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FABRICATION OF CALCIUM OXIDE CRUCIBLES FOR MELTING AND CASTING HIGH PURITY URANIUM AND PLUTONIUM

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ABSTRACT

The fabrication of dry pressed calcium oxide refractory crucibles and molds is described in detail. Specifications for raw materials are presented. Procedures for preparation of the materials and their pressing are described. Drying and firing of the pressed pieces are given. Comparative results using calcium oxide rather than magnesium oxide as container materials are included.

I. INTRODUCTION

The incentive for the development of a method to form crucibles of calcium oxide at Los Alamos resulted from a request for a container (crucible, liner or mold) to be used in the preparation of uranium and plutonium metals of high purity. The metals produced in the required containers were to be lower in silicon, boron, and magnesium content than the metal produced in conventional sintered magnesium oxide crucibles.

The two special requirements for a substitute crucible material were that it be capable of easy dissolution, so that any uranium or plutonium which soaked into the crucible could be removed; and that the primary constituent might not be a source of contaminating elements.

Reasonably procurable super refractory materials considered were zirconia and zircon, thoria, alumina, magnesia, beryllia and calcia. The easy dissolution requirement eliminated zirconia, zircon, and thoria while the factor of possible contaminating elements ruled out the alumina, magnesia, and beryllia. Therefore, the choice of materials was narrowed to calcia.

The dry press technique* is adaptable to the fabrication of refractory shapes of such design that relatively thick walls and uneven

* The dry press process consists of charging a suitably sized powdered ceramic material and a lubricant (waxes, stearates, etc., to increase flowability and to reduce friction on die walls) into a steel die and pressing at a few hundred to several thousand pounds per square inch.

[redacted]

sections can be tolerated. This technique was necessitated by the hygroscopic nature of the material being used - calcium oxide.

The slip casting technique* usually employed in the fabrication of special shapes when only a few pieces are required does not readily lend itself to casting hygroscopic materials because of the need for employing anhydrous liquids as suspending media. Such a process is not very suitable for quantity production of large shapes, owing to the rapid rate of evaporation of the suspending media, and the rapid deterioration of plaster molds due to chemical attack by the media.

* Essentially the casting process consists of pouring a slip (a suspension of ceramic materials in water) into a dry plaster mold which absorbs water from the slip until a layer becomes rigid enough to support itself; whereupon the liquid slip in the center is drained out leaving a uniform casting in the mold.

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II. RAW MATERIALS

Study of High Purity Calcia Availability

Several sources of calcium oxide were investigated before a material was secured satisfactory to the needs of the requesting agency.

Analyses of C.P. Grade calcium oxide from J. T. Baker Chemical Company showed that the purity of this material was not satisfactory. Group CMR-8 therefore decided to make some calcium oxalate to use as the raw material. J. T. Baker Chemical Company also was contacted and fifty pounds of special grade calcium carbonate was supplied by them. The Norton Company and the New England Lime Company also submitted samples of calcium oxide for evaluation. Analyses of these various materials as-received are noted in Tables I, II, and III.

After fabricating several liners of each source material and subsequently making reductions in each, the New England Lime Company calcia was chosen. This material was decided upon not only for its purity, but also its relative economy; for some of the other source material was very satisfactory but considerably more expensive.

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TABLE I

Element	New England Lime Co. Calcium Oxide		Norton Co. Calcium Oxide
	As-received*	Calcined, crushed, and ground**	Fused as-received
Li	0.6	<0.3	0.2
Be	<1	<1	<1
B	<3	<3	10
Na	12	<3	<1
Mg	90	200	5000 - 10,000
Al	80	500	1000 - 2,000
Si	500	1500	2000 - 10,000
V	<10	<10	<10
Cr	<5	10	3
Mn	5	5	90
Fe	150	300	800
Co	<3	<3	<3
Ni	8	5	<3
Cu	40	7	<0.5
Zn	700	150	<100
Ag	<0.1	2	<0.5
Pb	3	10	3

* Average results of analyses on five batches.

** Average results of analyses on three batches.

[redacted]

[redacted]

TABLE II

Element	J. T. Baker Co. C.P. Grade Calcium Oxide As-received	CMR-8 Produced Oxalate As-received*	CMR-8 Produced Oxalate After calcining,** crushing and grinding
Li	2	<0.1	<0.2
Be	<1	<1	<1
B	20	<1	8
Na	150	5	1
Mg	Approx. 20,000	3	1200
Al	1000	<2	45
Si	Approx. 10,000	8	110
V	<50	<10	<10
Cr	10	<3	5
Mn	100	<3	3
Fe	1000	4	60
Co	<5	<3	<3
Ni	<3	<3	<4
Cu	5	3	12
Zn	<500	<100	<100
Ag	<0.1	<0.2	2
Pb	<5	<0.5	<1

* Average results of analyses on two different batches.

** Average results of analyses on four different batches.

[redacted]

[redacted]

TABLE III

J. T. Baker Co. Special Grade Calcium Carbonate

Element	As-received	After calcining, crushing and grinding*
Li	0.1	<0.1
Be	<1	<1
B	<1	8
Na	3	0.6
Mg	3000	2000
Al	5	14
Si	60	200
V	<10	<10
Cr	6	15
Mn	1	4
Fe	15	50
Co	<3	<6
Ni	<3	<3
Cu	10	5
Zn	<100	<100
Ag	<1	3
Pb	5	<1

*Average results of analyses on four different batches.

[redacted]

