CALCIUM METAL:

LABORATORY PREPARATION BY VACUUM METALLURGY

BY

GEORGE ROBERT COUCH

A THESIS
SUBMITTED TO THE FACULTY OF
THE DEPARTMENT OF CHEMICAL ENGINEERING
OF
NEWARK COLLEGE OF ENGINEERING

IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

OF

MASTER OF SCIENCE
IN CHEMICAL ENGINEERING

NEWARK, NEW JERSEY
JUNE, 1953

APPROVAL OF THESIS

FOR

DEPARTMENT OF CHEMICAL ENGINEERING

NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: ______________________

____

____

NEWARK, NEW JERSEY

JUNE, 1953

ACKNOWLEDGEMENTS

The conduct of this investigation was made possible by the use of National Lead Company, Titanium Division equipment and facilities for equipment construction and repair. The cooperation of many Titanium Division personnel in the supply and repair of equipment, and the preparation of spectrographs and photomicrographs of product samples is gratefully acknowledged. The success of this investigation was greatly aided by the counseling of Dr. C. L. Mantell.

TABLE OF CONTENTS

APPENDIX

LIST OF FIGURES

LIST OF FIGURES (Cont'd)

LIST OF TABLES

INTRODUCTION

Background

Calcium is a silvery, white metal of the alkaline earth group that is light, ductile and reactive. It has a specific gravity of 1.55 which is lighter than beryllium, magnesium and aluminum but heavier than sodium and the alkali metals. The metal, of 13-16 Brinell hardness(1), is soft enough to be cut by a knife, and ductile enough to be extruded from cast ingots or rolled into sheet. The principal commercial applications, however, are based upon the chemical reactivity of calcium. It is less reactive than the alkali metals and can be, in general, safely handled like magnesium. Calcium does oxidize in air and decompose water but may be allowed to come in contact with the skin without danger. Its handling characteristics, high melting point (851°C), and high vapor pressure (1439°C boiling point) account for an increasing commercial acceptance as a reactive metal. Industrial applications listed by Mantell and Hardy(1) include uses as an alloying agent, a graphite control in cast iron, debismuthizer of lead, decarburizer and desulphurizer for ferrous metals and alloys, dehydrating agent, deoxidizer of metals and alloys,

---

(1) Mantell, C. L. and Hardy, C., Calcium Metallurgy and Technology, Reinhold Pub. Co., 1945, Chapt. I & II

desulphurizer of petroleum fractions, vacuum getter and reducing agent. During World War II calcium was used for hydrogen production, and has been since used as a reducing agent for titanium metal production.

Until the year 1939(1) commercial production of calcium metal was limited to France and Germany. However, by 1948 calcium production in Canada exceeded 1.1 million pounds(2).

Calcium metal is produced commercially by (1) electrolysis of a fused salt bath(3) and by (2) thermal reduction of calcined limestone with aluminum in vacuum retort furnaces formerly used for magnesium production.

Although the vacuum metallurgy process for magnesium production was not economically competitive with the large scale electrolytic magnesium processes in the United States(4), the small production units of the Pidgeon or ferrosilicon retort process are easily adaptable to the production of calcium metal at costs which offer competition with the electrolytic process for calcium metal pro-

---

(1) Mantell, C. L. and Hardy, C., page 1

(2) Minerals Yearbook, 1951, United States Dept. of Interior

(3) Includes calcium cathode "carrots" produced from fused anhydrous calcium chloride as well as calcium recovery from electrolytic sludges.

(4) Klagsbrunn, H. A., Ind. & Engr. Chem., 37, No. 7, p608-615, July 1945

duction. Loomis(5) estimated in 1945 that the use of low cost calcined limestone and aluminum would enable the thermal reduction process to produce calcium metal to sell at an estimated 50 to 75 cents per pound in 1000 to 3000 pound per day quantities, and possibly as low as 25 cents per pound if very large tonnages were produced. These were 1945 estimates at a time when calcium carrots (electrolytic product) were sold at $1.75 per pound. Calcium metal was quoted(6) at $2.40 to $4.55 per pound, in less than ton lots, delivered, in May 1953; the higher price being quoted for a distilled metal.

Details of the five former DPC owned ferrosilicon process magnesium plants have been published which describe process studies and production costs for magnesium production. Details of the commercial calcium metal process have not, however, been described in equal detail. Staub(7) and Loomis(5) described the New England Lime Company calcium metal production in the former ferrosilicon process magnesium plant. The process duplicates the ferrosilicon process with the substitution of calcined limestone for calcined dolomite and the substitution of aluminum for fer-

(5) Loomis, C. C., Trans. Electrochem. Soc. 89, p207-216, 1946
(6) Iron Age, Vol. 171, p181, May 21, 1953
(7) Staub, F. H., Chem. & Met. Engr. 52, p94-6, August 1945

rosilicon as the reductant. Reaction temperatures ranged 1170°C to 1200°C for calcium metal production compared with the 1170°F temperature used for magnesium production. The reported 12 hour reaction cycle was slightly longer and the 20 micron operating pressure was about equal to that reported for Pidgeon ferrosilicon process magnesium plants.

