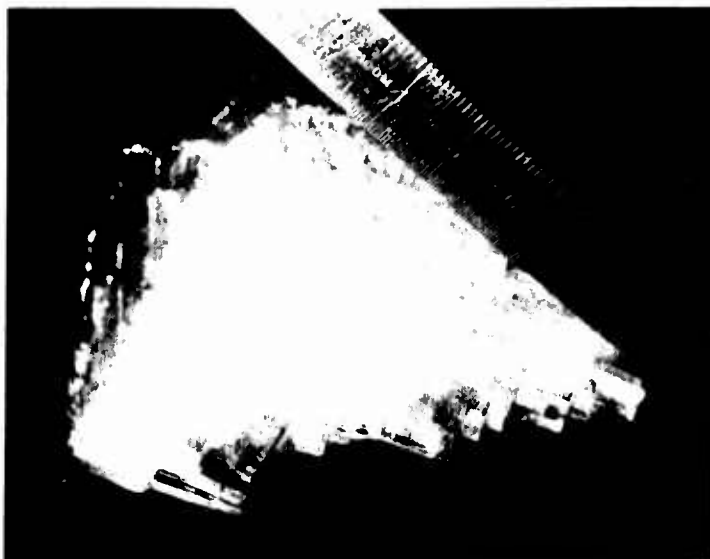


Figure 23 Growth on (0001) showing 3-fold symmetry of instabilities. Facets are r-form.

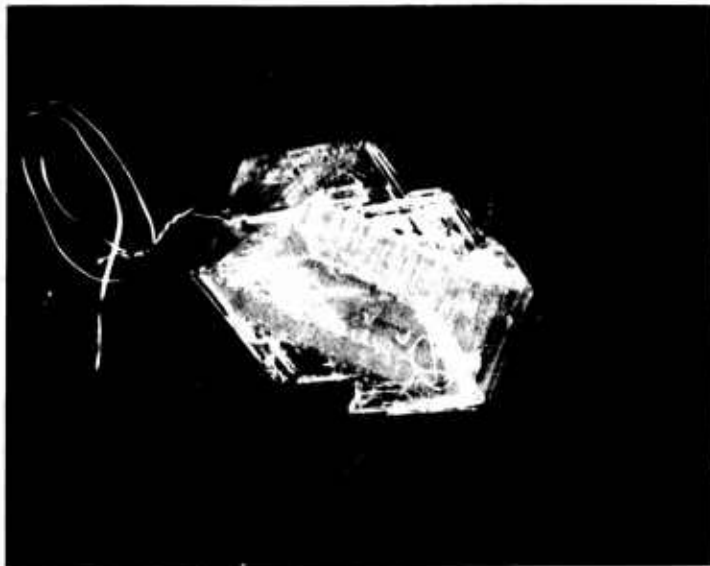


Figure 24 Growth on  $\{1012\}$  bounded by  $\{1101\}$ . Note rapid edgewise extension (and its preferred direction) of complementary r-face.

### Small Autoclave Experiments (Continued)

duration, a capped r-form would have been completed. As shown in Figure 24, edgewise growth on the adjacent r faces propagated in only one direction.

Earlier runs had indicated that growth at 450°C proceeded at relatively high rates when driven by a seed-to-nutrient temperature difference as low as 10°C. To confirm these and other observations, Runs CA-34 to CA-36 were made at 25,000 psi in 6 m  $K_2CO_3$  with the seeds held at 450°C and the nutrient at 455°C. Cleavage rhombs (r-form) and seeds having the e-form faces were also used. Equidimensional rhombs and rhombs having two equal sides and one of longer length were included to test for an aspect ratio effect. The data obtained in this run are summarized in Table XIII.

The growth rates were comparable with those of the earlier runs CA-32 and CA-33. The appearance of the deposits on the large plate cleavage rhombs were also similar. Figure 25 indicates the effect of the aspect ratio on the growth. The two seeds shown in the figure were placed on the same level in the autoclave and were of the same r-form yet the morphology of the deposited material was quite different. The slender seed at the right exhibited a surface that was almost optimum. Small amplitude perturbations of long wavelengths are observed on the surface. These irregularities are well rounded and are, by analogy to quartz growth, associated with high quality deposited material. The plate seed shown at the left in Figure 25, on the other hand, shows the ledges, steps, and scales that are typical for deposits on these forms.

The effect of temperature on the solubility of the transported species was central to the hydrothermal process. The nutrient/seed temperature difference, the average system temperature and the growth rate are interrelated through changes in solubility with temperature. All early studies of calcite solubility in 6 m  $K_2CO_3$  as a function of temperature at constant pressure indicated steadily increasing solubility with temperature. Run CA-42 was performed to investigate the potential of growth at temperatures somewhat higher than the norm for this work. It was reasoned that increased growth rates and growth quality might be achieved at higher temperatures. The conditions shown for this run in Table XIII were nominal except that the overall system temperature was 225°C higher. Although seed dissolution was experienced during the heat-up of this run, the morphology of growth was quite similar to that produced at lower temperatures.

Runs CA-46 and 47 were made to produce our best state of the art calcite in small autoclaves. Nominal conditions were used with low gradients being applied. The results of these runs are shown in Figure 26. These runs completed our work in the small autoclaves, since the conditions represented the upper limits attainable in our 9 inch diameter systems. By way of summary, these data showed that



Figure 25      Calcite seeds of different aspect ratio grown at the same level in the autoclave. The seed on the left is thin and shows ledge-flawed growth typical to this shape. The thickness of seed on the right is equal to its width. Note the absence of ledges.

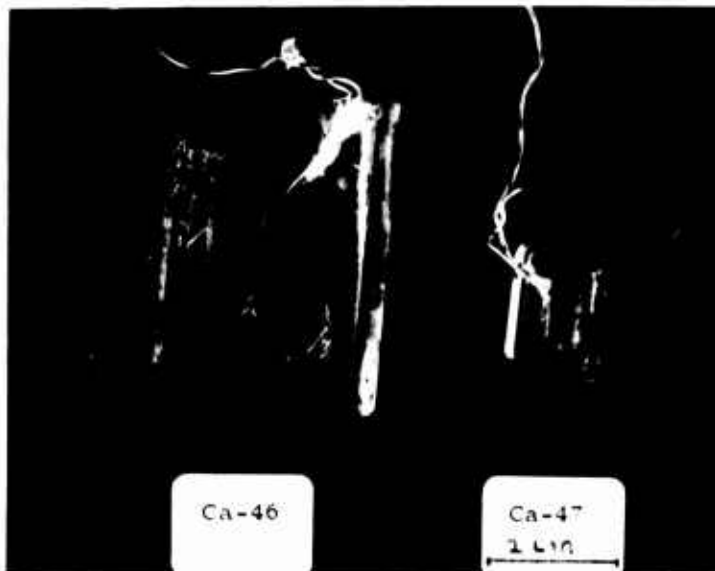


Figure 26 Hydrothermal calcite grown under low gradient conditions. The clarity of the grown material indicates current hydrothermal capability.

### Small Autoclave Experiments (Continued)

equidimensional rhombs of calcite seeds are preferred. Growth conditions were standardized at nutrient temperatures of 400 - 450°C, thermal gradients of 10 - 20°C between seeds and nutrients, and expected growth rates of 50 - 100  $\mu\text{m}/\text{day}$ .

#### 3.8 $\text{Li}_2\text{CO}_3$ Additives to Nutrient

The use of lithium as an added agent in the mineralizer was suggested by its role in the hydrothermal growth of  $\alpha$ -quartz<sup>35-36</sup>. Infra-red spectroscopy studies have shown for quartz that lithium additions to the mineralizer are effective in reducing the incorporation of hydroxyl ions in that material and thus increasing the Q. The role of mineralizer additives as they affect the growth habit of calcite material was clearly indicated as an area for examination since small amounts of  $\text{OH}^-$  are incorporated in calcite also. It was also thought that Li could be directly substituted for Ca in regard to ionic size even though some charge compensation scheme would have to be operative. The first test run in which  $\text{Li}_2\text{CO}_3$  was added to the mineralizer was CA-22 reported in Table XIII. This experiment was carried out in a mineralizer solution of 6 m  $\text{K}_2\text{CO}_3$  and 1.5 m  $\text{Li}_2\text{CO}_3$ . The results were much lower C-plane growth rates on natural calcite seeds. This was of note because C-plane growth in absence of  $\text{Li}_2\text{CO}_3$  had been shown to be faceted with  $\{10\bar{1}1\}$  surfaces forming in favor of the fast growing  $\{0001\}$  faces. The spontaneous nucleation in this run came out not as r-form rhombs but as thin c-form plates.

Based on the above observations, we pursued a series of runs that indicated the effect of lithium carbonate additions to the mineralizer on the growth morphology of several crystallographic faces. Three runs were performed CA-37, CA-38, and CA-39. The first two of these runs were made without Li while the latter contained  $\text{Li}_2\text{CO}_3$ . The autoclave conditions are given in Table XIII. The planes sampled for study are shown in Figure 27. They lie on the  $[1\bar{2}10]$  zone which includes one of the rhombohedral faces and the basal plane.

Natural cleavage rhombs were oriented and cut on a diamond saw to give slices having faces normal to the directions shown in the stereogram of Figure 27. These were then used as seeds in two growth runs with conditions similar to those in use of cleavage rhomb growth. The mineralizer was 6 m  $\text{K}_2\text{CO}_3$ . The orientations of the seeds of the two runs fall into two series. The poles of the seed surfaces of run CA-37 lie about  $[10\bar{1}0]$  and hence these surfaces were nearly perpendicular to  $(0001)$ , the basal plane. The poles of the surfaces used in run CA-38, on the other hand, lie on the same zone but spread between the  $[10\bar{1}1, r]$  and its complement, the  $[\bar{1}012, e]$ . These latter surfaces are nearly parallel to the basal plane. The development of faceting on the seeds of CA-37 was varied and depended on their orientation. Some of these showed a tendency to develop facets relating to  $e_1$ ,  $r_3$  and  $r_2$ . These are the two ( $S_1$  and  $S_2$ ) that lie at the end of the series nearest to  $e_1$ . The middle two ( $S_3$  and  $S_4$ ) were different. The

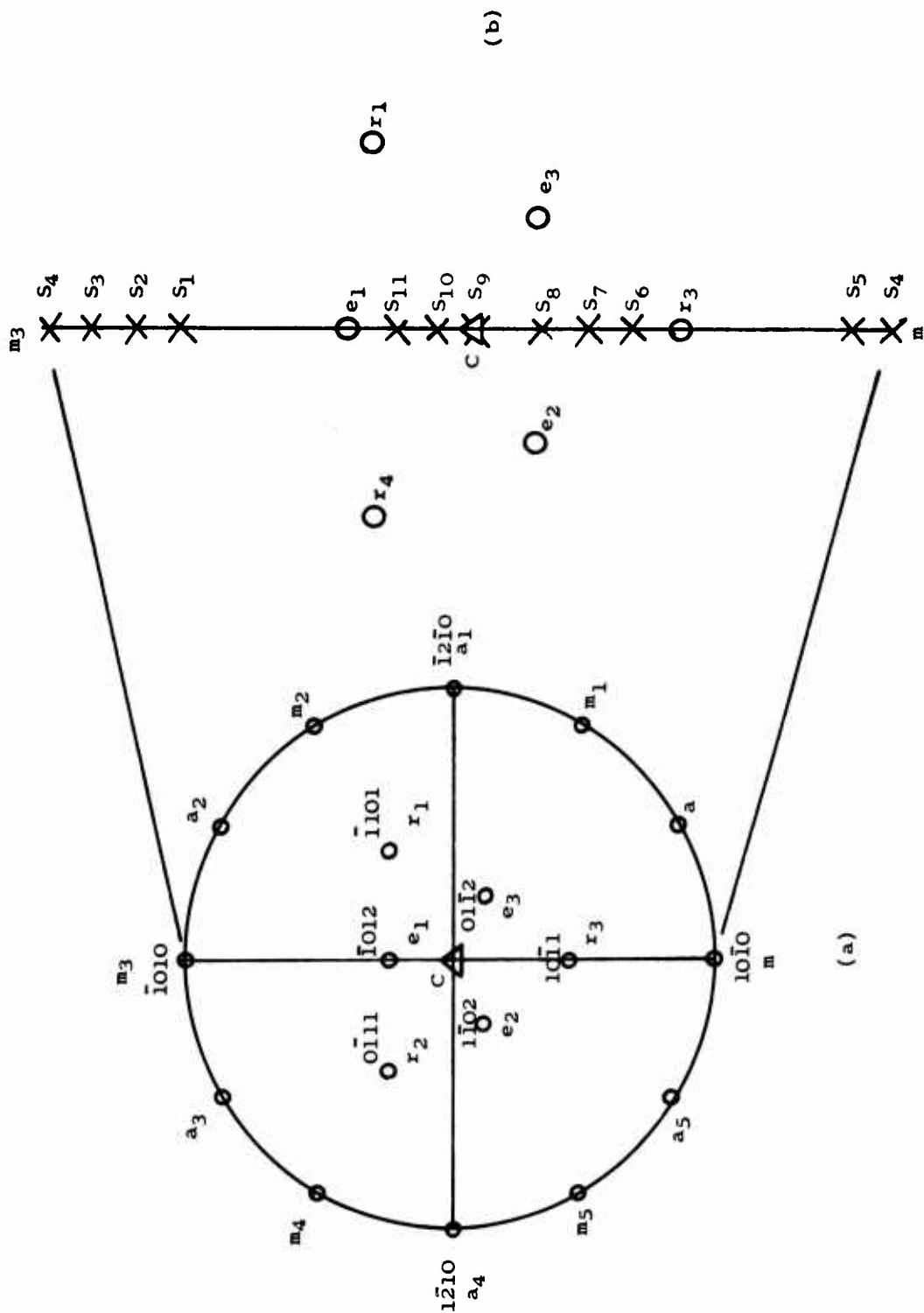


Figure 27 Seed orientations used in calcite runs CA-37 and CA-38.  
 (a) Stereographic projection on (0001)  
 (b) Seed surface normals  $S_n$  along  $[1210]$  zone

### Small Autoclave Experiments (Continued)

stable facet on  $S_3$  appeared to be  $e_1$  with some platelets of  $r$ , bounded on the thin side by  $r_3$  and  $r_2$  breaking out of the surface. This showed that as the orientation of the seed surface approached the horizon at  $m$ , the stable face moved from the pair of  $r$ 's to  $e_1$ .  $S_4$  which is very close to  $m$  appeared to be stable as it was cut. The third pair of this series lie below the horizon and are plotted in the lower half of the stereogram. These were approaching  $r$  and showed facets of this plane. Representative photographs of these seeds are shown in Figure 28 and 29.