III. FABRICATION

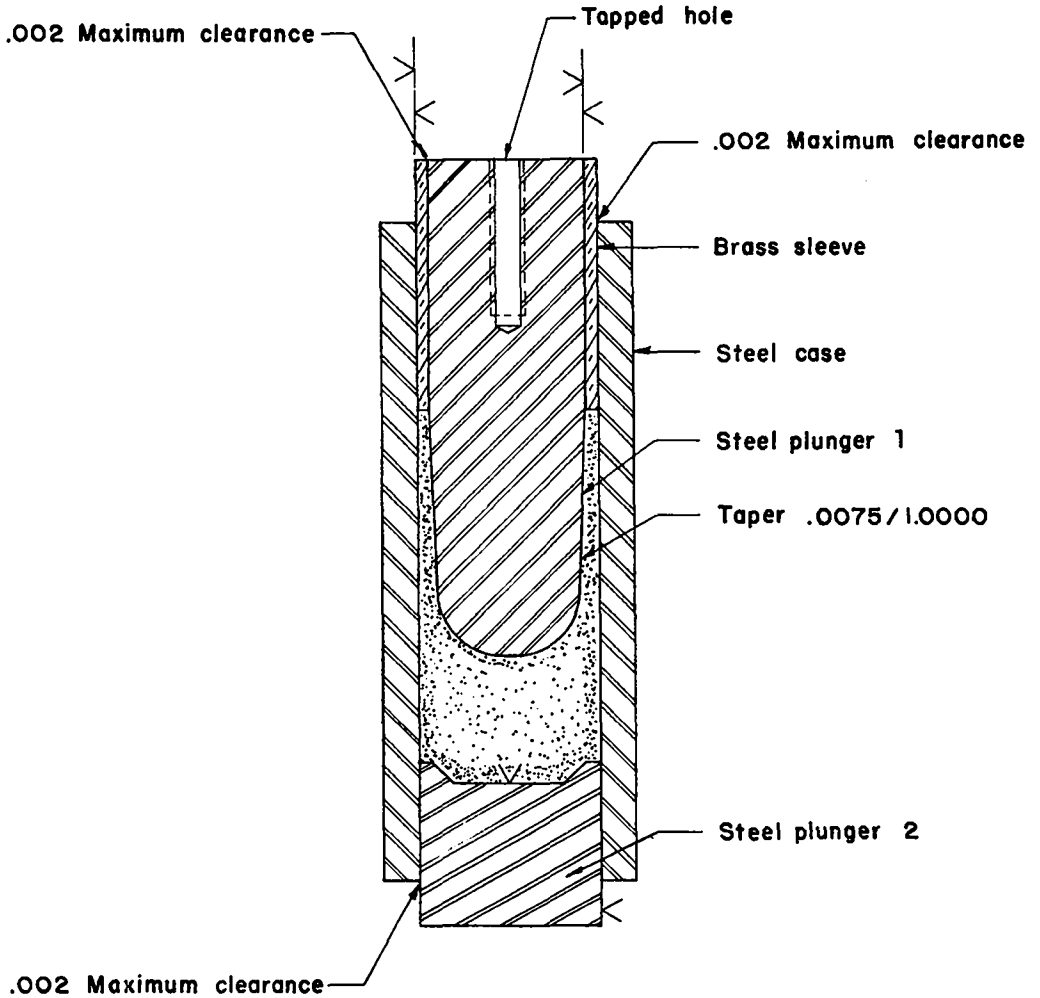
The steps involved in the fabrication of calcia refractory shapes by the dry press process method are: 1) fabrication of necessary dies; 2) calcination of the raw, as-received material; 3) adding and mixing of the binder; 4) pressing; and 5) firing.

A. Die Fabrication

The steel dies used were of a conventional type as illustrated in Figure 1, machined, hardened, and polished to the specifications listed.

B. Preparation of Calcia Pressing Mixture

The calcium oxalate was calcined in magnesia crucibles to a temperature of 1350°C in approximately 3-1/2 hours in a gas fired furnace. The calcined calcium oxide was crushed in an iron mortar and passed through a 6-mesh sieve then mixed with 3% of beeswax dissolved in carbon tetrachloride. The carbon tetrachloride was evaporated and the dry calcium oxide-wax mixture pressed at 10,000 psi in hardened steel dies into slugs 2-1/2 inches in diameter by approximately 1-1/2 inches thick. These slugs were calcined on a graphite plate in an induction coil to a temperature of 1700°C. The temperature was reached in one hour heating time (See Table IV for typical firing schedule). This accelerated heating rate usually caused fracture of briquettes thus facilitating the crushing operation. The slugs were held at this temperature for 5 minutes. The slugs, cooled in place in the coil (overnight), were removed and crushed in a laboratory jaw crusher to pass a 6-mesh sieve.



NOTES:

Steel materials noted are GSN or Hampden, hardened to Rockwell C 62-63 or K-46 or Mangano, hardened to Rockwell C 61-62

All finishes noted are $\overset{8}{V}$.

TYPICAL DRY PRESS DIE FABRICATION SPECIFICATIONS

Figure 1

[redacted]

TABLE IV

TYPICAL CONTROL PANEL SCHEDULE*
FOR FIRING CaO BRIQUETTES

Elapsed Time (min.)	Power (KW)	Current (amperes)	Temp. (°C)
0	13	57	R.T.
15	20	68	
30	25	74	
45	30	80	
55	15	62	1700
60	15	62	Off

*When using induction furnace shown in Figure 4.

[redacted]

The 6-mesh and finer material was then ground in a laboratory size pulverizer to minus 20 mesh size. This calcined and ground material was used to fabricate the crucibles.

The calcium carbonate was treated in the same manner as the calcium oxalate except that the 1350°C temperature of the first calcination was held for approximately 1-3/4 hours to insure complete calcination.

The calcium oxide, when received as such, was treated in the same manner as the oxalate and carbonate except that the first briquetting and 1350°C calcination step was omitted.

Spectrographic analyses of the various materials evaluated as-received and after calcination, crushing and grinding are shown in Tables I, II and III. The quantity of each element present is reported in parts per million.

1. Grain Size Distribution of the Sintered and Crushed Calcia Grain

Most desirable grain size distribution for fabrication of the various crucible sizes reported here was:

Screen Size, Mesh	Percent Retained
35	0.5 - 3.0
60	6.0 - 9.0
80	7.0 - 6.0
100	10.0 - 6.0
150	12.0 - 6.0
200	15.0 - 5.0
thru 200	49.5 - 65.0

[redacted]

2. Pressing Die Materials.

The dies were usually machined of K-46 or Mangano, which are general purpose oil hardening steels, (typical analysis of 0.95 C, 0.35 Si, 1.60 Mn, 0.2 Cr) or GSN or Hampden chrome-carbon wear resisting steels (typical analysis of 2.20 C, 0.40 Si, 0.40 Mn, 12.25 Cr).

C. Binder Addition

One percent by weight of beeswax, dissolved in sufficient carbon tetrachloride to thoroughly wet the calcium oxide, was added to the calcined, ground calcium oxide. The carbon tetrachloride was then evaporated from the mixture until no detectable odor was noted. This wax addition was necessary to bind and lubricate the non-plastic grains of calcia composing the mixture.

D. Pressing

The dry calcium oxide - beeswax mixture was formed into the desired crucible shapes by hand-tamping into the steel dies and subjecting the assembly to a pressure of 10,000 psi in a conventional type hydraulic press. See Figure 2 for steps in pressing.

The crucible was removed from the die employing the method illustrated in Figure 3.