The reactions used in these two processes were reported as follows:

(1) Magnesium Process

$$2\ MgO\cdot CaO + Si \xrightarrow[\text{Vacuum}]{1170°C} 2\ Mg + 2\ CaO\cdot SiO_2$$

(2) Calcium Process

$$6\ CaO + 2\ Al \xrightarrow[\text{Vacuum}]{1200°C} 3\ Ca + 3\ CaO\cdot Al_2O_3$$

The only detailed study of the vacuum metallurgy process for calcium metal production published at this time are the reports of the Government Chemical Industry Research Institute of Tokyo(8). These reports describe the use of a vacuum thermobalance of the quartz spiral type. The effects of reaction temperature, cycle time, blend ratios and vacuum upon calcium yield were reported. The investigation sought to determine the optimum condition of this reduction process. These Research Institute (Tokyo)

---

(8) Fujita, E., Reports Gov't. Chem. Ind. Research Inst., Tokyo, February, 1951

test data indicated that the laboratory furnace could in a two hour cycle simulate the recoveries that might be expected in the 12 hour cycle used in commercial practice. The optimum conditions outlined by this investigation indicated that best results were obtained at temperatures over 1200°C from charges containing calcium oxide and aluminum in the proportion of 6 mols of CaO to 4 mols of Al (100 percent in excess of the stoichiometric quantity of aluminum). A comparison of yields based on the calcium recovery from the calcium oxide charged indicated a slightly higher calcium recovery was obtained from the 6 mols CaO: 4 mols Al charges than was obtained from charges containing 6:6 and 6:2 mol ratios of CaO:Al. The report described many tests to determine the mechanics of the reaction which indicated that the calcium oxide was principally reduced by aluminum vapor at temperatures above 1200°C and by molten aluminum at low temperatures. The composition of the metal produced was not reported in the three reports of the Government Chemical Industry Research Institute of Tokyo which have been issued.

Present Investigation

The following report presents the results of a laboratory investigation of the thermal reduction process for the preparation of calcium metal. The investigation was conducted in a laboratory size vacuum retort of a size intermediate between the thermal balance, as used by the Japanese Industrial Chemistry Research Institute, and the pilot plant vacuum furnace as used for the study of the Pidgeon retort process for magnesium production. The tests herein reported provide a preliminary indication of the effect of the reduction temperatures and concentration of the aluminum reducing agent in the calcium oxide charge upon the calcium metal yield and the reduction efficiency of the aluminum.

TEST EQUIPMENT

The first problem was the design and construction of a vacuum reduction furnace in which the major process variables could be studied. A horizontal heat resistant, alloy retort with a removable heat radiation shield was adopted, after the fashion of the ferrosilicon or Pidgeon process vacuum retort. A mechanical vacuum pump system was sized to provide a nominal thirty minute pump-down to operating pressures in the range of 20 microns Hg.

A retort furnace capable of temperature control and operation within the 1100°C to 1200°C range, with retort temperature measurement by potentiometer with a platinum-13% Rhodium thermocouple compensated for the cold junction temperature, was obtained. The condenser system and retort vacuum seal system were designed for this specific installation to provide flexibility in the control of the calcium condenser temperature and to provide a simply constructed and easily removable metal condenser.

The relative locations of the briquette charge, radiation shield, condenser, as well as choice of the retort vacuum seal system, vacuum pumps, retort mounting, condenser size and cooling were modified to provide best operating conditions as determined by the initial eight test runs which were conducted for this purpose (Appendix C, Table 3).

The laboratory scale vacuum reduction furnace and auxiliary equipment which was constructed and assembled for these preliminary tests are shown in Figures 1 - 4. The following principal pieces of equipment were used:

(1) Lindberg electric furnace, Model CF-1 and Time Relay switch
(2) Vacuum retort, radiation shield and condenser
(3) Vacuum pumps, (a) Welch Duo Seal and (b) Cenco Hyvac
(4) McCleod Vacuum gages (Florsdorf type)
(5) Potentiometer (L & N)

Furnace

A single tube Lindberg combustion furnace designed for 1370°C combustions, with three "Globar" resistance rods, was used for the retort furnace. The furnace has an effective heating length of 8-3/4 inches of which the middle 4½ inches are maximum and most uniform in temperature. The power rating was 1500 watts, the heat up time at full load was about four to five hours depending upon the ultimate temperature attained. Fine and coarse rotary tap switches permitted adjustment of power input rates and compensation for changes in element resistance.

The furnace was equipped with a Platinum-13% Rhodium thermocouple which was located in the heating chamber below the combustion tube space.