The seeds of the second series from CA-38 displayed again the strong preference of this system for the  $r$ -form. Figures 30 and 31 showed this. Each of the facets without exception were rhomb faces. While a direct comparison between these two runs was made tenuous by the premature termination of CA-37 (autoclave failure), the runs do establish the difference between the two series.

The ease with which calcite formed  $r$ -form caps over non-rhomb surfaces was described before. However, growth on seed  $S_{10}$  of the second series showed the speed at which this can take place. The growth rates in certain directions on this sample were as high as 1 mm per day, almost 200 times as fast as  $r$ -face growth! This capped rhomb is shown in Figure 32. The implication was clear that if the growth rate shown in capping could be utilized, the growth of calcite might be economical and rapid.

The third experimental run of this series was CA-39. It showed the marked effect of lithium additions to the potassium carbonate mineralizer. Faces parallel to the crystallographic basal plane became stable on some of the seeds. Others showed  $r$ -type faces and the familiar  $r$ -forms. The results are summarized in Figures 33 through 39. While most of these are interesting from a theoretical viewpoint, several facts were of immediate practical significance. Growth rates using  $Li_2CO_3$  additives were not different from those using only  $K_2CO_3$ . Thus the rate is still controlled by the autoclave variables. Morphology changes may be helpful to grow orientations that require a specific direction of the optic axis in relation to polarizer use.

### 3.9 Nutrient Form

While undertaking the development of a satisfactory method for pure nutrient preparation, small autoclave experiments using pure calcite powder as nutrient were run to indicate the quality of material that can be expected. Run CA-40 was performed with this objective. The very low surface growth rate of  $10 \mu \cdot \text{day}^{-1}$  indicated that the reduced nutrient surface area of the powder limits the process under these conditions. However examination of the grown calcite confirmed the improved optical quality of this material. The thin layer appeared to the eye to be without color, scattering sites, cracks,

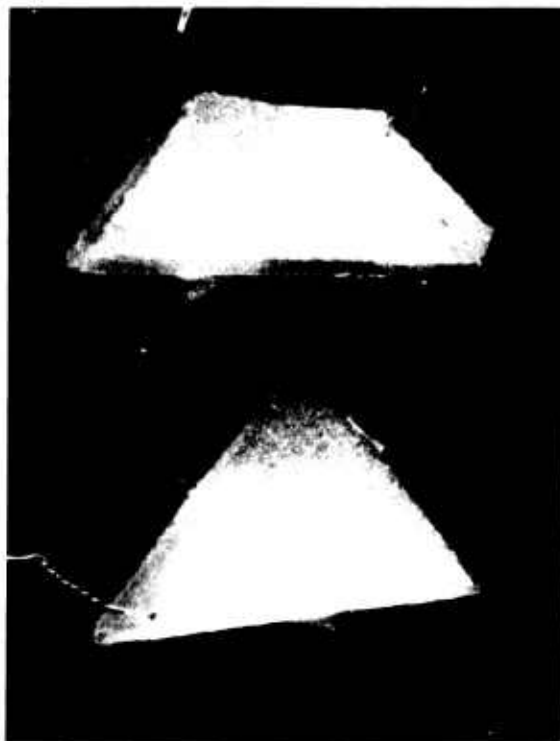


Figure 28 Hydrothermal growth on calcite seeds  
S<sub>1</sub> and S<sub>2</sub> (upper) from Run CA-37.



Figure 29 Hydrothermal growth on seeds  $S_4$  and  $S_5$  (upper) from Run CA-37.



Figure 30 Hydrothermal growth on calcite seeds  
S<sub>6</sub> and S<sub>7</sub> (upper) from Run CA-38.



Figure 31 Hydrothermal growth on calcite seeds  
S<sub>8</sub> and S<sub>9</sub> (upper) from Run CA-38.

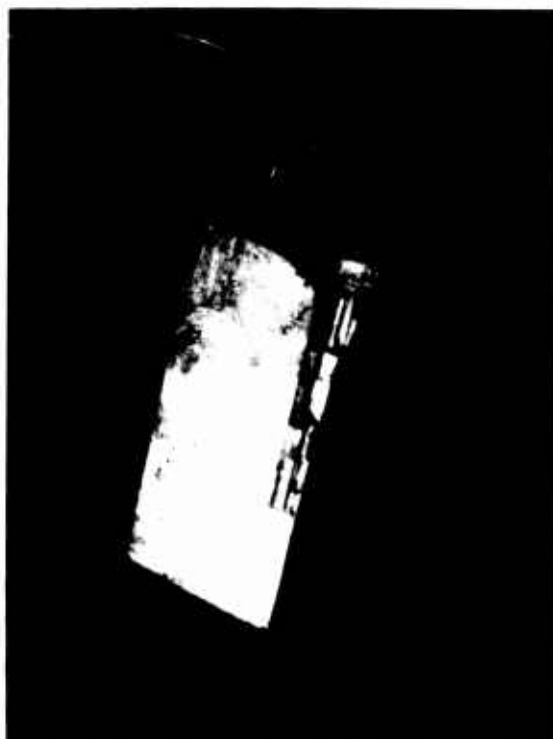


Figure 32 Hydrothermal growth on seed  $S_{11}$  (Run CA-38). The r-form surfaces are hollow caps that have grown over a thin plate having  $S_{11}$  major faces.



Figure 33 The effect of lithium mineralizer additions on growth on c-form faces. Inclusion of lithium in system produces smooth growth (left) on (0001) faces. Growth without lithium (right) is faceted with rhomb faces.

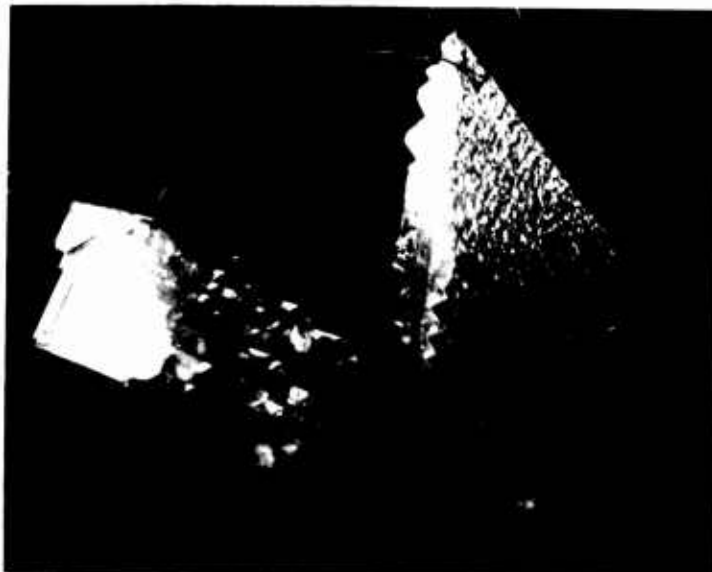


Figure 34 Calcite growth on orientation  $S_1$  (Ref. Figure 27) with lithium mineralizer additions (left) and without (right).

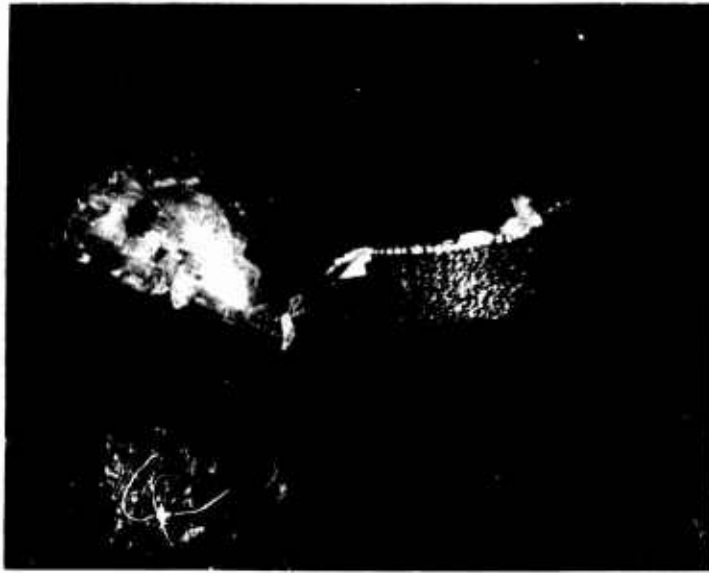


Figure 35     Calcite growth on orientation  $S_3$  (Ref. Figure 27) with lithium mineralizer additions (left) and without (right).

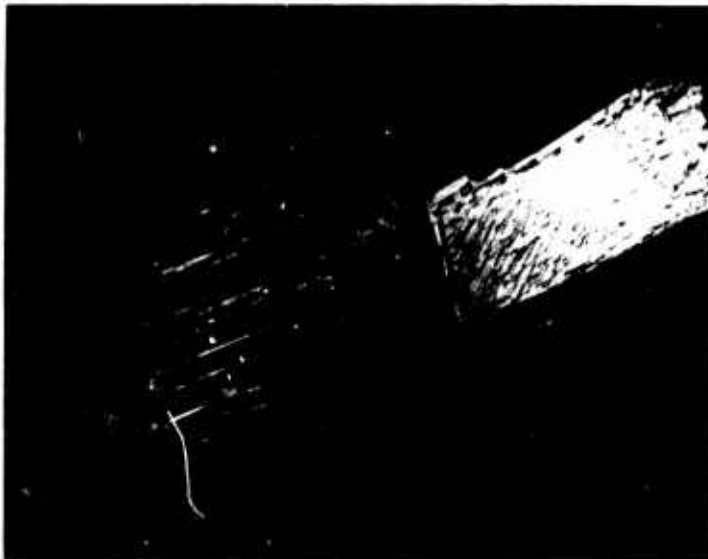


Figure 36     Calcite growth on orientation  $S_5$  (Ref. Figure 27) with lithium mineralizer additions (left) and without (right).

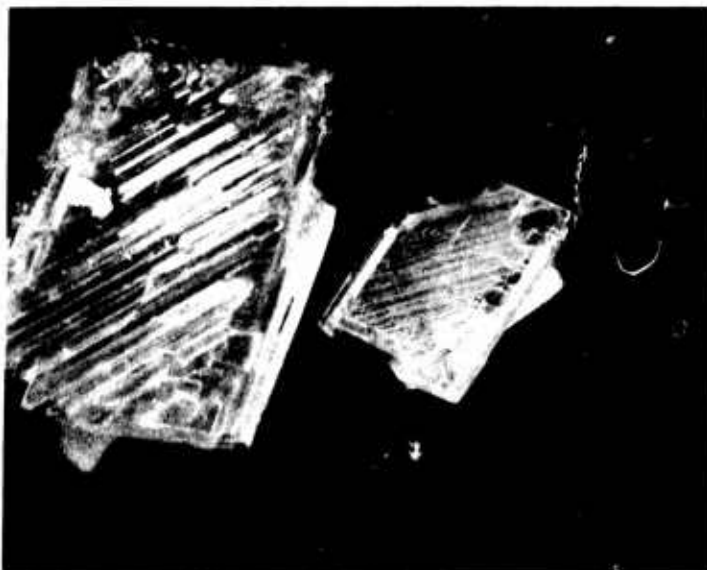


Figure 37      Calcite growth on orientation  $S_0$  (Ref. Figure 27) with lithium mineralizer additions (left) and without (right).

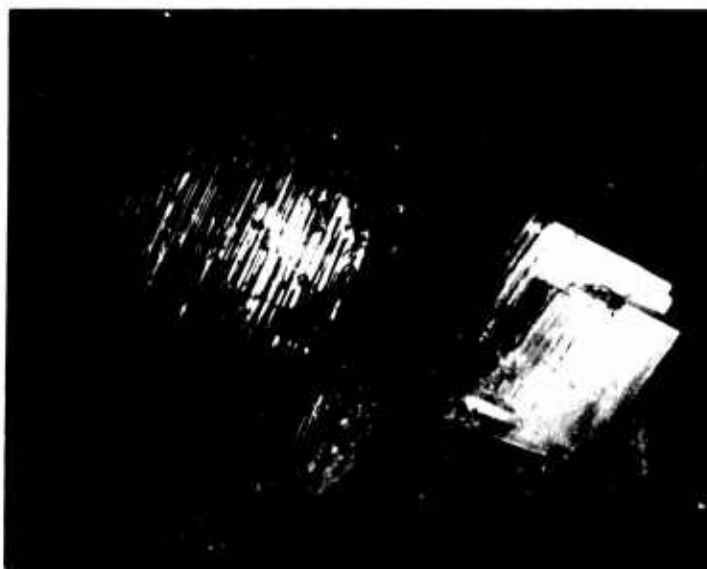


Figure 38      Calcite growth on orientation  $S_7$  (Ref. Figure 27) with lithium mineralizer additions (left) and without (right).



Figure 39    Calcite growth on orientation S9 (Ref. Figure 27) with lithium mineralizer additions (left) and without (right).

## Small Autoclave Experiments (Continued)

or other defects. Run CA-45 was made under a higher nutrient temperature and gradient with a large increase in rate.

In the event that natural calcite had to be used as nutrient material, it is quite possible that purification by recrystallization (in the chemist's sense) may be useful as described in Section 2.3. Run CA-41 was made using standard conditions except that the nutrient source was spontaneous nucleation from earlier runs. This experiment suggested that partially recrystallized natural calcite would be quite satisfactory provided the initial chemical analysis is uniform.

### 4.0 LARGE AUTOCLAVE PROGRAM

#### 4.1 Purpose and Goals

Under the original production schedule this portion of the program commenced nearly one year after contract initiation. The purpose of the time lag was to allow full consideration of autoclave and associated structural design to be accomplished. Furthermore nearly six months were allotted for autoclave alloy preparation, fabrication, and full testing of components before delivery to Airtron.