E. Firing

The pressed pieces were fired in an induction furnace having a graphite heating chamber whose inside dimensions were 9 inches in diameter and 19 inches high. See Figure 4 for schematic diagram of furnace assembly. The crucibles were set in an upright position on unfired plates

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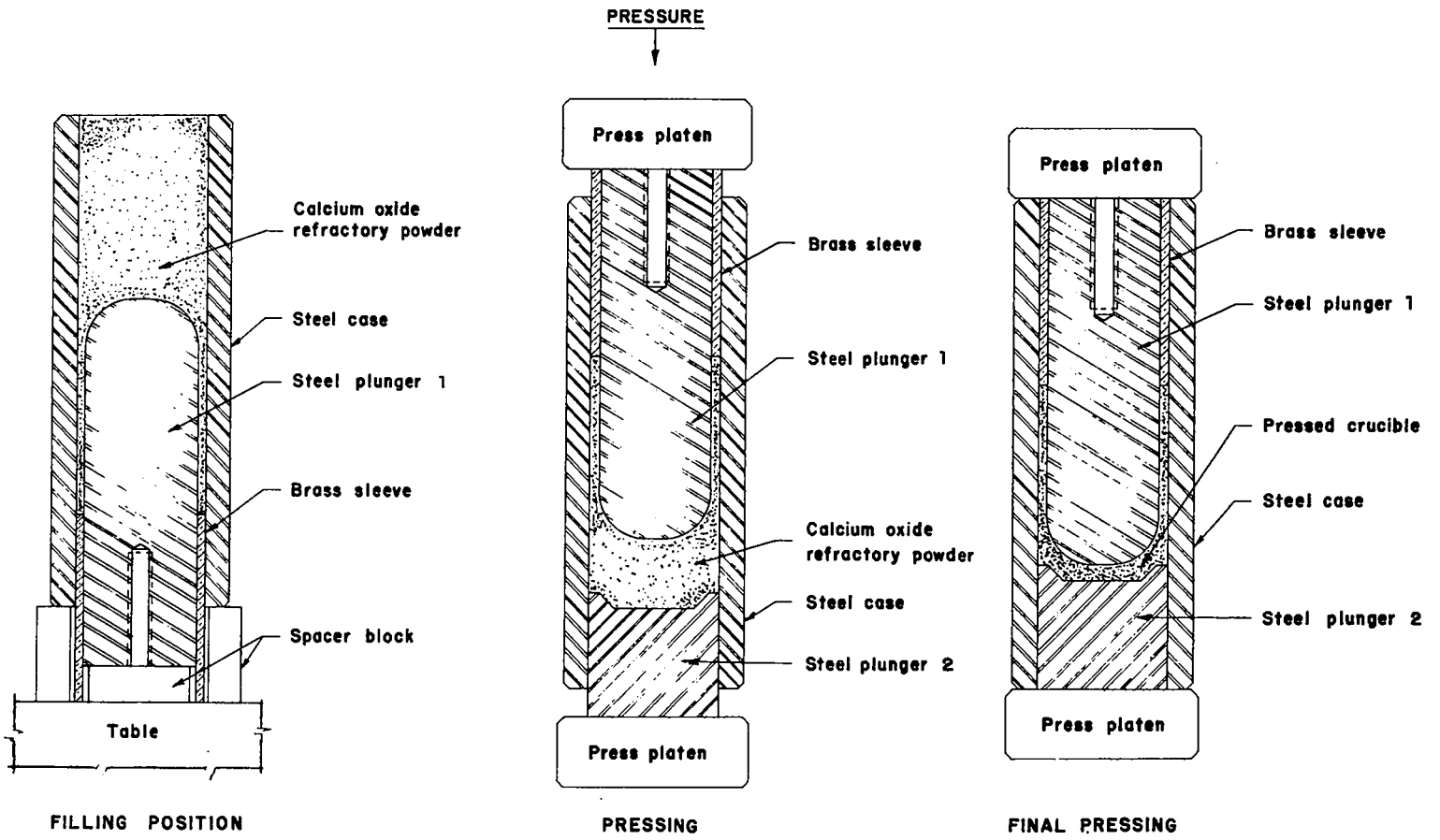

TYPICAL DIE AND METHOD OF DRY PRESSING CRUCIBLES

Figure 2

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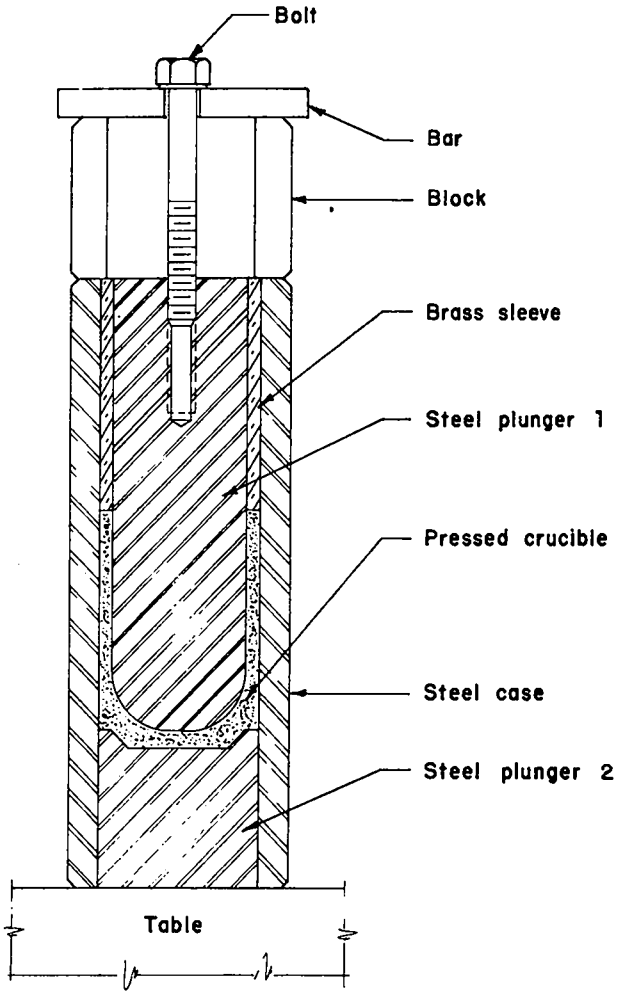
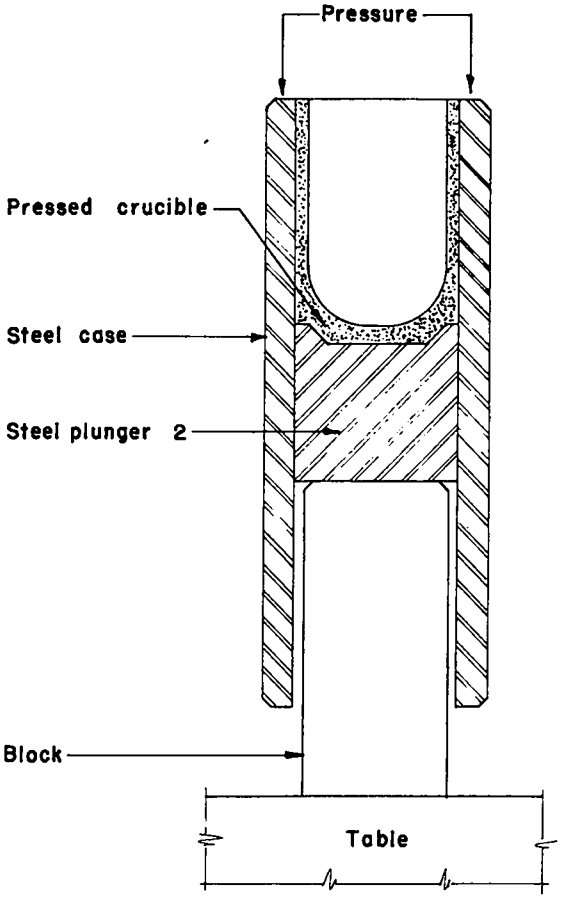