The conventional combustion tube and adapters were

EQUIPMENT ASSEMBLY

Fig. 1 - Assembly

Fig. 2 - Assembly

Fig. 3 -Vacuum Pumps & Furnace

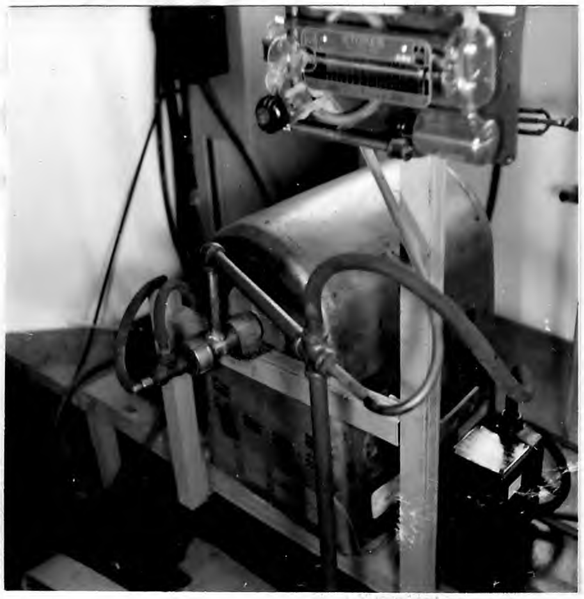
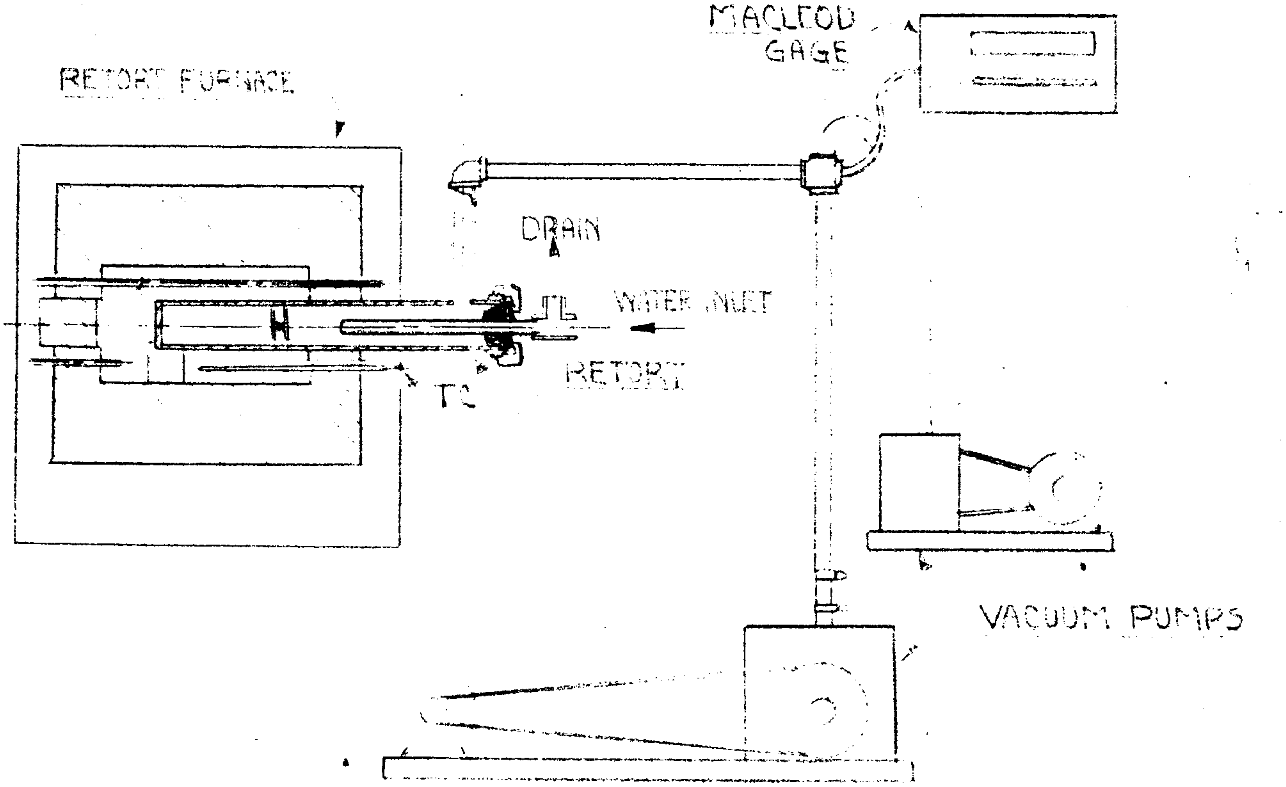