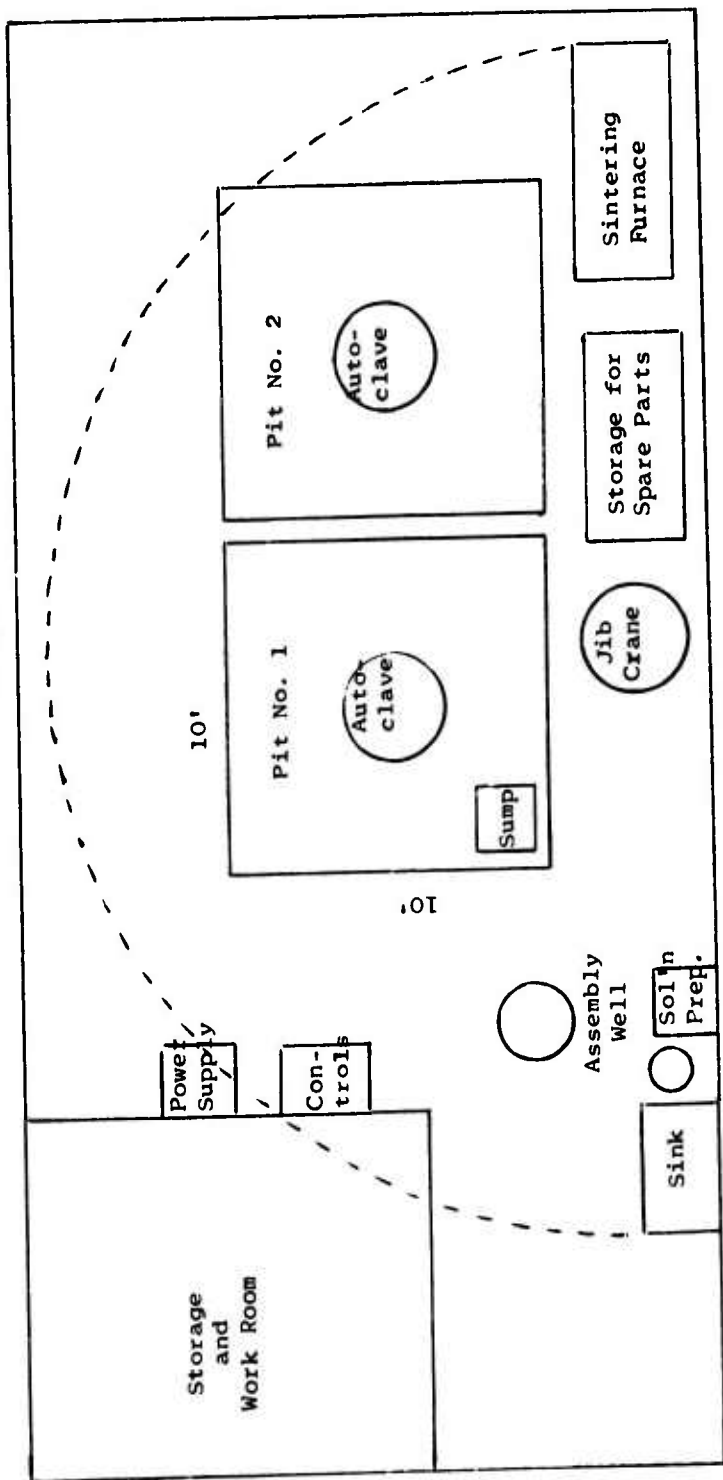
Deliveries of state of the art crystals of calcite were to occur at four month intervals and consisted of 20 lbs each of grown material. Established growth rates of 75 - 125  $\mu\text{m/day}$  were easily achieved in the small autoclaves. Assuming a similar rate in the large systems, we estimated that a full production run would take nearly 100 days of growth and yield from 40 - 100 lbs of crystals if a full complement of seeds were utilized. Seed crystals of high quality were intended to be provided from 3 inch autoclave runs. As the 9 inch systems were brought into service more seeds could be produced from natural sources, and finally the process could be self sustaining.

Two major problems prevented a rigid adherence to our program schedule. One of these was a strike of several months at the autoclave manufacturer. The other was an internal difficulty of operating autoclaves with metal liners. The latter is more fully discussed in Section 4.7 and was solved within a few months.

#### 4.2 Description of Laboratory

For large autoclave growth runs, a new laboratory was constructed in the main factory area. The laboratory measured 43.5 x 21.5 feet. The floor plan and arrangement of equipment are shown in Figure 40. In this room are two adjoining 10 x 10 x 11 feet deep pits in which the 9 inch diameter autoclaves are housed. A steel grating covers the pits and provides access to the autoclaves for operational activities at floor level. Removable panels and ladders permit access to the autoclaves for any work to be performed in the pits.

43-1/2'



Scale: 1" = 5'

Figure 40 Laboratory Floor Plan Showing Arrangement of Equipment

## Large Autoclave Program (Continued)

In addition to the autoclaves, the room contains the necessary power supply and temperature control monitoring equipment. A base-mounted jib crane<sup>37</sup> with electric hoist was installed at the edge of the pit area and was used for loading and unloading the autoclaves. The location of the crane with respect to the pit area is illustrated in Figures 40 and 41. To facilitate charging the silver can liners with seeds and nutrient, removal of crystals at the end of the run, and the usual maintenance operations, a 1 foot diameter x 6 feet deep work well was set in the floor adjacent to the pit area. The solution preparation area included a mixing tank, sinks, wash tank, platform scales, and a disposal system for the spent mineralizer solution. The largest version of our pressure sintering vessel was located in a corner of the room within reach of the jib crane. Provision was made for several storage areas to stock additional vessels and spare parts. An enclosed area has been constructed as a work room for seed rack assembly, record keeping and clean storage of chemicals. An early view of the laboratory is given in Figure 42.

### 4.3 Autoclave Design and Construction

Two large autoclaves were used in the crystal growth program and were manufactured at an experienced company<sup>38</sup>. Except for a two month strike the production timing schedule of Table XIV projected by the manufacturer was adhered to. General design details are shown in Figure 43. Autoclaves were fabricated of Ni-Cr-Mo alloy steel<sup>39</sup> and were designed for operation at 850°F (450°C) and 25000 psi. The closure of the vessels is of the modified Bridgman type. The inside growth chamber is 9 feet long with an inside diameter of 9 inches. The overall length is 11 feet with an outside diameter of 18.5 inches.

The autoclaves were positioned on steel and insulating brick supports in the 10 x 10 x 11 feet deep pits for operational and safety reasons. They were not moved from their positions in the normal course of the crystal growth program. Handling of closure assemblies as well as the autoclave liners was by means of the crane hoist. Side bracing was also employed in addition to a bolted-on bottom plate to insure positional stability of the autoclaves. The top of the autoclave contains a metal leak deflector in event of a seal failure and loss of hot steam. Figure 44 shows one autoclave with the deflector in position. Figure 45 shows the autoclave with deflector removed but with insulating jackets surrounding the body. Figure 46 is a picture of the autoclave with band heaters in place and half the insulation jacket removed. The top sealing nut is also removed.

### 4.4 Heaters and Control System

The autoclaves were heated by means of electric resistance band heaters<sup>27</sup> clamped around the outside of the vessels at spaced intervals along the length of the vessels. There was provision for 15 band heaters in the lower or nutrient zone, and 9 band

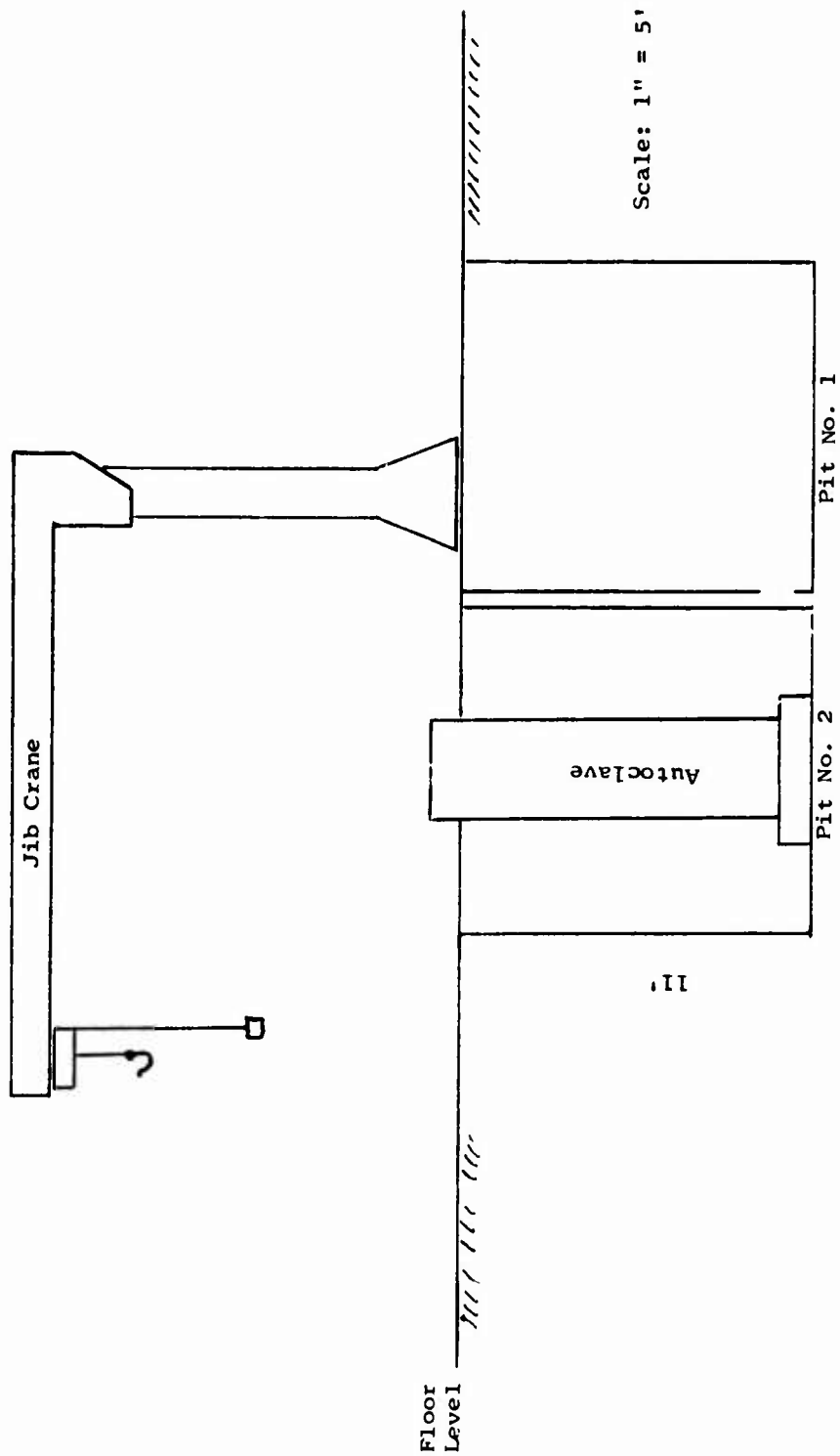


Figure 41 Longitudinal Cross Section of Pit Area

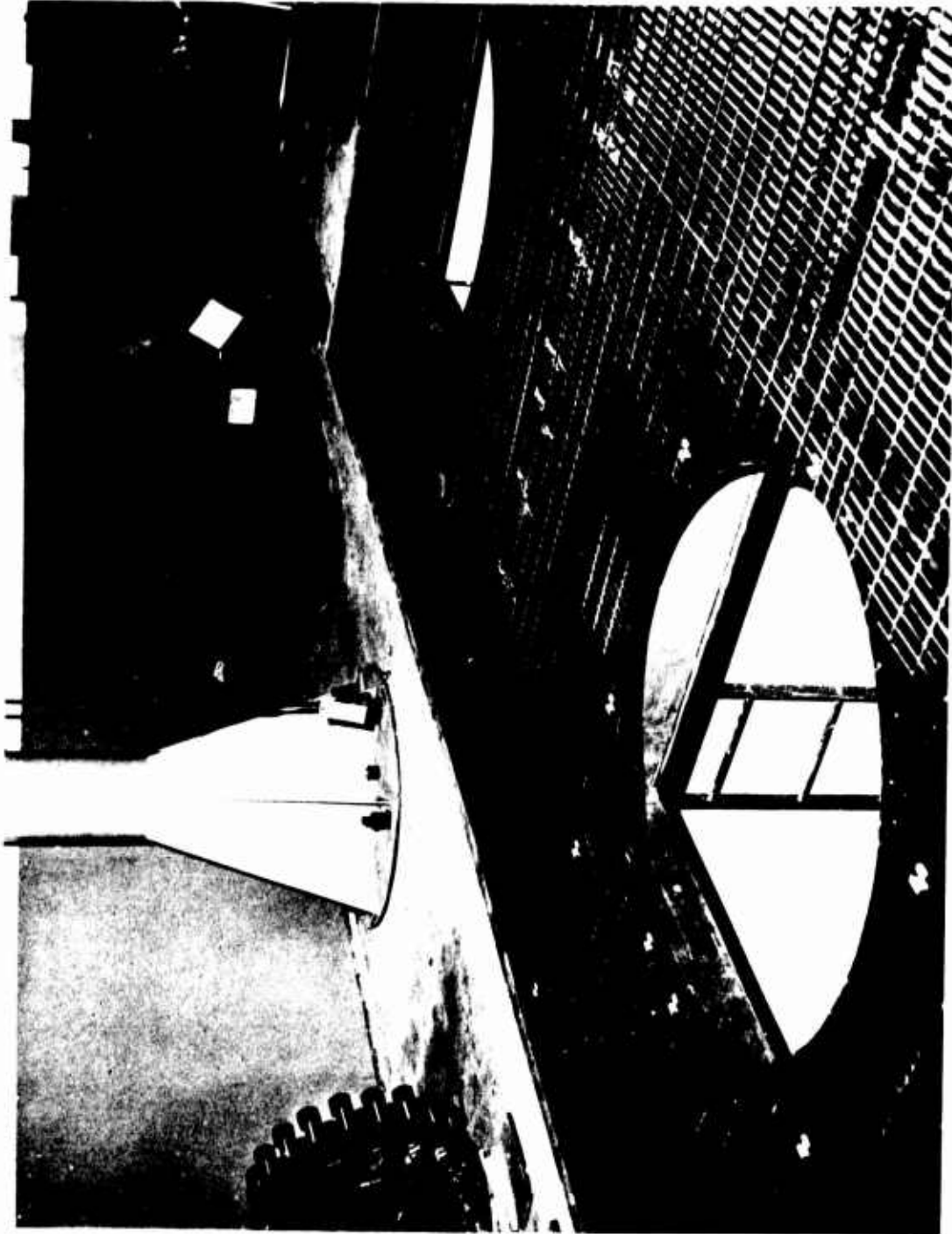


Figure 42 Completed pits for large autoclaves

Table XIV  
Large Autoclave Fabrication Schedule

<u>Item</u>	<u>Weeks</u>
Engineering and Planning	4
Melt and Forge	4
Receive Technical Information	1
Post Forge Heat Treatment of Vessel	2
Rough Machine Vessel Components	2
Heat Treat and Test Vessel Components	2
Finish Machine Vessel Components	2
Layout Temperature Controllers	1
Receive Two (2) Sets of Heaters	1
Assemble and Hydro-test Vessel No. 1	1
Assemble and Hydro-test Vessel No. 2	1
Dissassemble and Inspect Vessls After Hydro-test	1
Assemble Heatersand Insulation	1
Performance Test	2
Disassemble and Inspect Vessel No. 1	1
Disassemble and Inspect Vessel No. 2	1
Ship Vessel No. 1	2
Ship Vessel No. 2	2
Ship Spare Cover	1
	<hr/>
Total	32