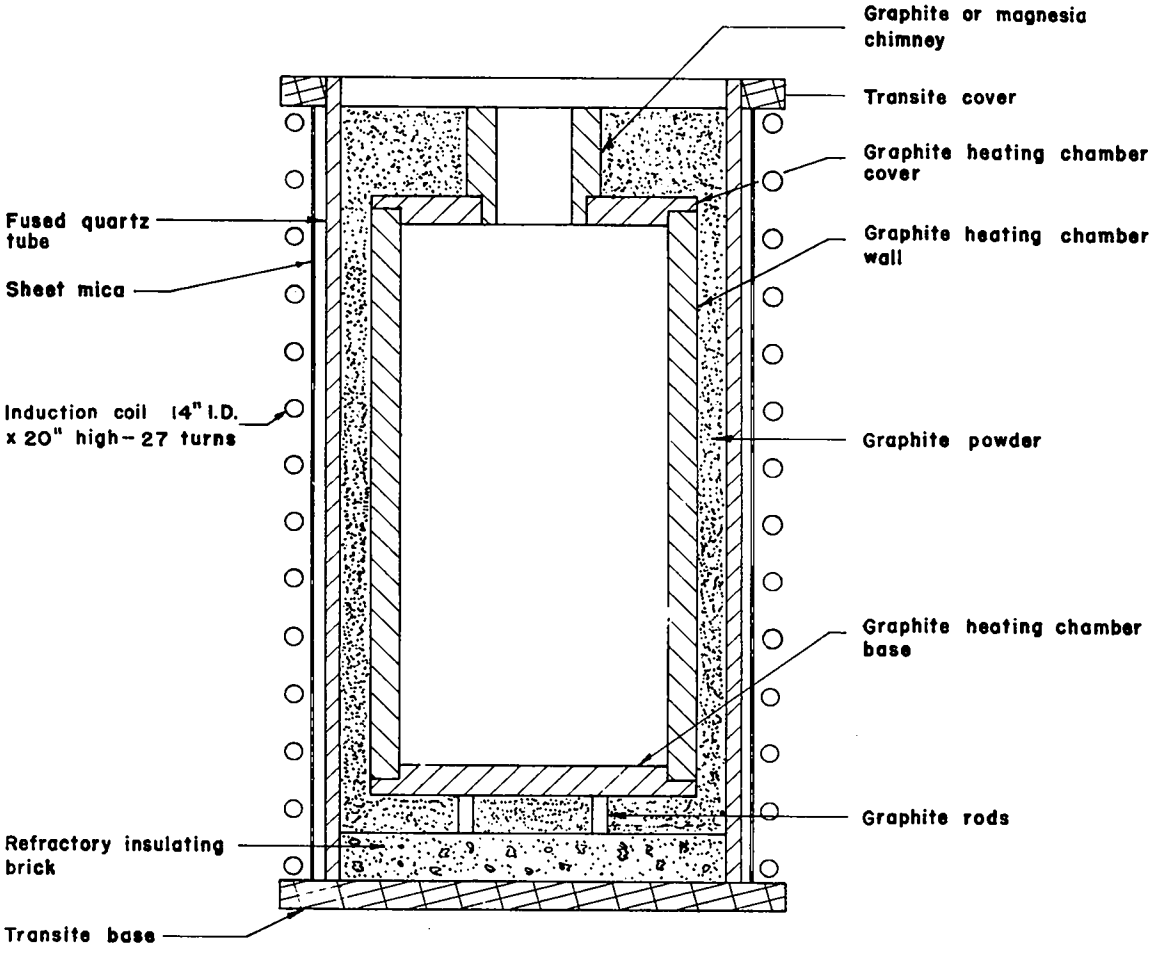
CORE PULLING



FINAL EXTRUSION

METHOD OF REMOVING DRY PRESSED CRUCIBLE FROM DIE

Figure 3



SECTION THROUGH CENTER OF INDUCTION FURNACE

Figure 4

pressed of the same mixture as the crucibles. This procedure minimized warpage and excessive carbon discoloration during the firing operation. Power for the furnace was supplied to a 14 inch inside diameter induction coil from a 100 KW, 800 volt, 3000 cycle motor generator set. A temperature of 1700°C was reached in 1-1/2 hours with a maximum (20°C/min. firing rate) power input of 40 KW (See Table V for typical firing schedule). After the peak temperature was reached, a 15 minute soak at this temperature was allowed before the power was cut off. The loaded furnace was allowed to cool naturally until the contents were at a temperature of approximately 90°C. The cooling period was 18 to 20 hours.

At this point the crucibles were discolored to a very pale grey at the surface - a carbonaceous deposit probably due to the graphite heating chamber. This grey color was completely removed by re-firing the crucibles in the oxidizing atmosphere of a globar-type resistance furnace to a temperature of 1100°C.

Group CMR-8 discovered earlier* that this re-firing was very beneficial in reducing the carbon content in the button product of the reduction. Carbon content of the CaO liner was reduced from 800 - 1200 ppm to 120 - 200 ppm, with a resulting drop in button carbon content from 500 - 600 ppm to 20 - 40 ppm.

* Prior to the re-firing process described, CMR-8 had ignited crucibles to 900°C in vacuo employing a two hour schedule in a nickel reaction chamber to accomplish this.