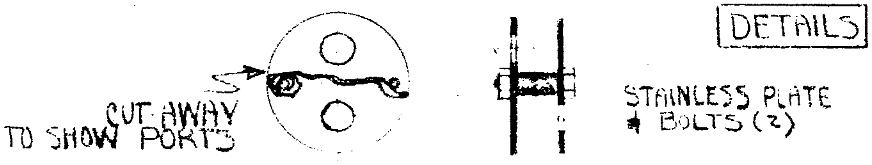
Fig. 4 -Retort Furnace & Vacuum Gage

FIGURE · 5

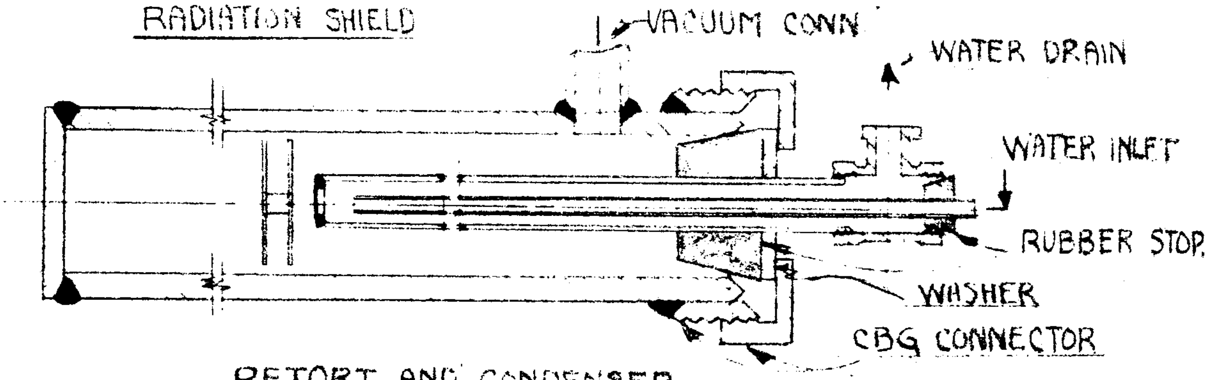
VACUUM REDUCTION EQUIPMENT



DETAILS



RADIATION SHIELD



RETORT AND CONDENSER

replaced with an alloy steel retort, located as shown in Figure 4 page 9, and Figure 5 page 10.

A Tork time relay switch was used to turn the furnace on five hours before anticipated use.

Retort

The available Lindberg GF-1 furnace which could accommodate a tube 1-3/4" in outside diameter when used without the usual combustion-tube adapters, determined the maximum diameter of the reduction retort. The 4½ inch maximum temperature zone of this furnace determined the size and location of the reduction zone in the retort.

The retort, Figure 5 and 6, was constructed by welding a disk of ¼ inch thick plate to one end of the 1¼" ID x 14½" long pipe section. A ½" diameter hole was drilled into the retort 1½ inches from the open end of the retort. A 5 inch length of ⅛" pipe was welded onto the retort at this point to serve as the vacuum connection. A ½" long threaded section of CBG connection was cut, tapered and welded to the outside surface of the tube at the open end of the retort. The CBG connection and vacuum connections were carefully welded to prevent obstruction of the retort opening, or marking of the open end of the retort so that a rubber stopper inserted in the end of the retort would seat in the original cut pipe. This threaded section was attached to the retort to receive the CBG cap which was

VACUUM RETORT

Fig. 6 - Vacuum Retort

assembled on the condenser section, Figure 8. This seal which was obtained with the CBG connector was satisfactory for the 5 micron minimum pressure during vacuum operation and was satisfactory for 100 psi air pressure for leak detection.

The condenser section, Figures 7 and 8, consisted of an 8 inch length of 3/8 inch standard black iron pipe, sealed at the extreme end with a plug of 1/8 inch plate, Figure 5. The plugged end of this pipe was the metal condensing section. The plug was welded in place and the whole end was ground and polished to a smooth surface. A 3/4" diameter washer was drilled to fit over the condenser pipe; this washer was forced on and ground to a 3/16 inch width. This washer served as a divider or baffle on the condenser to divide the metallic calcium which collected on the sealed end from the sodium and potassium which collected behind the collar, on the cold stopper end of the condenser. This washer was located 1½ inches from the end of the condenser, as shown in Figures 5 and 8, by trial. A No. 8 rubber stopper was drilled to accommodate the 3/8 inch pipe and sealed on the pipe with Glyptal lacquer. By trial this stopper was located to allow the condenser to project 6½ inches into the retort. The CBG connector cap, and a special washer which was cut to fit inside of the CBG connector cap, on the pipe, are shown in Figure 7. This

RETORT CONDENSER

Fig. 7 - Disassembled Condenser

Fig. 8 - Assembled Condenser

cap when assembled on the condenser pipe as shown in Figure 8 forced the rubber stopper into the retort to form a vacuum tight seal. The condenser was cooled by passing water into the condenser pipe through the 1/8" copper tube shown attached to the pipe tee in Figure 7 disassembly view. The copper tube was assembled to fit in the center axis of the condenser pipe, water passing down the center, around and out the ¼ inch top fitting of the pipe tee.

The retort was used at temperatures up to 1200°C and under a vacuum so that materials and methods of construction were of great importance. Three different retorts were used in the conduct of these tests. The first retort was constructed of FA 20, a 29% Ni - 20% Cr alloy steel. The second retort was constructed of Incoloy, a 35% Ni - 20% Cr alloy steel (International Nickel Company). The third retort was constructed of ordinary steel pipe. The alloy pipes were capped and welded with Inconel. The ordinary steel pipe was gas welded with ordinary steel rod; three attempts to alloy weld this cap on the ordinary steel failed to yield pressure tight welds.

The radiation shield shown in Figure 5 consisted of two 1½" diameter 16 gage Incoloy plates, each drilled with an off-center ½" diameter hole. The two plates were drilled and fitted together with stainless steel nuts and bolts. The 3/8" spacing of these two plates was fixed by 3/8" lengths of 1/4" pipe spacers on each of the two bolts which held the two plates together. The plates were assembled so that the off-center holes were not opposite each other. Direct radiation from the charge to the condenser and rubber stopper seal was prevented without an objectionable restriction of gas flow from the charge.