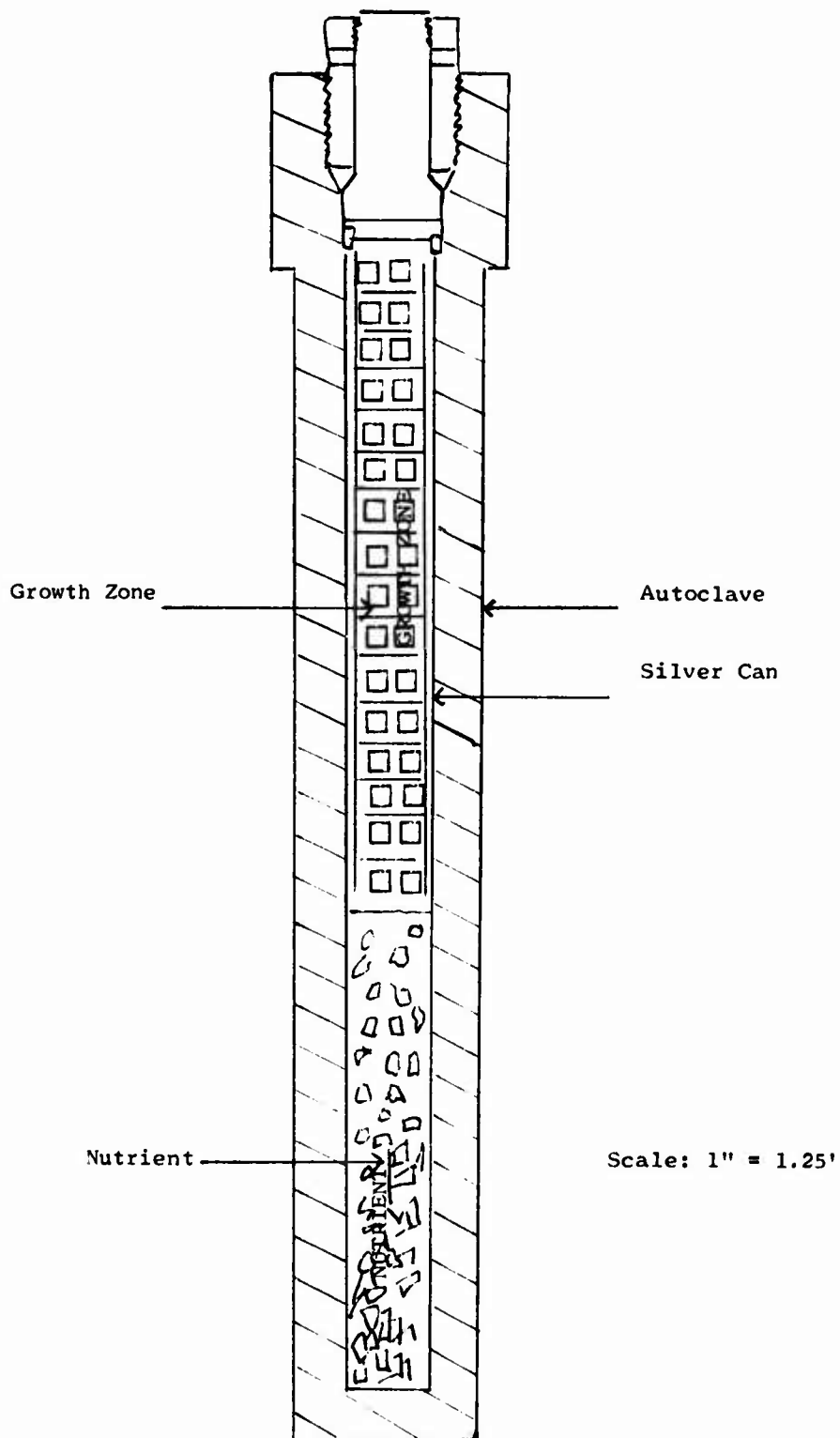


Figure 43

Nine-inch I.D. Autoclave with Silver Can in Position

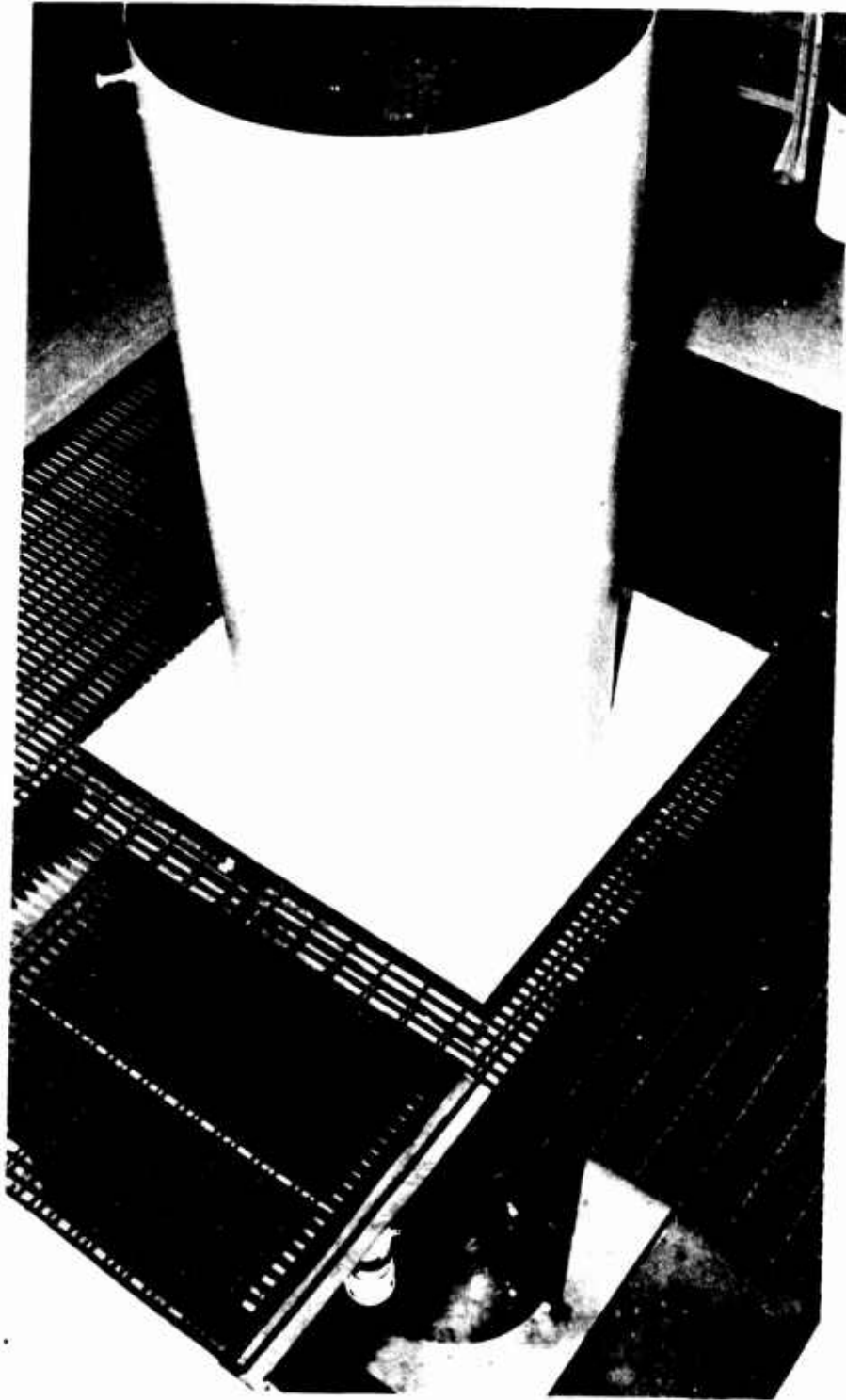


Figure 44 Nine-Inch Autoclave Installation



Figure 45 Nine-Inch Autoclave Installation - Leak Deflector Removed.



Figure 46 Nine-Inch Autoclave Installation -  
Insulation Jackets Removed.

### Large Autoclave Program (Continued)

heaters in the growth zone. There were also 3 larger diameter band heaters strapped to the very top of the system which included the silver lid. The advantage of such a heater system is that a whole range of thermal gradients can be obtained by positioning the band heaters along the length of the autoclave. Within each of the nutrient and growth zones the desired temperature can be adjusted to arrive at the optimum  $\Delta T$  between the two zones for desirable hydrothermal growth of calcite. The vessels were completely surrounded by an insulating jacket mounted in removable sections for easy access to the heating elements.

The temperature control system consisted of three units per autoclave. One unit controlled the temperature of the lower portion of the vessel in which solution of the source or nutrient material takes place. The second unit controlled the temperature of the upper portion of the vessel in which crystal growth takes place. The third unit controlled the very top to prevent extensive spontaneous nucleation. Functionally, temperature control was accomplished by interaction of low-level signals generated by chromel/alumel thermocouples positioned at key points on the autoclave and proportional band digital set-point controllers. Current output to the heaters was increased, decreased or held constant according to the relationship between the thermocouple input to the controller and set point.

The actual control units consisted of Bruce<sup>40</sup> Series 550 Master-Slave Overtemperature Module Controllers with digital set point, proportional reset, and thermocouples. The units included overtemperature failsafe protection units with audible alarm and signal deviation lights. Bruce Model 350 zero crossover forming SCR power controllers with voltage feedback and current limits were also incorporated. The system also included pressure sensors and recorders with appropriate interlocks to the power source. The completed rack system is shown in Figure 47. The power and controls were chosen with a design limit of  $\pm 0.5^\circ\text{C}$  stability over an operating period of 2 - 3 month runs. In actual practice few difficulties were encountered except for burned out heating elements. However, these could be easily replaced and one or two failures during a run did not significantly affect the zone temperature or gradients.

#### 4.5 Silver Can Liners and Equipment Fabrication

Because of the corrosive nature of the  $\text{K}_2\text{CO}_3$  mineralizer solutions, calcite cannot be grown in the steel vessel cavity as is the usual practice in the growth of cultured quartz. It is necessary that the reacting system be isolated from the autoclave by means of a noble metal chamber insert or "can". We have designed a flanged silver can held within a stainless steel jacket for support rigidity. Preliminary design details are shown in Figure 48. After the can is loaded with the nutrient, mineralizer solution, and rack of seed crystals, it is sealed by means of a flexible silver lid and lowered



Figure 47      Instrumentation and power  
supplies for production  
autoclaves.

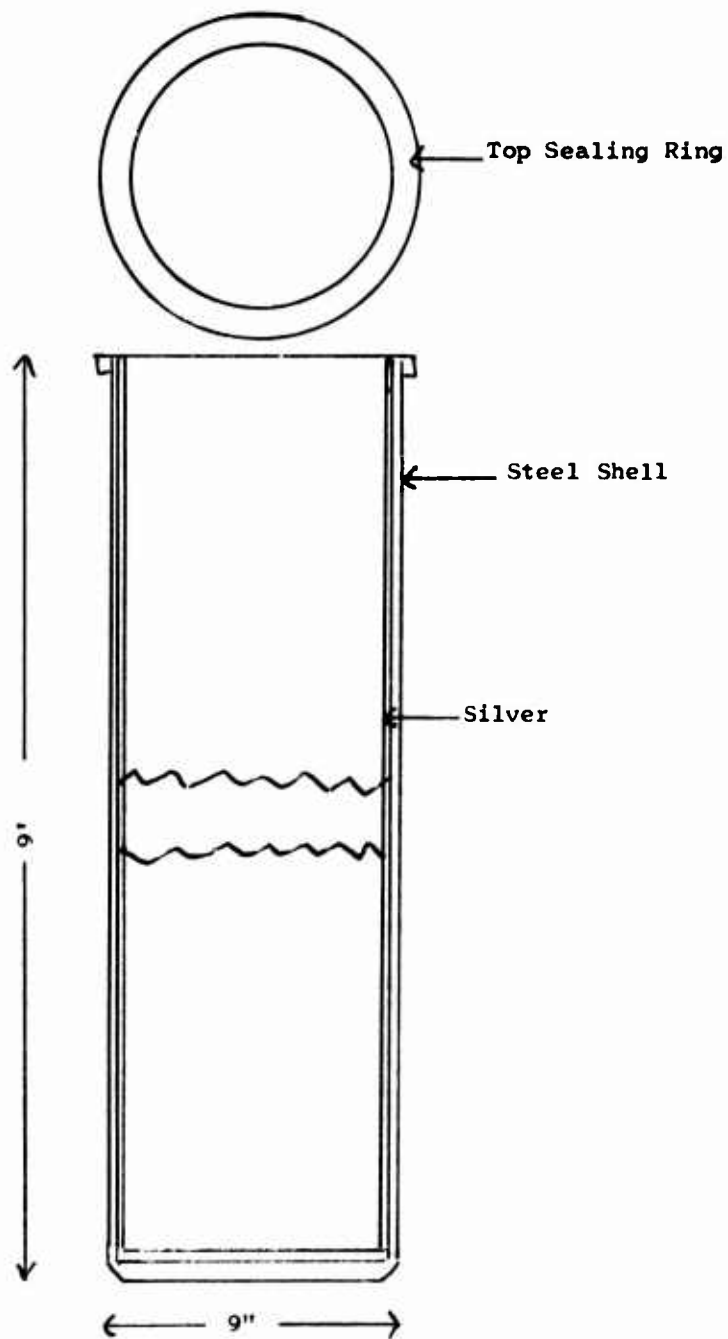


Figure 48

Silver Can Design

### Large Autoclave Program (Continued)

into the autoclave. Depending upon the amount of internal filling of the can, the space remaining in the autoclave cavity after placement of the silver can is filled to the extent necessary for external/internal pressure balance at run temperature.