[redacted]

[redacted]

TABLE V

TYPICAL CONTROL PANEL SCHEDULE*
FOR FIRING CaO CRUCIBLES

Elapsed Time (min.)	Power (KW)	Current (amperes)	Temp. (°C)
0	7	48	R.T.
20	13	56	
40	17	64	
55	20	72	1100
70	30	80	
85	40	92	
95	15	63	1700
110	15	63	Off

*When using induction furnace shown in Figure 4.

[redacted]

[redacted]

IV. STORAGE

After firing, the refractory pieces while still warm (approximately 75-90°C) were placed in warm dessicators or warm air-tight cans in which a suitable drying agent had been placed. Crucibles stored in this manner have been kept satisfactorily over six months with no detrimental effects.

V. RESULTS

Employing the pre-calcination method described, crucibles weighing up to 2.5 Kg have been fabricated successfully with very little change in chemical composition other than slight increases in iron and magnesium content. See Appendix for representative crucible drawings and photographs of typical crucibles.

The calcium oxide crucibles and/or liners have been used in the production of high purity uranium and plutonium metal lower in silicon, boron, and magnesium content than any produced heretofore*. The analytical data presented in Table VI reveal the difference in purity of the resulting metal buttons.

Inasmuch as higher purity materials were used in the metal reductions in the calcium oxide liners than in the MgO liners, the more favorable purity results tabulated in Table VI must not be construed to be wholly because of the change in liner materials. However, the data

*See also "Preparation of High Purity Uranium Metal" by R. W. Kewish, et.al. LA-1652; and "Preparation of High Purity Plutonium Metal" by K. W. Johnson, LA-1680.

[redacted]

TABLE VI

COMPARISON OF ANALYSES* OF URANIUM BUTTONS PRODUCED IN MAGNESIUM OXIDE AND CALCIUM OXIDE LINERS

Element	With MgO Liner**	With CaO Liner***
Li	<0.1	0.1
Be	<0.1	0.01
B	0.18	0.1
C	66	25
O	-	70
Na	0.6	1
Mg	15	3
Al	1.6	2
Si	47	7

* The values < 0.1 represent the lower limits of detection for the spectrochemical methods then used. Analyses were not routinely made for oxygen.

** Average results of analyses on 50 samples.

*** Average results on analyses on 10 samples.

tabulated do evidence what purities are possible employing this type of reduction liner.

VI. DISCUSSION AND RECOMMENDATIONS

Prior to use, it is desirable to re-heat crucibles to 1000°C in vacuo as it appears inevitable that some calcium carbonate is formed on crucible surfaces in handling. This requirement is generally fulfilled by the requesting agency just prior to use in process described in earlier footnote.

For exceptionally high purity crucibles, raw material as-received has been mixed with 3 percent by weight beeswax and fabricated into small crucibles without pre-calcination, using identical firing techniques. This method, however, precludes the fabrication of large (2 inch diameter or larger) crucibles due to the excessive fired shrinkage of the uncalcined material. It has been very satisfactory for fabrication of crucibles weighing up to 150 grams.

A slow heating rate (15°C/min.) to red heat is advisable for the calcium oxide bodies. Removal from the furnace at temperatures greater than 90°C is to be avoided, because of the excessively poor thermal shock resisting properties of calcium oxide bodies.

In comparing the liners fabricated of different CaO sources, (see Table VII), it is worthy of note here that crucibles containing up to 30 ppm boron did not result in buttons containing more than 0.1 ppm boron. This fact should probably prompt a more thorough investigation

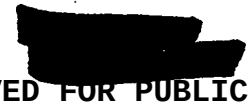


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TABLE VII

COMPARISON OF ANALYSES OF BUTTONS WITH ANALYSES OF CaO LINERS IN WHICH THEY WERE PRODUCED

Element	Crucible[1]	Button	Crucible[2]	Button	Crucible[3]	Button	Crucible[2]	Button
Li	0.1	<0.1	0.1	<0.1	0.2	<0.1	0.4	<0.1
Be	<1	<0.1	<1	<0.1	<1	<0.1	<1	<0.1
B	20	<0.1	7	<0.1	1	0.1	8	<0.1
C	150	20-30	145	20-30	110	<25	200	<25
Na	100	<1	100	<1	1-2	<1	0.4	<1
Mg	5000 - 10,000	2	4000	2	400	2	2000	4
Al	50	<2	40	<2	500 - 5000	2	10	2
Si	1	6	30	4	400	6	300	12
Ca	VS	<10	VS	12	VS	<10	VS	<10
V	<10	<10	<10	<10	2	<10	<10	<10
Cr	5	2	<3	2	2	4	50	2
Mn	10	12	1	5	2	5	8	7
Fe	150	>100	10	24	300	70	70	100
Co	<3	<5	3	<5	<3	<5	<10	<5
Ni	<3	6	4	8	5	20	50	10
Cu	40	4	50	<1	10	2	1	1

1. Crucible fabricated of CMR-8 produced calcium oxylate.
2. Crucible fabricated of J. T. Baker Co. calcium carbonate.
3. Crucible fabricated of N. E. Lime Co. calcium oxide.

[redacted]

as to what purity specifications on other of our ceramic materials are really necessary and realistic.