Vacuum Pumps

Mechanical vacuum pumps which were rated at 5 and 0.3 micron ultimate pressure were used to evacuate the retort and maintain pressures of 40 to 5 microns Hg. Two pumps were used in parallel to give a quick vacuum pull down to an operating pressure. The two pumps used in this test were described as follows:

(a) Welch Duo-Seal (1403-B). A single stage rotary vacuum pump with ½ Hp motor, rated at 100 liters/minute (free air displacement); capable of pumping to 5 microns of mercury pressure (0.005 mm Hg).

(b) Cenco Hyvac (P8830). A single stage rotary vacuum pump with ¼ Hp motor, rated at 10 liters/minute (free air displacement); capable of pumping to 0.3 microns of mercury pressure (0.0003 mm Hg).

Vacuum Gage

Vacuum was measured in the ½ inch diameter vacuum line, 18" from the retort connection and 24" above the vacuum pump intake. Vacuum was measured with a McCleod gage, (Flosdorf type, Gage No. 276 BB, Lot B2191J, manufactured by the F. J. Stokes Machine Company, Philadelphia). The vacuum gage was checked, for accuracy, against another McCleod gage and with a factory checked Pirani thermocouple type gage. The McCleod gage incorporated a dust filter and drier in the vacuum line to protect the gage mercury from contamination by dust and/or water vapor.

Temperature Measurement

A Pt-13% Rhodium-platinum thermocouple, with protection tube was used with an L & N potentiometer to measure furnace temperature. The hot end of the thermocouple was located 4½ inches inside the furnace wall, about 1" below the center of the vacuum retort. The potentiometer was compensated for the cold junction temperature as measured at the potentiometer thermocouple terminals.

TEST PROCEDURE

The second problem was the determination and standardization of test procedures to obtain reproducible process results. The investigation was confined to the specific process in which calcium metal is produced from a briquetted charge of calcium oxide and aluminum which has been heated to a temperature of the order of 1100°-1200°C under a vacuum. The calcium metal is sublimed or distilled out of the heated briquette charge and collected on a water cooled condenser as solid, crystalline calcium metal.

Preliminary tests in the reduction retort indicated that four one-inch diameter briquettes which would supply about 10 grams of calcium metal to the condenser could be satisfactorily used. Therefore, the following test procedure was adopted as the basis of these tests.

Raw Materials

A reagent grade ground calcine analyzing 94.09% CaO, 1.41% MgO, 0.49% R_2O_3, 1.03 acid insoluble, and 2.87% loss on ignition was used for all reduction tests. The reducing agent was a granular analytical grade aluminum of 99.5% (minimum) aluminum and 0.04 magnesium content.

The calcine was a milled minus 100 mesh size, with a pack bulk density of 1.25 grams/cc (79 lbs/cu. ft.). A

20-30 mesh granular aluminum of a pack bulk density of 0.61 grams/cc (39 lbs/cu. ft.) was used as the standard reducing agent. An 8-20 mesh granular aluminum of a pack bulk density of 0.40 grams/cc (26 lbs/cu. ft.) was used for comparison tests. Raw material data are tabulated in Appendix A.

Charge Preparation

All raw materials were received and kept in sealed jars and every effort was made to reduce the time of exposure of the charge materials to the atmosphere to avoid H_2O and CO_2 pickup. Calcine and aluminum were weighed out in ½ retort charge quantities and were immediately sealed in 2 ounce jars in which they were then blended. Each half charge was removed from the sealed jar only for briquetting, weighing and for immediate measuring and charging into the furnace.

All charges were prepared with the same weight of calcine, weighed on the analytical balance, to which the proportional weight of aluminum was added as weighed on the analytical balance. Charges were weighed in one half charge quantities to insure uniformity of blend and simplify regulation of briquette size. The base quantities of calcine and aluminum weighed for each charge of the respective blend ratios were as follows:

Blend Ratio	Calcine	Aluminum	Blend Weight
6:2	15.0266 grams	2.2994 grams	17.3260 grams
6:4	15.0266 grams	4.6000 grams	19.6266 grams
6:6	15.0266 grams	6.8981 grams	21.9247 grams

These blend ratios are nominal values as the metal charge compositions were initially calculated on the approximate suppliers analysis. The exact blend ratios as recalculated from the analysis of the representative sample of the calcine used in these tests are compared as follows with the nominal blend ratios:

Nominal	Corrected
6:2	6:2.01
6:4	6:4.03
6:6	6:6.05

The weighed charges were shaken in 2 ounce sample bottles until the mixture of calcine and aluminum were visually uniform. Each 2 ounce jar contained one half charge, or a 2 briquette quantity of charge. Each jar of blend was divided in half and briquetted to form two one inch diameter by approximately one quarter inch thick, pill shaped, briquettes. In this way each pair of briquettes would have the same combined thickness although the individual briquettes of each pair might differ.

All briquettes were prepared at pressure of 25 tons per square inch (39,500 pounds force on a one inch dia. die plunger) in hand filled plunger die, in a Blackhawk hydraulic press of the type normally used for metallurgical sample mounting. A charge that was briquetted in this press is shown in Figure 9. These briquettes were sufficiently strong to withstand, for test purposes, a ten foot drop to a concrete floor; repeated dropping produced chips or cracked briquettes but produced no powdered fines. The 25 ton pressure was arbitrarily used although preliminary briquetting tests indicated that lower pressures could be used with these specific materials and briquetting process. No briquette binders were used. The briquette die was lubricated with graphite.