The silver can was fabricated by welding five sections together to form a unit approximately 9 feet long x 8.5 inches diameter x 0.060 inch thick. The sheet silver for the can was purchased from a commercial supplier<sup>41</sup> and welding was performed at a local metal shop<sup>42</sup>. A special fluted can lid was constructed from silver. The lid and closure are shown in Figure 49. It should be noted that this type of lid provided for moderate expansion and contraction caused by pressure differences between the can and autoclave. Seed racks were constructed from silver-encased stainless steel, and the silver baffle plates were made of pure silver. Figure 50 shows the hardware that was used in the autoclave during crystal growth. The stainless steel jacketed silver growth container is shown at the left. The silver convection baffle, seed rack and tripod stand are shown at the right. Figure 51 shows the completed assembly being lowered into the autoclave.

#### 4.6 Initial Pressure Tests

Our approach to the initial start-up of the large autoclaves was to segment the procedures used in running our small vessels. At the end of each of the segments, the condition of the equipment was checked to verify the scale-up analogy. The first tests prior to the introduction of mineralizer into the system are reported in Table XV. Having passed each of the tests to the point of including all the elements of a growth run, the inner can was filled with  $\text{CaCO}_3$  nutrient,  $\text{K}_2\text{CO}_3$  mineralizer solution, and seeds. It then was sealed, and lowered into the autoclave. The external fill of pure water was added and the autoclave sealed. Power was then turned on and the autoclave brought to about  $375^\circ\text{C}$ , the critical point of water. With the equipment at the end of another procedural segment, the autoclave was shut down and cooled overnight to room temperature. When the autoclave was opened, the inner can and lid were severely deformed by crushing due to pressure differential. In order to understand this situation, a discussion of the pressure-balancing hydrothermal method is necessary.

At the temperatures and pressures used for hydrothermal growth, both fluids in the autoclave are above their critical temperatures. Consequently, they behave like highly compressed gases. Each fluid has a constant volume and density since these conditions are imposed by the rigid autoclave and the volumetric fills. Thus the temperature and pressure of each fluid are almost linearly related. It has been common practice to fill the volume between the outside of the thin walled growth can and the inside of the autoclave with



(a)



(b)

Figure 49 Growth can closure. (a) without seal or clamping ring. (b) sealed and ready for growth.



Figure 50 Production autoclave accessories.  
Left to right - Growth container,  
convection baffle, seed rack, rack  
support stand, and handling tanks.

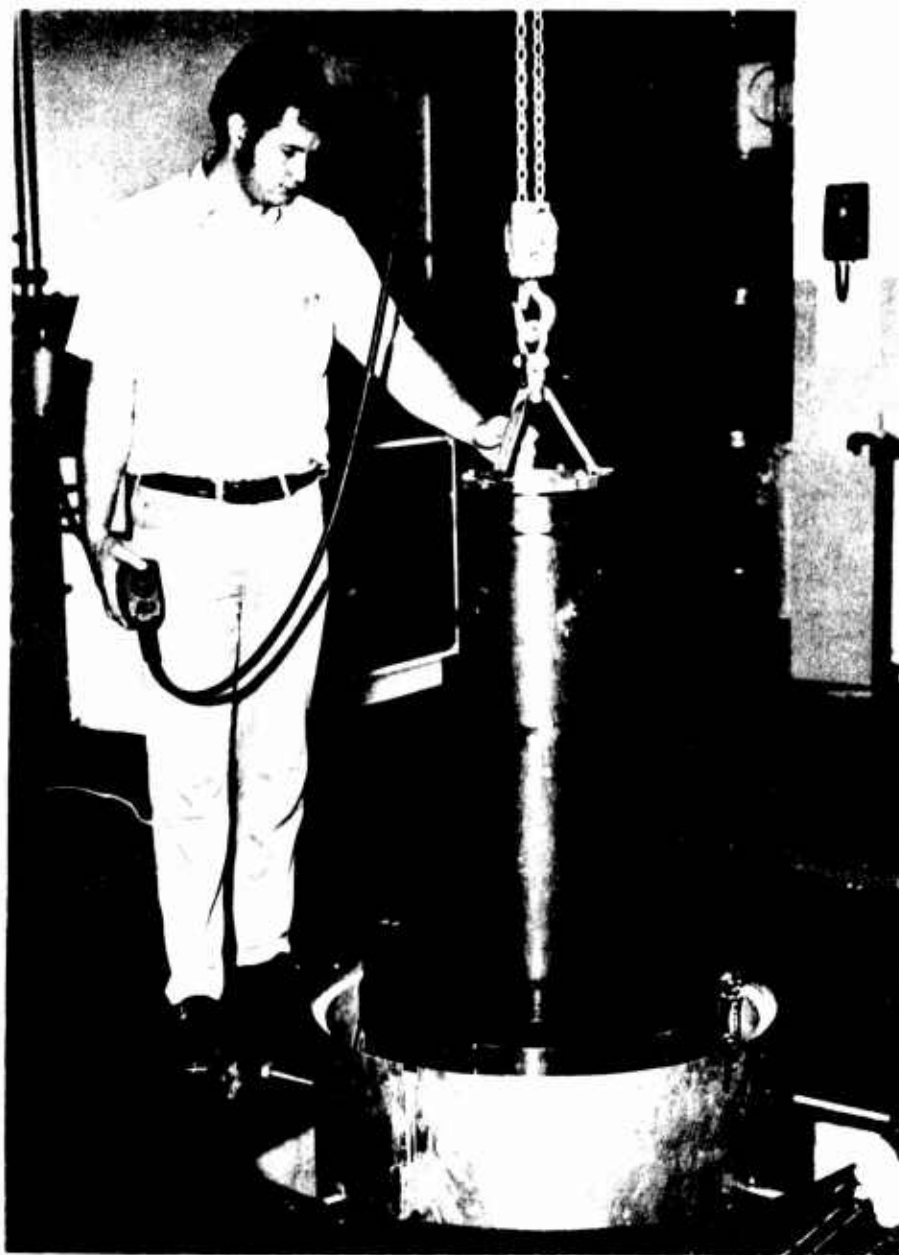


Figure 51 Placement of the growth container into the autoclave.

Table XV

## Production Facility Test Running

Test No.	Temperature (°C)		Pressure (10 <sup>3</sup> psi)	Duration (hrs.)	Fills (v/o, material)		Remarks
	Nutrient	Seed			Internal	External	
1	400	390	18.5	10	-	74.7, water	Initial in-house pressurization
2	400	390	21.1	36	-	74.5, water	
3	400	390	18.8	24	74.7, water	74.7, water	Initial run with growth can in place
4	400	395	18.8	24	74.5, water	74.5, water	
5	400	395	22.3	27	75.1, water	73.5, water	Initial run with all the elements of a growth run except the mineralizer

### Large Autoclave Program (Continued)

an amount of water that will create a pressure equal to that exerted by the growth solution. With equal pressure on both sides of the wall, the can retains its shape and integrity. Clearly the success of this method is based on the gas-like property of both of the fluids. With the external volume kept very small, slight distortions of the can cause large pressure changes in the external volume<sup>43</sup>. Mechanical equilibrium is thereby easily obtained in small autoclaves.

The substantial success achieved over a number of years with this method for small autoclaves apparently diverted a critical examination of the transient periods at the beginning and end of each run. During warm-up and cool-down, the fluids are not above their critical points and, hence, do not behave as gases. Two phases, a liquid and its saturated vapor, are present in both the internal and external volumes. In this situation, the pressures exerted by the fluids at a given temperature do not change with small changes in volume. Expansion and compression results not in a pressure change, but in a mass transfer across the liquid-vapor interface. This situation is pictured in Figure 52.

At constant temperature, the pressure of the vapor in the left hand cylinder at (a) is simply the vapor pressure of the fluid at that temperature. If the piston is moved downward as in (b) at constant temperature, the pressure remains constant. The only change that takes place is the condensation of some of the vapor. Only when the piston contacts the liquid will the pressure increase as the liquid begins to be compressed slightly.

In the hydrothermal autoclave, with water on one side of the container and a concentrated aqueous solution within it, large differences between the vapor pressures of the fluids occur. Because two phases are present in both the volumes, by analogy to Figure 52, large deflections of the flexible lid cannot relieve this difference. The source of the differences between the vapor pressures of the two liquids lies in their thermodynamic properties. These will now be discussed to complete our explanation of this problem.

In the absence of strong solvent-solute interactions, the vapor pressure of an aqueous solution will be less than that of pure water and will be approximately proportional to the relative number of water molecules. Thus a solution containing 55 mole % water molecules and 45 mole % of solute molecules will exert a vapor pressure of .55 that of pure water. This is the simplest case and is known as the ideal solution model. It applies well for dilute solutions which have a little or no heats of mixing. When there are strong interactions between a solute and solvent and heat is either liberated or absorbed during the dissolution, the model does not accurately predict vapor pressures. This situation requires a more involved explanation that leads to the regular solution model which says in effect that, "the higher the temperature, the more ideal the system; the lower the temperature the more important are molecular

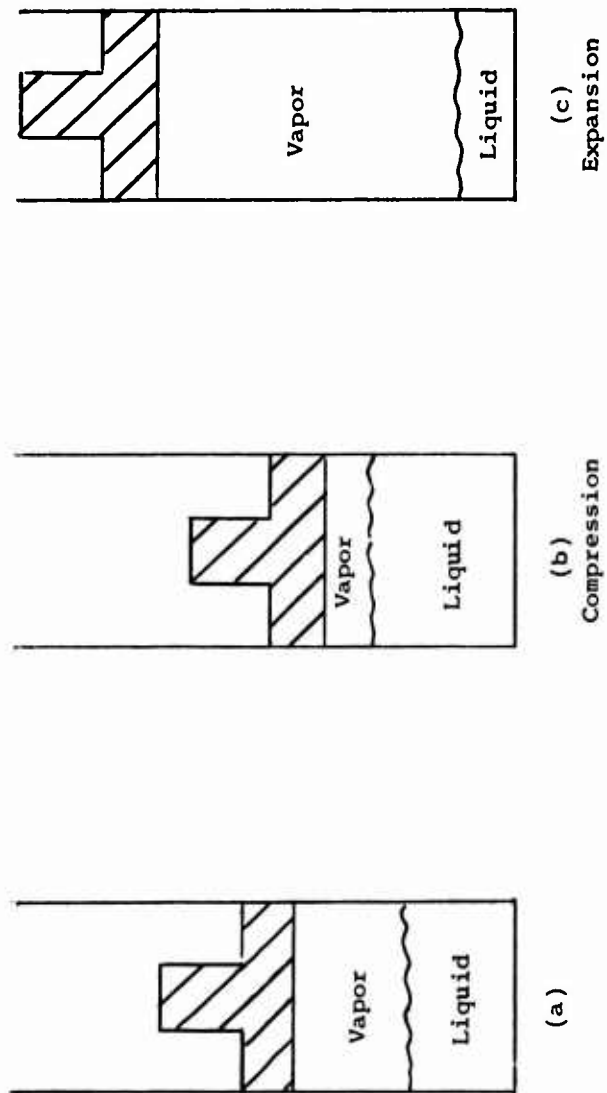


Figure 52 - The behavior of a liquid and its saturated vapor with volume change. At constant temperature, the pressures in (a), (b) and (c) are equal

### Large Autoclave Program (Continued)

interactions". These two models give the following descriptions of the solute effect on vapor pressure:

(Ideal Solution)

$$P_v = (1-x) P_v^0$$

(Regular Solution)

$$P_v = (1-x) \left[ \exp \left( \frac{x^2 Q}{kT} \right) \right] P_v^0$$

where  $P_v$  is vapor pressure at absolute temperature  $T$  of a binary solution having a mole fraction  $x$  of solute and a solvent that exerts a vapor pressure  $P_v^0$  when it is pure at this temperature;  $Q$  is related to the heat of mixing, and  $k$  is Boltzmann's constant. Using these relations, the tabulated vapor pressures of pure water and the value of  $Q$  indicated by the tabulated vapor pressure<sup>44</sup> of 6 M  $K_2CO_3$  at 100°C the curves shown in Figures 53 and 54 were calculated. These figures show that great pressure differences that cannot be relieved by small deformations of the thin-walled growth can are present in the autoclave below about 370°C. This pressure difference will exist until either the can has ruptured or crushed to the point where either the inside liquid fills the can or all the external liquid evaporates to fill the external volume with superheated steam. Based on these calculations the observed inward deformation of the 100-liter can lid was to be expected.

The process presented us with a choice; either a rigid growth container that withstands the pressure difference must be used, or the difference must be relieved by changing the nature of the fills. We have chosen to do the latter. A system of monitoring the position of the lid has been designed and a pump was used to meter in the external fill. The low pressure within the can was matched with steam pressure in the external volume.

#### 4.7 Pressure Balancing Technique

The large difference between the vapor pressures of the internal and external fills was eliminated as a problem by confining the external fill to the gaseous phase with controlled pressure equal to the internal pressure. During the warm-up period of a run, water is pumped into the autoclave using a commercially available air-driven pump. An exact amount of water is injected so that the resultant superheated steam in the external volume balances the pressure within the silver can. The termination of a growth run requires only a controlled venting of the system. The system has been operated successfully to pressures of 1.7 kbar (25 ksi) and 450°C for all of our large growth runs.