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APPENDIX

TYPICAL REDUCTION LINER AND CRUCIBLE SHAPES

AND PHOTOGRAPH OF TYPICAL CaO CRUCIBLES

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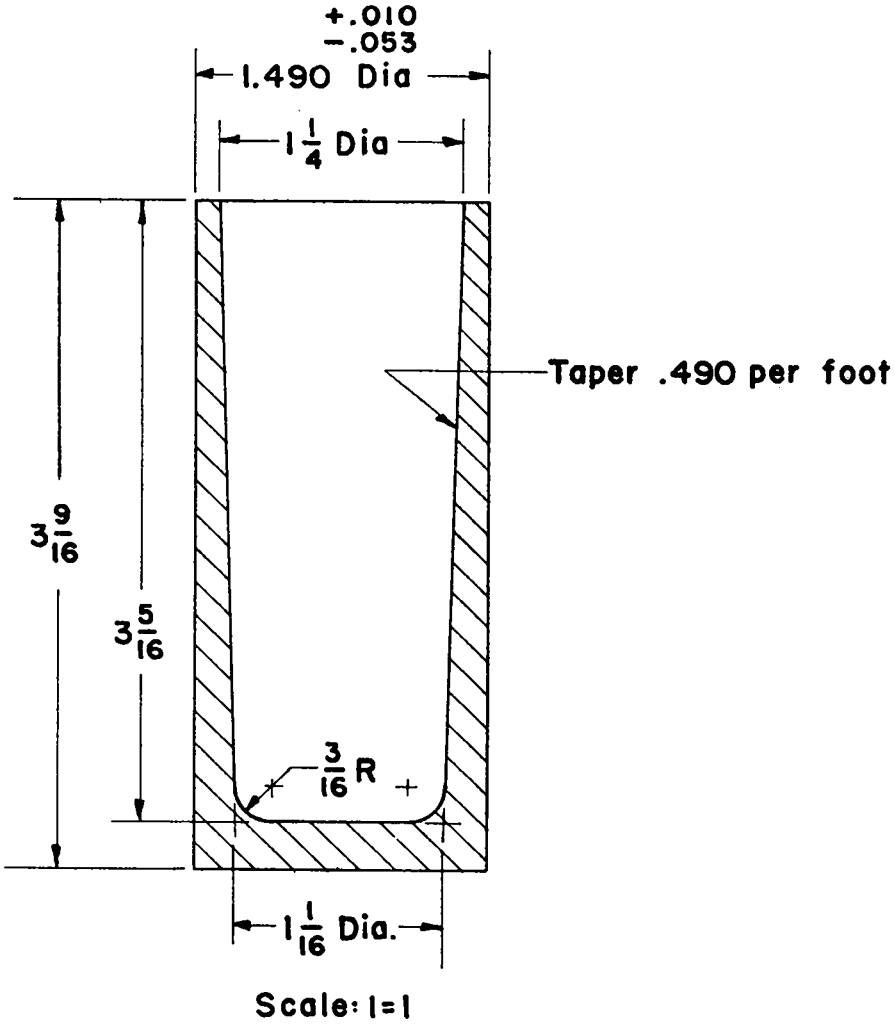

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Figure A-1

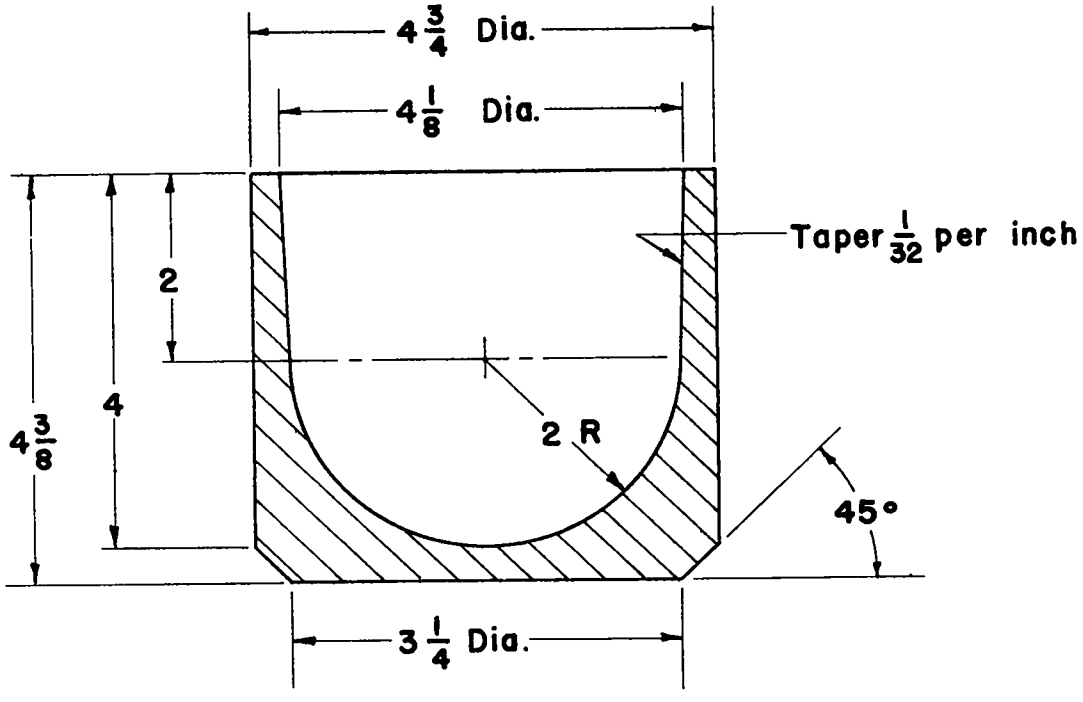

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Figure A-2

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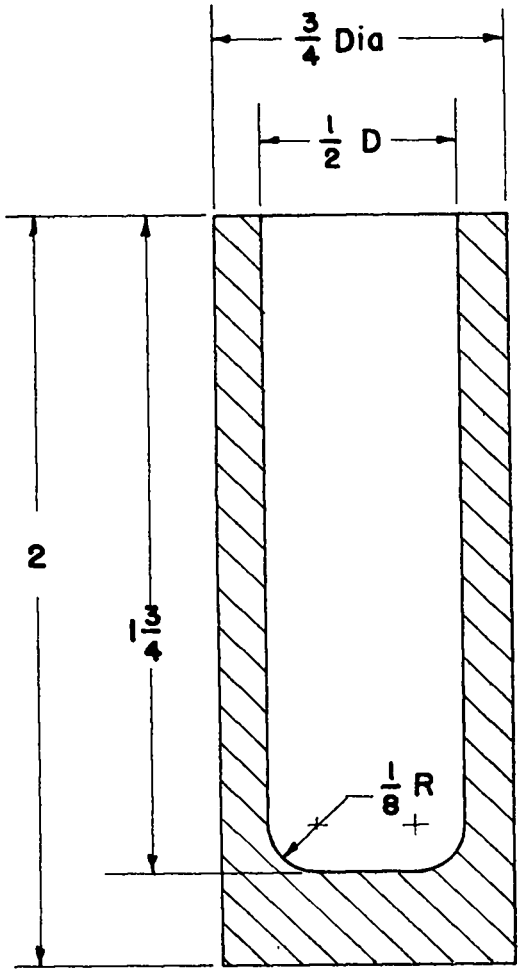