Some blend was lost in the briquetting so that each pair of briquettes was weighed on the analytical balance and resealed in the 2 ounce jar for storage until use.

Charging

The briquettes were removed from sealed jars, measured and charged into the furnace one briquette at a time. The briquettes were placed in a row, one briquette per inch, to spread over four inches of length of the retort hot zone. This was measured at 10½ to 14½ inches from the outside end of the retort.

A double plate ("Incoloy") radiation shield was located at 9½ inches from the retort cold end after preliminary tests at shorter distances. This shield screened the condenser and retort vacuum seal (rubber stopper) from direct radiation of the retort hot zone. The radiation shield

BRIQUETTED CHARGE

Fig. 9 - Briquetted Charge

was located in the retort as shown in Figures 10 and 11.

The condenser, which was coated with graphite, before charging, was inserted into the retort to seat the rubber stopper into the cold end of the retort, as shown in Figures 10 and 12. The condenser extended 6½ inches into the retort. The condenser cooling water was adjusted to 1-2 liters per minute.

The vacuum pumps were started after the condenser stopper was seated in the retort as shown in Figure 13.

Reduction Cycle

The reduction time was measured from the time a 40 micron Hg pressure was measured with the McCleod gage. The vacuum pumps were kept in continuous operation during the reduction cycle.

Temperature control was by manual adjustment of the power input to the "Globar" resistance elements. Temperatures were controlled to within ± 10°C of the chosen operating temperature as measured by a Platinum-13% Rhodium thermocouple located 3/4 of an inch below the retort in the maximum temperature zone.

The reduction cycle was ended by stopping the vacuum pumps and breaking vacuum to atmospheric pressure.

The condenser was withdrawn and allowed to cool to

EQUIPMENT ASSEMBLY

Fig. 10 - Radiation Shield

Fig. 11 - In Place

Radiation Shield Installation

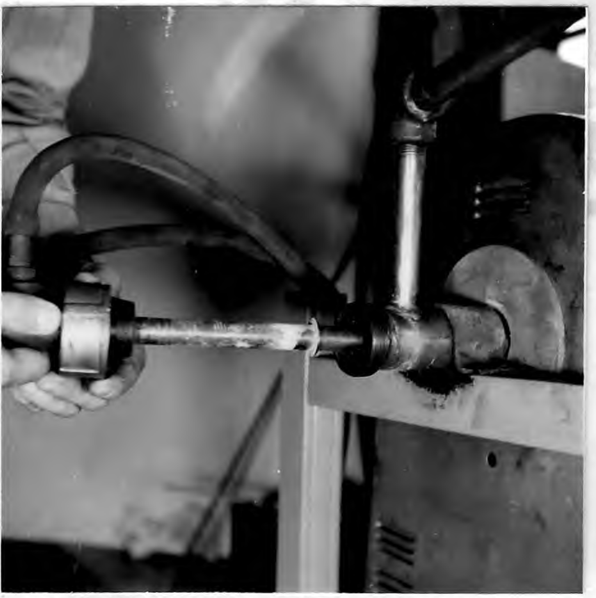


Fig. 12 - Condenser

Fig. 13 - In Place

Condenser Installation

room temperature. The calcium crystals were then scraped off of the condenser and collected and sealed in a 2 ounce sample jar. The briquette residue which was still in briquette form, was removed, cooled and then placed in a 2 ounce sample jar for storage.

SUMMARY OF VACUUM REDUCTION TESTS

The following equation is considered(5) (8) to represent the overall reaction between the calcium oxide and the aluminum for the production of calcium metal:

$$6\ CaO + 2\ Al \xrightarrow[Vacuum]{Heat} 3\ Ca + 3\ CaO \cdot Al_2O_3$$

Vacuum reduction tests were conducted to indicate how the rate of this reaction changed with reaction time, temperature and charge composition. Reductions were conducted at temperatures of 1100°C, 1150°C and 1200°C for test times ranging from ½ to 8 hours under vacuum. Charges composed of the equated 6 mols of CaO:2 mols of Al, 6 mols CaO:4 mols Al and 6 mols CaO:6 mols Al were tested at 1200°C reaction temperatures over ½ to 8 hour cycle times.

The experimental data on forty-eight reduction tests which were conducted for this study are summarized in Table 3 of Appendix C. These data include tests conducted to test condenser design and test procedures which include metal losses caused by equipment failures (vacuum leaks) and fires that damaged the calcium yield. The useful metal yields are extracted from the Appendix C, Table 3 and summarized in the following tables and graphs.

Metal Yields are shown as percent calcium recovered

(5) Loomis, page 3
(8) Fujita, page 4

from the theoretical amount of calcium in the reduction charge. It should be noted that this method of representing yields differs from that used by Fujita(8); Fujita expressed calcium yield as percent of CaO in the reduction charge.