The complete growth assembly is shown schematically in Figure 55. It is made up of two systems, the autoclave and its associated electrical and hydraulic equipment, and the differential

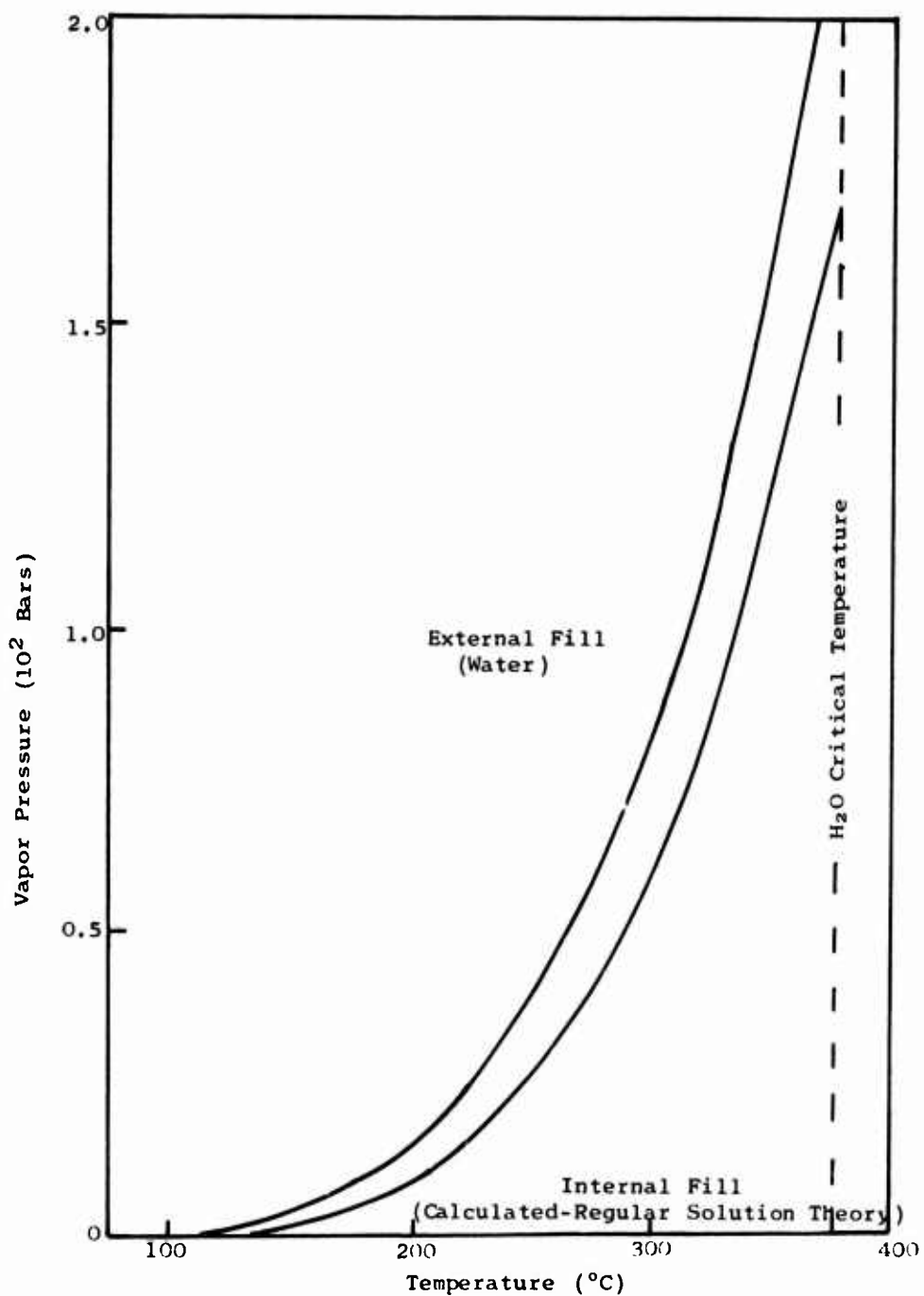


Figure 53 Vapor Pressure of Internal and External Fills.

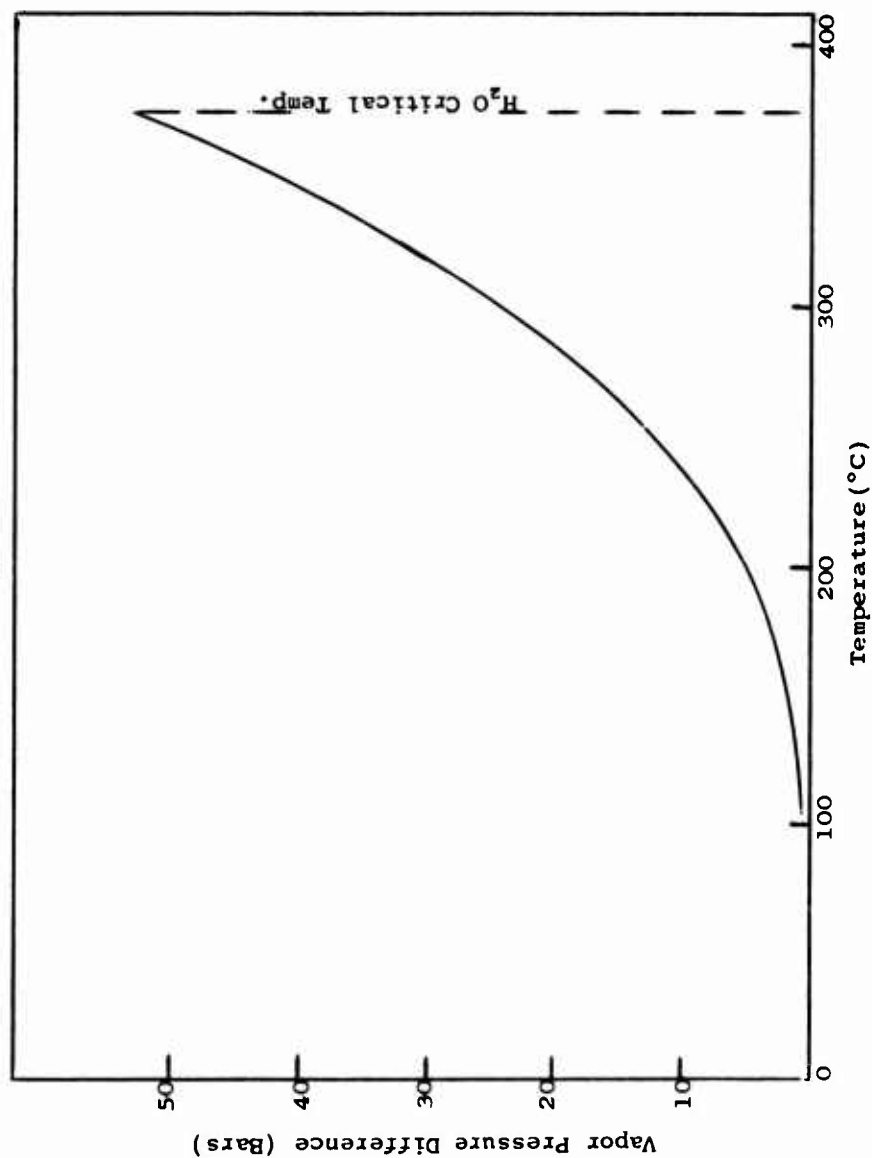


Figure 54 Calculated Vapor Pressure Difference of Water vs. 6M  $K_2CO_3$  (Regular Solution Model)

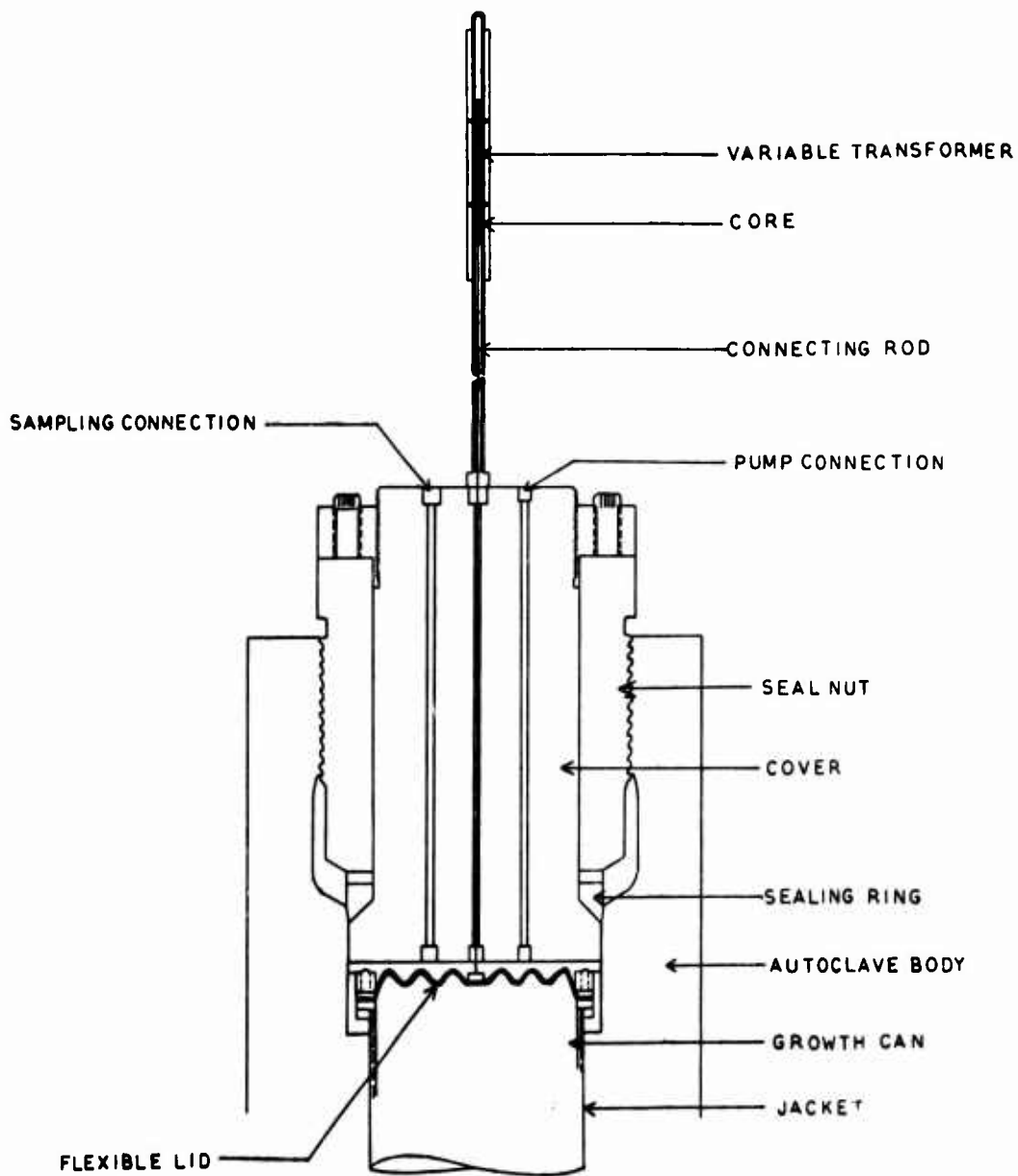


Figure 55 The LVDT Pressure Balancing System

### Large Autoclave Program (Continued)

pressure indicating device. The former are rather straightforward and have been described in Sections 4.3 - 4.5. However, the use of the linear variable differential transformer (LVDT) as a pressure differential indicator is new and deserves more explanation.

The position sensing ability of the LVDT is based on the use of a movable ferromagnetic transformer core that couples the magnetic field of a toroidal coil to two other coils placed on either side of the first. With the core placed at the center of the transformer, the primary is coupled equally to each of the secondaries. When these are connected in opposition, no net output is observed. Displacement of the core causes asymmetry in the coil coupling and, hence, a net secondary output. The device is simple, has been proven over many years of operation in other applications, and can operate with 3 mm of paramagnetic metal between the core and the coils. Figures 56 and 57 show the actual equipment. The degree to which this system solved the pressure differential problem is indicated by the fact that during warm-up and cool-down of a run, the operator can control the flexible lid while observing its position in tenths of a millimeter.

During the first half of the heating cycle of a run in the production equipment, the temperature of the internal growth can lag behind that of the external autoclave. When the system reaches the point where the exterior water fill goes single phase (374°C) large water additions to the external fill are required to maintain pressure balance across the growth can lid. Heat transport through the now dense single phase accelerates the temperature rise of the growth solution. The system's demand for water at this point often exceeds the capacity of our pump. Hence another source of external pressure is needed at the peak demand time. We have completely solved this problem by connecting a commercially available 6000 psi nitrogen cylinder to our system. Whenever the water pump cannot deliver sufficient water to hold the growth can lid horizontally, nitrogen is injected. This system was developed for routine use and has proved to be more than adequate. We note with emphasis that the connection of this equipment to a system that develops pressure five times higher than the cylinder pressure has the potential of great hazard if left connected to the autoclave after the gas injections have been completed. We have, therefore, installed a check valve rated at 60 Ksi between the high pressure piping and the lower pressure of the autoclave equipment. Our normal procedure is to disconnect the gas cylinder from the valve immediately after the injections have been completed. During the early development of the pressure balancing technique, the large production autoclaves were started five times. After some minor difficulties, a detailed procedure was perfected for our growth conditions.