Scale: 2 = 1

Tolerance: $\pm \frac{1}{64}$

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Figure A-3

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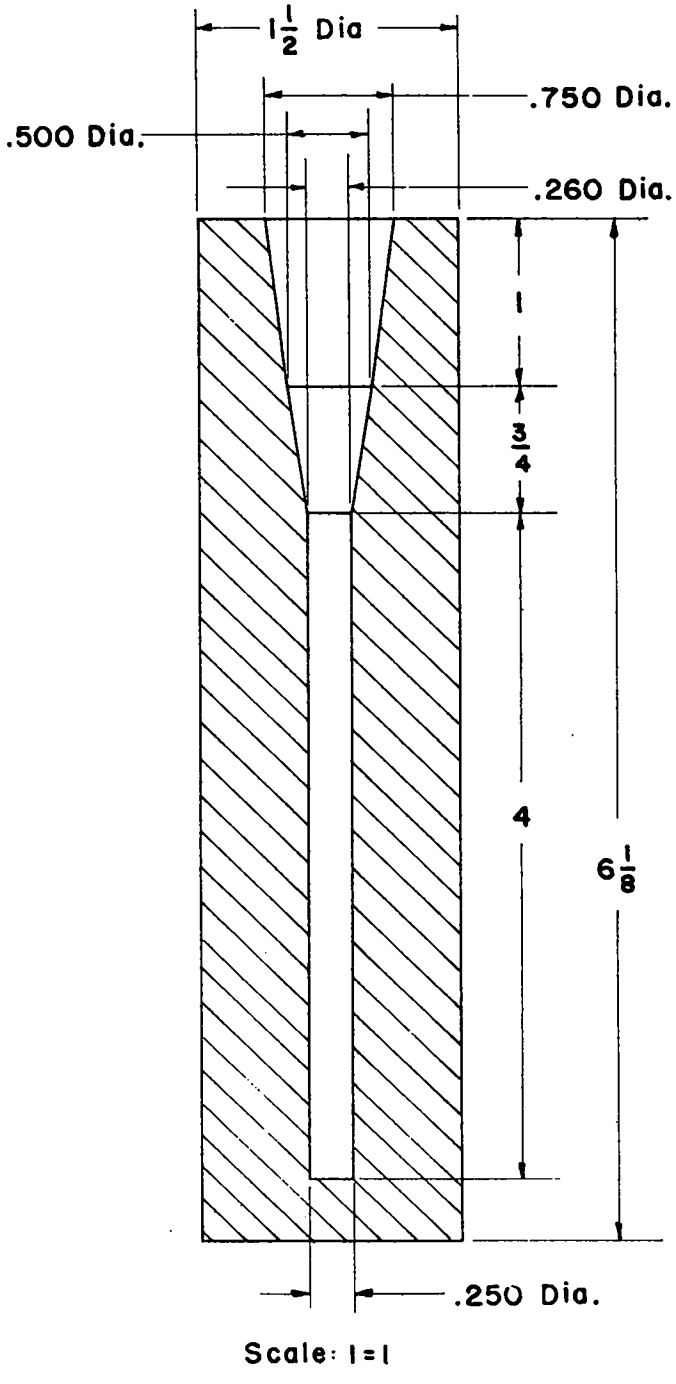

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Figure A-4

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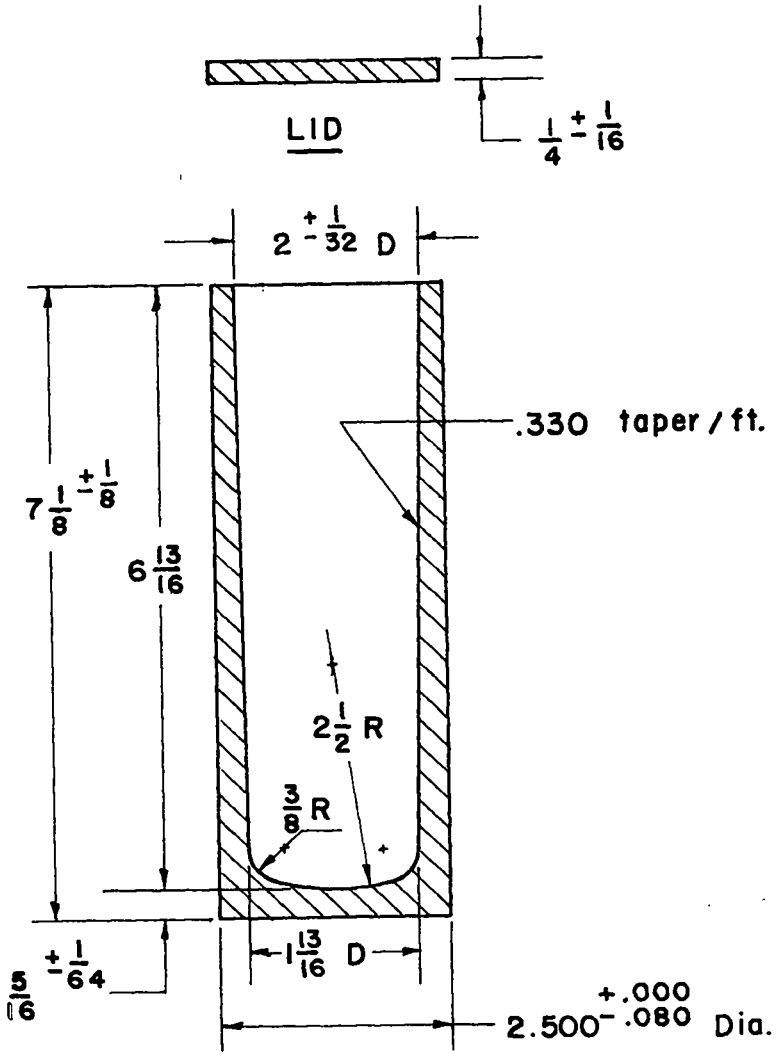