Calcium yields are also expressed in terms of the efficiency of the reducing agent which is calculated from the weight of calcium recovered as compared with the stoichiometric calcium metal equivalent of the aluminum in the charge. Expressing completeness of the reduction reaction in terms of the efficiency of the reducing agent was a standard practice in reference to the ferrosilicon of Pidgeon process for magnesium production. The efficiency of the reducing agent is of commercial significance in the calculation of the economic charge composition, the aluminum being the most expensive reduction charge ingredient.

Effect of Blend Ratio and Cycle Time on Reduction

The stoichiometric quantity of CaO and Al indicated by the preceding equation is 6 mols of CaO to 2 mols of Al. Investigations of the effect of CaO:Al mol ratios of 6:6, 6:4 and the stoichiometric 6:2 upon metal yield are tabulated in Table 1 and graphically represented in Figures 14 and 15. These tests were conducted at a temperature of

---

(8) Fujita, page 4

1200°C for reduction cycle times of ½ to 8 hours under vacuum.

TABLE I

Effects of Blend Ratio and Cycle Time on Reduction

(A) Calcium Yield

Hours under Vacuum	Calcium Recovery, Percent 6:2	6:4	6:6
½	--	8.0	9.5
1	7.1	14.5	22.5
2	8.3	25.0	--
3	15.4	34.9	45.9
5	--	47.5	--
8	31.9	45.0	--
8-3/4	35.2	--	--

(B) Aluminum Efficiency

Hours under Vacuum	Aluminum Efficiency, Percent 6:2	6:4	6:6
½	--	7.8	6.1
1	13.8	14.-	14.7
2	16.1	24.3	--
3	30.0	33.9	29.7
5	--	46.1	--
8	62.1	43.7	--
8-3/4	68.3	--	--

Based on calcium recovery, these data indicate a higher yield from the higher aluminum content charges, 6 mols CaO:6 mols Al and 6 mols CaO:4 mols Al. The spread between these Figure 14 curves is greater than that indicated for similar charges in the thermobalance tests reported by Fujita(8).