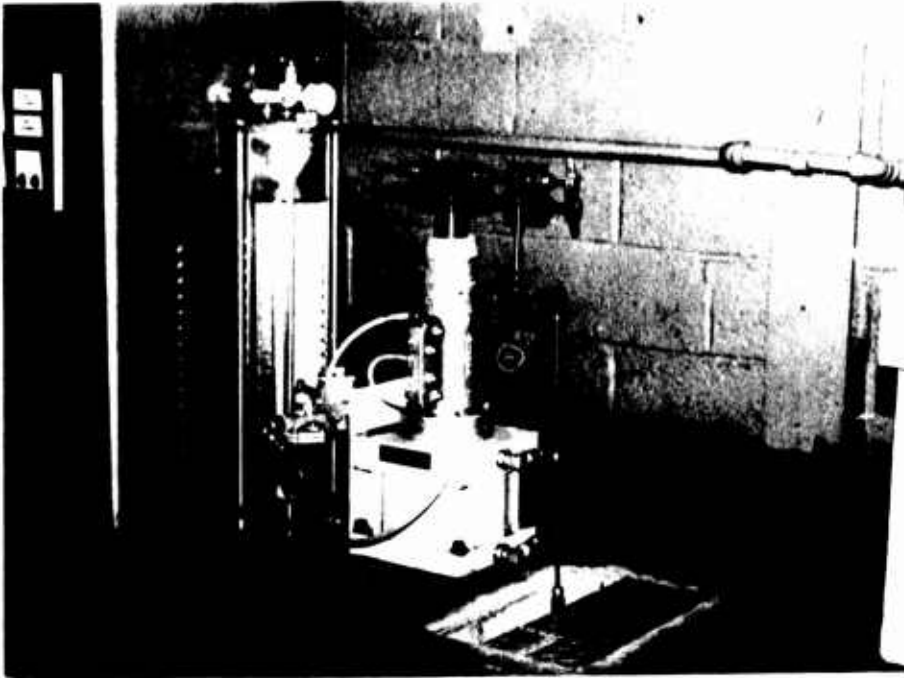


Figure 56 Air-driven high pressure pump for autoclave pressure pump for autoclave pressure balancing system.

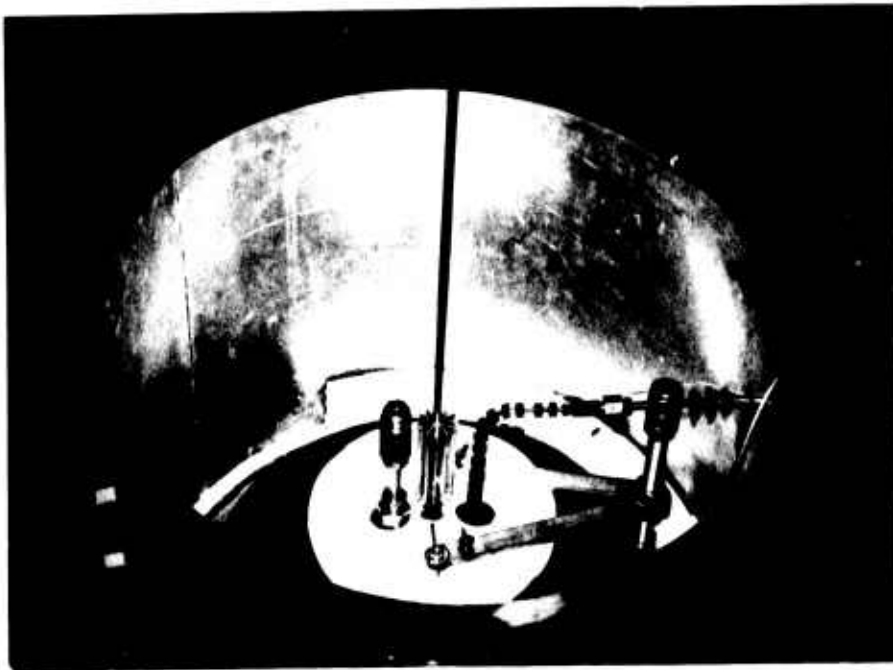


Figure 57 Top view of nine inch diameter autoclave showing pressure and LVDT connections.

## Large Autoclave Program (Continued)

### 4.8 Summary of Large Runs

The primary objective of the large runs was the establishment of a viable process for the routine production of superior quality calcite. Nearly 18 months of work preceeded the attainment of this goal but runs finally became routine. Experiments during our operation of the nine inch production vessels are summarized in Table XVI. Both units were started eleven times during this portion of the program. Several of these starts resulted in successful production runs that yielded many pounds of transported calcite. Some attempted runs were aborted because of leaks in the hydraulic piping or in the growth can. In one instance a slag inclusion had been rolled into the silver plate for the growth can. This caused the can to leak so slowly that two to three days examination by the supplier were needed before the leak could be detected. With the entire assembly of can, jacket, and flexible lid new and untried, many runs were attempted with this can on the assumption that the leak was in the lid. Only after the jacket was cut away and the can pressurized, did the leak become apparent.

From our small autoclave runs, an optimized nutrient temperature was 420 - 440°C, a seed temperature of 410 - 430°C, and thermal gradients of 10 - 25°C. All pressures were close to 25 ksi. Runs 5 - 9 were made in the large systems but only 5 and 6 of Table XVI showed any transport of material. Also runs 7, 8, 9, 11, and 12 had to be discontinued because of leaks. In all of our runs the seeds racks were filled with 100 - 150 cleavage rhomb seeds which had 20 - 30 cm<sup>2</sup> of surface and were 2 - 4 mm thick. One of the completed seed racks is shown in Figure 58. In all cases the nutrient was composed of natural calcite pieces.

Four large autoclave runs were completed during the period of this contract. These represented the beginning of routine operation of the pressure balanced units. Data from runs 10, 13, 14, 15 are given in Table XVI. These runs are essentially identical except for systematic changes in the nutrient-seed temperature difference. Using a 7% baffle, our experience has shown us that at 450°C/1.7 Kbar, a temperature difference of approximately 15 degrees yields optimum growth. Examples of the material grown in these runs are given in Figures 59 - 61. It can be seen that the quality of the crystals has progressively increased to where crystals from Run CA 9-15 were almost totally transparent. In regard to growth rate, the large autoclaves reflected previous data from 3 inch systems. The fastest rates were attained on {1011} equidimensional rhombs and measured no more than 75 µm/day.

### 5.0 PHYSICAL TESTS ON HYDROTHERMALLY GROWN CALCITE

The previous sections of this report have demonstrated that

Table XVI  
Production Autoclave Operation

<u>Run No.</u>	<u>Conditions Achieved</u>		<u>Pressure kbar/ksi</u>	<u>Duration of Run (days)</u>	<u>Material Transported</u>
	<u>Nutrient</u>	<u>Temperature (°C) Seeds Top</u>			
Ca 9-5	433	416 420	1.72/25	18	1
Ca 9-6	430	412 418	1.72/25	7	2
Ca 9-7	Run aborted because of leaks.				
Ca 9-8	Run aborted because of leaks.				
Ca 9-9	Run aborted because of leaks.				
Ca 9-10	434	407 408	1.72/25	44	20
Ca 9-11	Run aborted because of leaks.				
Ca 9-12	Run aborted because of leaks.				
Ca 9-13	420	410 409	1.72/25	34	6.3
Ca 9-14	445	427 428	1.72/25	49	21
Ca 9-15	433	419 420	1.72/25	40	14

Note: All runs were at an internal fill fraction of 0.86



Figure 58 Completed seed rack for nine inch diameter autoclave.



Figure 59 Hydrothermal calcite grown in the production facility.



Figure 60 Hydrothermal calcite grown in the production facility.



Figure 61 Hydrothermal calcite grown in the production facility.

## Physical Tests on Hydrothermally Grown Calcite (Continued)

calcite can be grown in our large autoclaves at experimental rates of 50 - 75  $\mu\text{m}/\text{day}$  for  $\{10\bar{1}1\}$  faces. Two large runs were achieved where growth continued for 30 - 60 days. The longest run yielded about 3 mm of hydrothermally grown calcite on a seed. This thickness of crystal permitted us to evaluate certain quality factors even though it does not allow the complete fabrication of calcite polarizers of different types. Most of the following data were obtained by physically cutting or cleaving the portions of hydrothermal growth from the seed crystal.

### 5.1 Composition and Crystal Perfection

An elemental analysis is important in hydrothermal growth to determine correctly which elements may lead to impurity phenomena, defects, or purification. Table XVII gives an extended quantitative optical spectroscopic analysis of nutrient and hydrothermally grown crystal. The nine elements were chosen from their relative abundance in natural crystals of various geographical origins. It can be seen that the nutrient crystals, which were of good optical grade, reflect a very low level of impurities. The most extensive impurity is potassium. The regrown crystals show almost the same level of impurities as the nutrient. A slight increase of magnesium occurs while a decrease of strontium is effected. This might be expected on the basis that  $\text{MgCO}_3$  has the calcite structure while  $\text{SrCO}_3$  has an aragonite structure. It is also interesting that the level of potassium remains stable even though  $\text{K}_2\text{CO}_3$  is used as the solvent. The exact percentage of silver was not determined in this analysis but is known to be very low.  $\text{Ag}_2\text{CO}_3$  also has a structure quite different from calcite. Apparently very little  $\text{Ag}_2\text{CO}_3$  forms in the silver autoclave can liner or transport is difficult. We have noticed very little silver corrosion in our systems since a small amount of calcium is used as a reducing getter for  $\text{O}_2$ .

Figure 62 is a comparison of the infrared spectra of a portion of nutrient crystal and hydrothermally grown calcite. For all practical purposes the spectra are identical from 1 - 15  $\mu\text{m}$ . The principal bands in the 6-15  $\mu\text{m}$  region are from the  $\text{CO}_3^{2-}$  molecular vibrations. Those in the 2 - 6  $\mu\text{m}$  region are from small amounts of  $\text{OH}^-$ ,  $\text{HCO}_3^-$ , and trace organics. Whatever the exact nature of these bands may prove to be, the amounts in our crystals are nearly equivalent. Very little purification or augmentation occurs as a result of our hydrothermal process.

Another indication of crystallographic quality or general perfection may be obtained from etch pit results. Ordinarily a crystal surface must be prepared carefully before specific etch solutions are attempted. However in our hydrothermally grown crystals, natural etching of the surfaces occurs after the growth process is terminated. This etching may be caused by impurity accumulation,

Table XVII  
Spectrographic Analysis of Calcite

<u>Element</u>	<u>Calcite Nutrient, CA915</u> (%)	<u>Grown Crystal, CA915</u> (%)
Al	< 0.001	< 0.001
Ca	major	major
Fe	< 0.001	< 0.001
Mg	< 0.005	< .001
Mn	< 0.001	< .001
Na	< 0.001	.001
Si	< 0.001	< .001
Sr	.003	.002
K	.01	.01

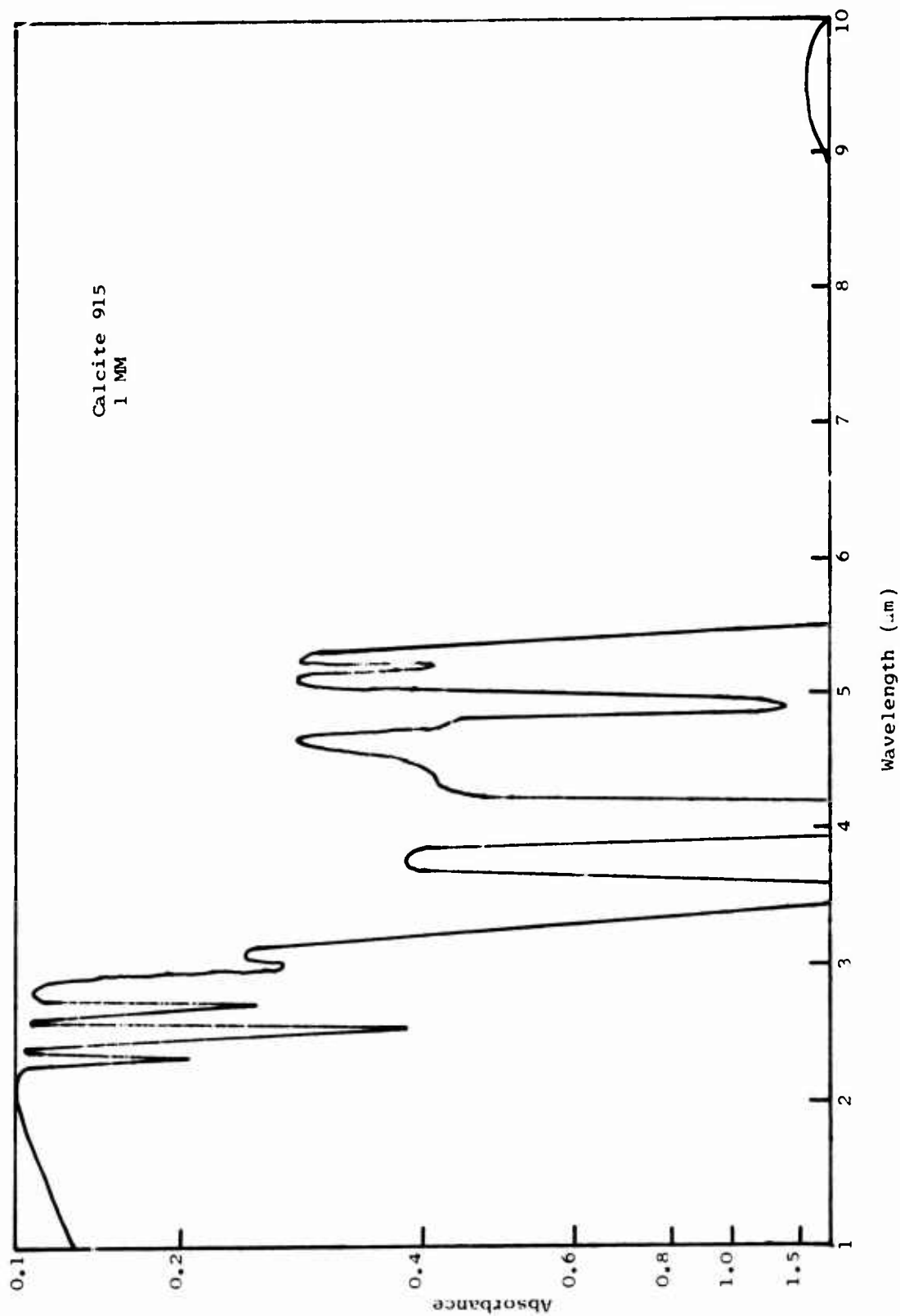


Figure 62 Infrared spectrum of natural seed and hydrothermally grown calcite.

## Physical Tests on Hydrothermally Grown Calcite (Continued)

a slight retrograde solubility at lower than growth temperatures, or the effects of a new species in the hydrothermal environment as the temperature is decreased. Figure 63 gives an example of etch pit formation on a cleavage rhomb face of hydrothermal calcite. The pit density was counted at  $10^3$  lines/cm<sup>2</sup> which indicates a high quality crystal. The rhombohedral shape of the pits follows the growth morphology. The regular pit shapes on the surface indicate that most dislocation lines are nearly normal to the  $\{10\bar{1}1\}$  growth surfaces.