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Scale: $\frac{1}{2} = 1$

250 GRAM REDUCTION BOMB LINER
A-183

Figure A-5

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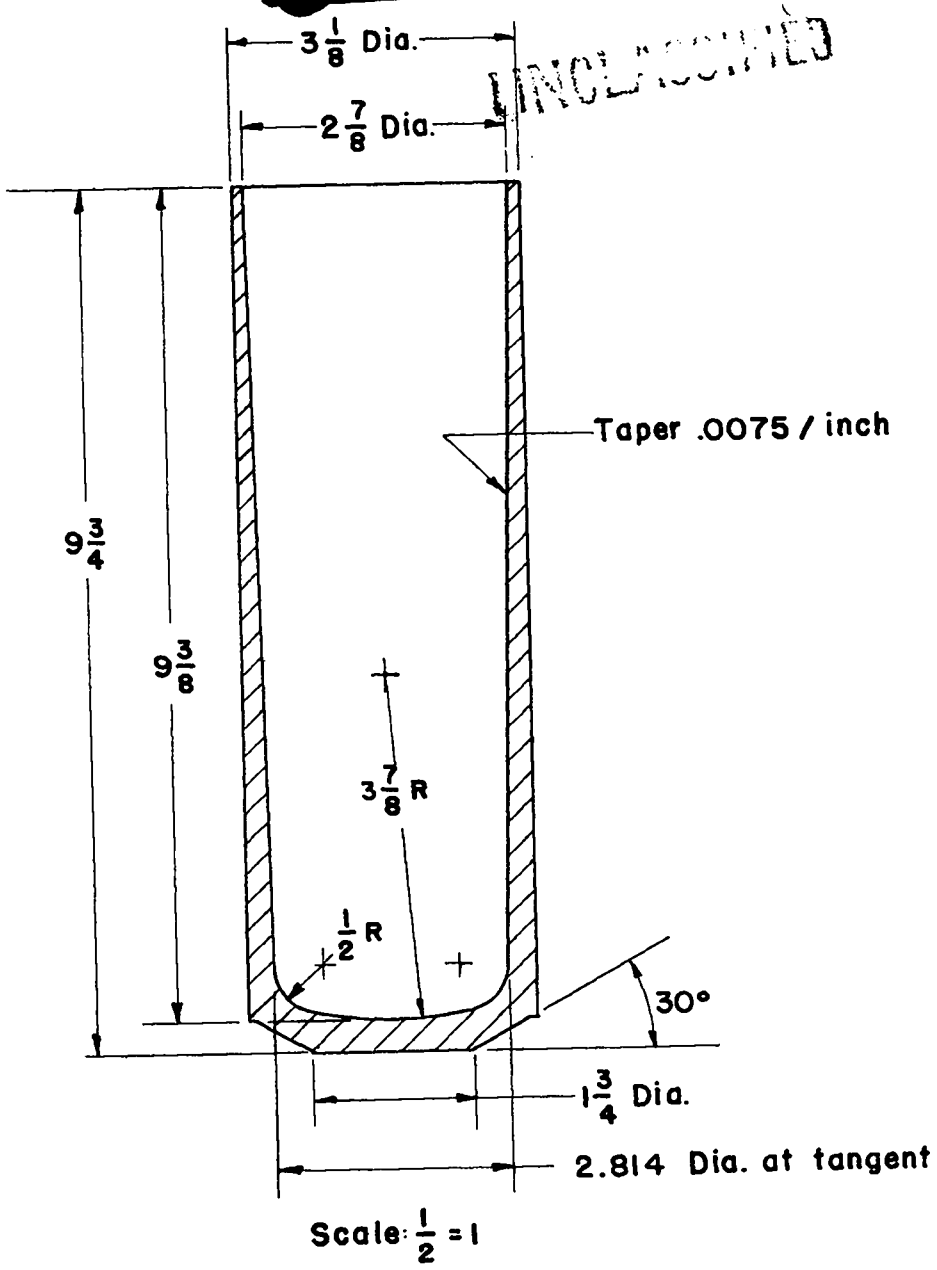

500 GRAM REDUCTION BOMB LINER
A-406

Figure A-6

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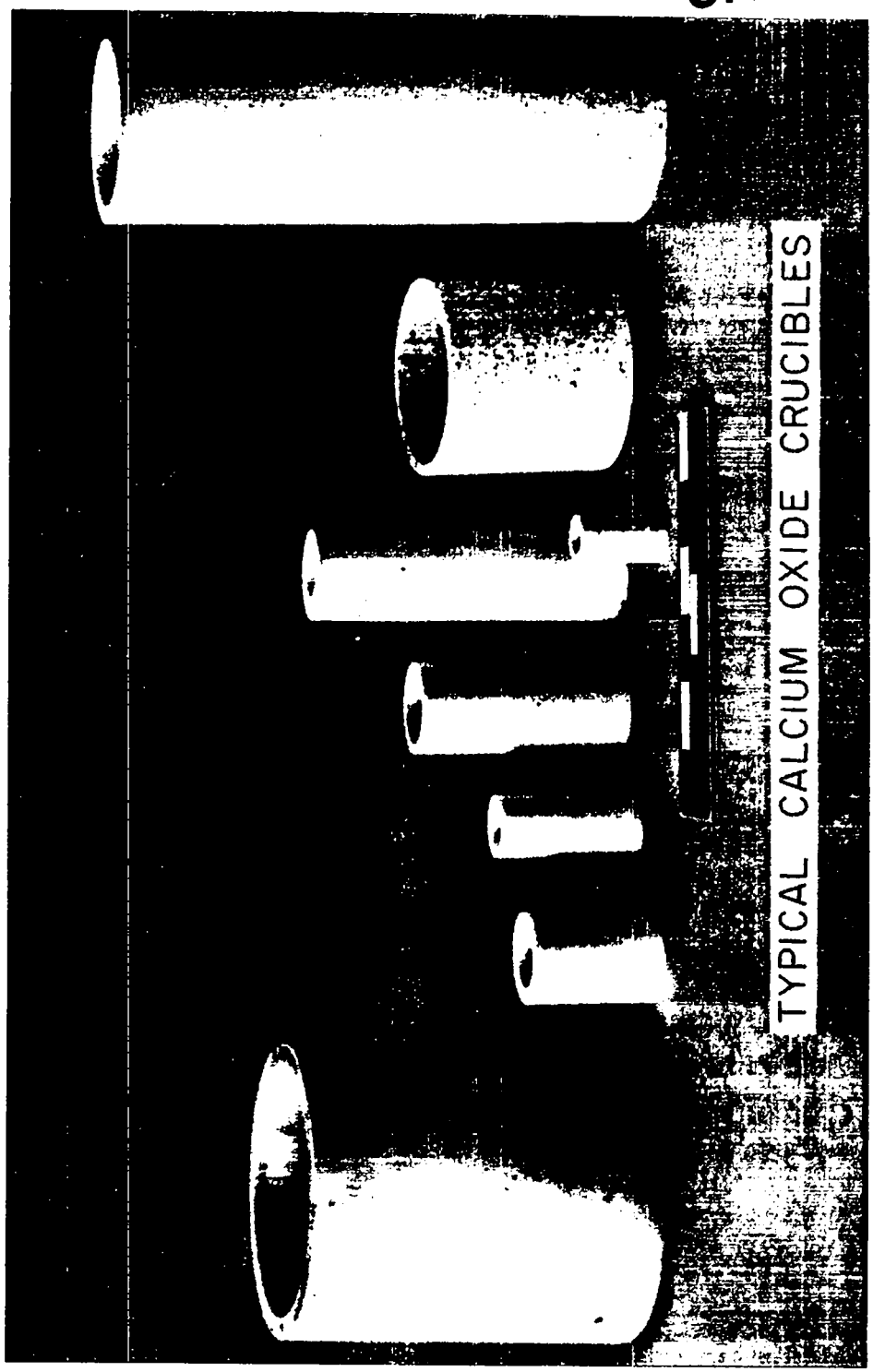

Figure A-7