The etching data have also been confirmed independently by x-ray topographic techniques. Cut sections of hydrothermal calcite were mechanically polished, chemically polished in  $\text{NH}_4\text{Cl}$  solution, and thinned to about 0.5 mm. The area of a cleavage plane 1 cm x 2 cm was examined in transmission by using  $\text{AgK}\alpha$  radiation and a Lang x-ray topographic camera. Diffraction was from  $(10\bar{1}2)$  planes which were at  $20^\circ$  to the  $(10\bar{1}1)$  plane. Figure 64a shows the results of one topograph. Tiny areas of strain and one large area in the upper left hand corner were the predominant features. Few dislocation lines were resolved since most lines were parallel to the x-ray beam and traversed the thin dimension of the slice. Most defects tend to lie in planes which were parallel to the large area  $\{10\bar{1}1\}$  planes. Figure 64b is an additional topograph of a slice of calcite which was cut similarly to that of Figure 64a. However, in the present situation the cut traverses both the seed crystal and hydrothermally grown calcite on the top and bottom surfaces. Diffraction was from  $(10\bar{1}2)$  planes. The seed crystal is characterized by several groups of strained areas all lying parallel to each other horizontally on the figure. About 3 mm of regrown crystal are shown at the top and bottom. This material shows no planar defects which relate to the seeds. In fact the crystallographic quality of the grown calcite is much better than that of the seed. Only a few defects are present and some of these were propagated from the seed.

Some preliminary tests were performed on the damage sensitivity to laser radiation<sup>45</sup>. Briefly they consisted of an irradiation of our hydrothermally grown calcite with a Q-switched Nd:YAG laser. The reported damage level for our calcite was found to be within 1 db of that measured for a polished and coated natural calcite crystal. Some variations occurred in the damage level from area to area but these were thought to be due to the poor optical quality of the samples available at that time. We have not submitted samples from our last two large runs of calcite where large areas several mm thick were obtained.

### 5.2 Optical Properties

The crystalline perfection in terms of the optical properties was evaluated through visual examination for color, light scatter, and particulate inclusions. Examinations were also made



Figure 63a Natural etch pits on hydrothermally grown calcite rhomb surface.

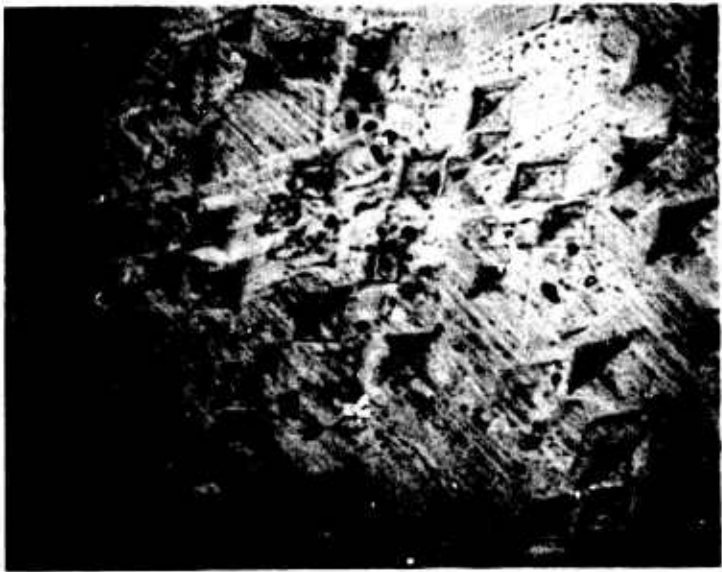


Figure 63b Detail of etch pits on calcite.

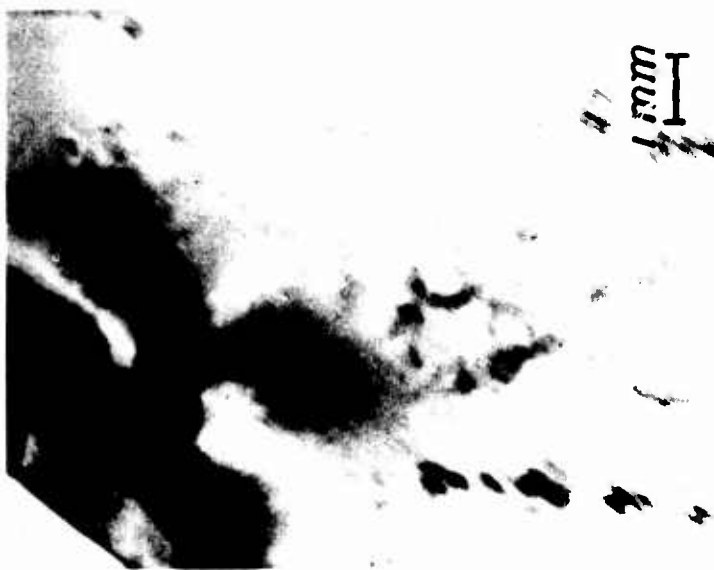


Figure 64a X-ray topograph of hydrothermally grown calcite, slice cut parallel to cleavage plane.



Figure 64b X-ray topograph of hydrothermally grown calcite on natural calcite seed.

### Physical Tests on Hydrothermally Grown Calcite (Continued)

for optical distortion, optical homogeneity and measurement of polarization performance. These measurements were performed on samples of natural and hydrothermally grown calcite. The latter were usually 3 - 4 mm sections cut from seed crystals.

Visual examination was accomplished by observing the material against a white background and also at  $90^\circ$  to a He-Ne laser beam passed through the material. The hydrothermally grown samples examined were colorless and no distinct visible scattering was observed. Several of the natural calcite samples did contain small particles which gave visible amounts of light scattering.

No cm size samples of hydrothermal calcite were fabricated for examination by Twyman-Green Interferogram because of availability. However several 10 mm samples of natural calcite were prepared. The interferograms of these samples are shown in Figure 65 with the beam parallel to  $[10\bar{1}0]$ . The isogyre patterns of these samples were also examined and very little distortion was observed. The prepared natural crystals were to be used as standards for the hydrothermal material.

Polarization performance of natural and hydrothermally grown material, which included some spontaneously nucleated crystals of cm size, was measured by passing an unpolarized He-Ne laser beam through the material at an angle to the optic axis, and then measuring the polarization of the output beams. In all materials extinction ratios in excess of 100:1 were measured for each beam. The aperture size used was less than 3 mm for some of the hydrothermally grown material.

### 6.0 CONCLUSIONS

Efforts to prepare a hydrothermal nutrient from sintered high purity  $\text{CaCO}_3$  powder were not entirely successful. Further work should be done on hot pressing or other procedures which can operate below the decomposition point. A satisfactory nutrient is uniform purity natural calcite of sub-optical grade. An alternate nutrient may be recrystallized  $\text{CaCO}_3$  powder to enlarge particle size.

Small 1.5 or 3.0 inch diameter autoclaves were used to determine correct operating conditions for large systems. At  $400 - 450^\circ\text{C}$  and 20 - 25000 psi 6 m  $\text{K}_2\text{CO}_3$  is a satisfactory solvent for calcite. Below  $375^\circ\text{C}$  there is a tendency to form a new phase  $\text{K}_2\text{Ca}(\text{CO}_3)_2$ . The solubility of calcite at  $425^\circ\text{C}$  is approximately 0.7 wt. %.

The most favorable conditions for small autoclaves were found to be a nutrient temperature of  $425^\circ\text{C}$ , a seed temperature of  $400-420^\circ\text{C}$ , thermal gradients of  $10 - 20^\circ\text{C}$ , a pressure of 24000 psi, and baffle openings of 10%. Under these circumstances growth rates were found to be 75 - 125  $\mu\text{m}/\text{day}$  on  $\{10\bar{1}1\}$  cleavage rhomb seeds.



Figure 6.3 Twyman-Green interferometer patterns of 10 mm lengths of natural calcite, beam parallel to  $[1010]$ .

### Conclusions (Continued)

A morphological study of seed orientation was made to optimize growth rate and crystal size. It was found that the best seeds and growth were from nearly equidimensional cleavage rhombs. The addition of  $\text{Li}_2\text{CO}_3$  to the nutrient changed the growth morphology to  $\{0001\}$  plates but at a rate less than  $25 \mu\text{m}/\text{day}$ .

Large autoclaves with 9 inch diameter by 9 feet long cavities were constructed and operated for periods of 2 months. The routine use of silver can liners for the autoclaves presented a problem in avoiding can rupture or crushing when filled with mineralizer solution. The problem was solved by a pressure balancing method for the internal fill and external pressure.

Growth runs were performed in the large autoclaves with a full complement of 150 natural calcite seeds which measured  $1 \times 5 \times 6 \text{ cm}$ . Nutrient consisted of crushed natural calcite. At a growth temperature of  $425^\circ\text{C}$  and 25000 psi, nearly 20 pounds of calcite was transported to the seeds. Five runs were made under these conditions. Measured growth rates on  $\{10\bar{1}1\}$  were  $50 - 75 \mu\text{m}/\text{day}$  averaged over two months. For most seeds 3 - 4 mm of new growth occurred uniformly over the seeds.

Chemical and physical tests were performed on the grown portions of crystals. Elemental analysis, infrared spectra, etching, x-ray topography, optical examination, and laser damage threshold all confirmed the essential reproduction of high quality calcite.

Under the terms of the contract, three deliveries of 20 pounds of calcite grown crystals were made at intervals of 4 months. First article and production run were not completed due to a reduction in scope and actual use of the material.

## 7.0 IDENTIFICATION OF PERSONNEL

During the many phases of this program, the following personnel were contributors to the experimental work.

Dr. Roger F. Belt	Research Manager
Mr. Richard C. Puttbach	Production Manager
Dr. D. Reed Kinloch	Project Engineer
Dr. Joseph Hutta	Engineer - Growth
Dr. Robert Arlett	Engineer - Growth
Mr. Robert Uhrin	Staff Physicist - Growth
Mr. David Dentz	Staff Physicist - Testing
Mr. William Dorman	Technician
Mr. Christopher Schreiber	Technician

Several discussions on polarizers, optical testing, and laser system use were held with Drs. L. Gillespie and D. Horowitz of the Night Vision Laboratory, Fort Belvoir, Virginia. This project was performed under the administrative direction of Mr. Louis Goldberg and Mr. David Biser of the Industrial Preparedness Division, Production and Procurement, U.S. Army Electronics Command, Fort Monmouth, N. J.

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## APPENDIX I

### Process Flow Chart

A process flow chart for the entire calcite growth program is given in Table XVIII. The main parts of our process are concerned with materials preparation, the autoclave and its appurtenances, growth run procedures and testing. For convenience all the steps in our operation are placed in their chronological order even though practical applications demanded some deviations. In general the process is repetitive each time production runs are made. Some steps can be omitted by a judicious effort to anticipate quantities of materials required for sustained operation.

The amount of testing on the prepared crystals is limited to a few optical procedures. The scope of the program did not include polarizer fabrication in any particular prism configuration.

Table XVIII

## Process Flow Chart for Hydrothermal Calcite

<u>Step</u>	<u>Materials Preparation</u>
1	Evaluate high purity $\text{CaCO}_3$ powder
2	Sinter or hot press to briquettes
3	Weigh out $\text{CaCO}_3$ nutrient
4	Prepare dionized water
5	Prepare $\text{K}_2\text{CO}_3$ mineralizer solution
6	Orient seed crystals
7	Cut seeds on blade saw
8	Polish and etch seeds
	<u>Autoclave and Associated Equipment</u>
1	Grind down sealing area on silver vessel to a smooth, even finish
2	Pressure test vessel with air at 5 psi
3	Clean inside of vessel and internal parts with dilute HCl
4	Rinse vessel and parts thoroughly with water
5	Place baffle stand inside of vessel
6	Add nutrient to nutrient area of vessel
7	Place baffle on baffle stand
8	Lower seed rack onto baffle stand
9	Add prescribed amount of mineralizer
10	Place silver sealing ring and silver lid on vessel sealing surface

Table XVIII (Continued)

<u>Step</u>	<u>Autoclave and Associated Equipment</u>
11	Turn down steel sealing ring onto lid
12	Seal vessel by torquing down sealing ring bolts
13	Lap sealing surface on autoclave
14	Clean inside of autoclave by flushing with water
15	Clean autoclave sealing parts with Acetone
16	Apply anti-sieze compound to threaded parts of sealing apparatus
17	Lower silver vessel into autoclave
18	Assemble sealing parts and screw into autoclave as a unit
19	Seal autoclave by torquing down sealing ring bolts to 150 foot pounds
20	Attach to autoclave connections for LVDT, pressure gauge, water pump and gas feeds; bleed pipe valve and base check valve
21	Make initial temperature settings - note a slightly hotter top was found to be most favorable for easier lid control during warm up
22	Turn on power
23	Increase control temperature set point in steps of 25 to 50°C
24	Closely monitor lid position, pump in water in response to rising lid, bleed system in response to falling lid
25	Employ high pressure gas boost primarily during critical period in response to rapidly rising lid

Table XVIII (Continued)

<u>Step</u>	<u>Autoclave and Associated Equipment</u>
26	Disconnect high pressure gas after critical period
27	Upon approach of desired run temperature set final temperature gradient
28	At desired run temperature set temperature and pressure deviation alarms
29	Make base check
30	Monitor lid position temperature and pressure daily
31	Make periodic base checks throughout the run
32	At end of run disconnect alarm system, turn off power and turn on cooling fans
33	During cooling period monitor lid position until lid movement subsides. Periodic venting will be necessary
34	When autoclave reaches room temperature and pressure disconnect all fittings
35	Unscrew sealing ring bolts and unscrew sealing apparatus as a unit
36	Withdraw silver vessel
37	Unscrew silver vessel sealing ring bolts and unscrew sealing ring
38	Break seal between lid and vessel sealing surface
39	Withdraw seed rack
40	Pour or pump out mineralizer
41	Recover residual nutrient

Table XVIII (Continued)

<u>Step</u>	<u>Testing Procedures</u>
1	Examine under 10X for gross defects
2	Gas laser beam probing for scattering
3	Prepare cube for interferometer testing
4	Run optical absorption spectra
5	Measure polarization performance
6	Laser damage resistance
7	Final packaging and delivery