---

(8) Fujita, page 4

FIGURE 14

EFFECT OF BLEND RATIO ON CALCIUM RECOVERY

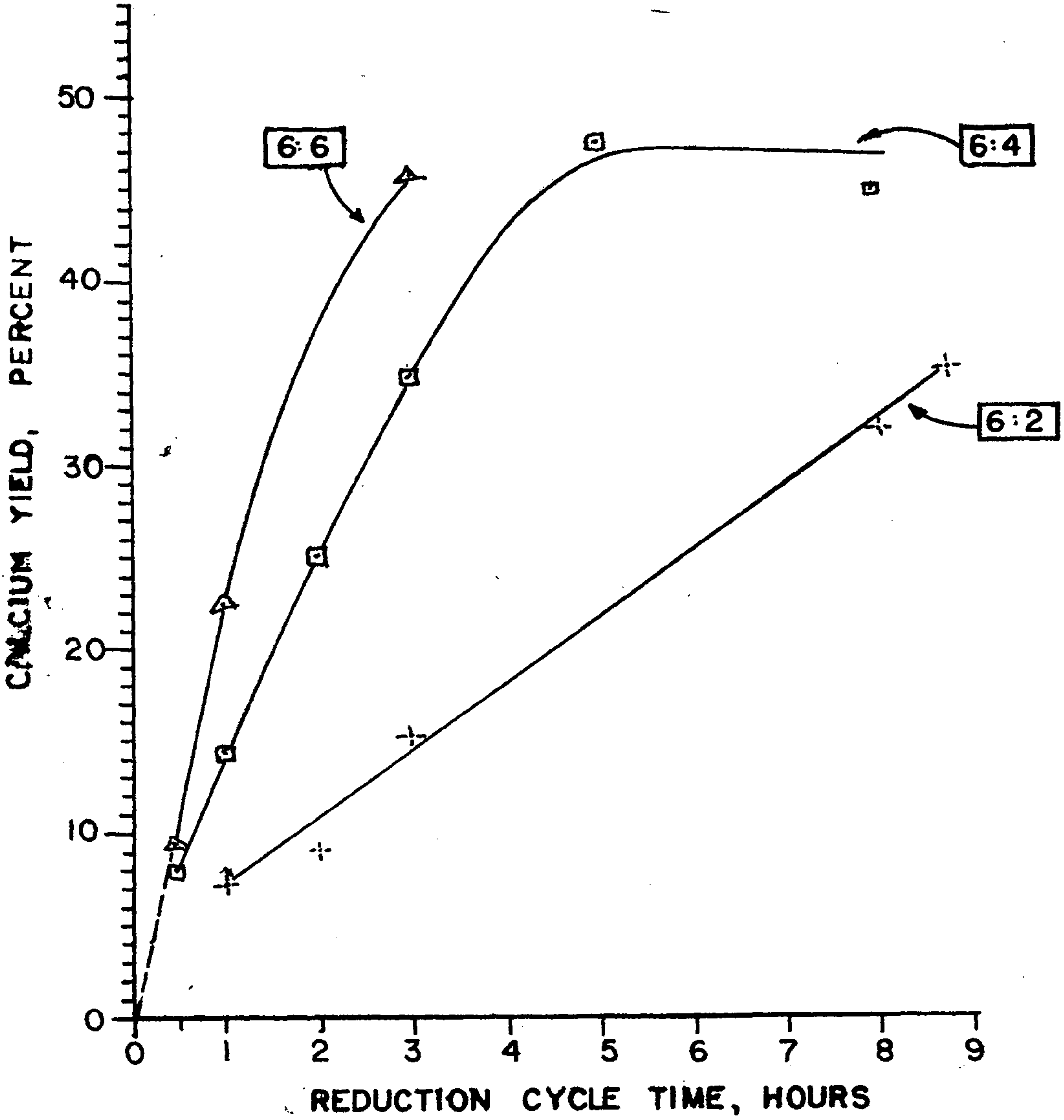
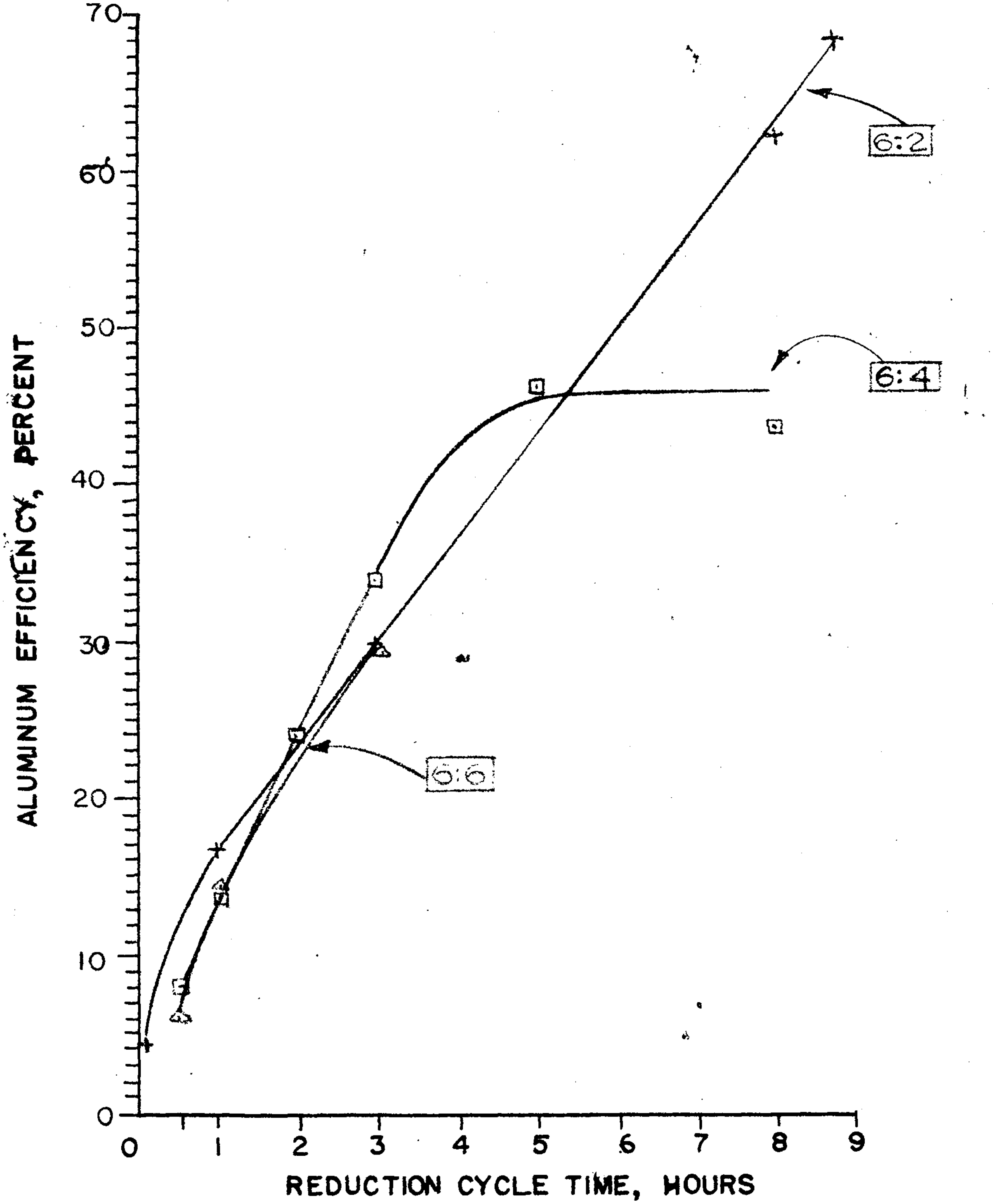


FIGURE · 15

EFFECT OF BLEND RATIO ON ALUMINUM EFFICIENCY



Inspection of these data in terms of the aluminum efficiency, as shown in Figure 15, indicates that the higher rates of calcium recovery shown by the 6:4 and 6:6 blends were obtained at the expense of the efficiency of the reducing agent. The 6:2 blend produces calcium at a lower rate, but achieves the highest aluminum efficiency. The choice of which of these or intermediate charge compositions is the optimum reduction charge could only be determined by an economic balance of the manufacturing costs for a specific installation.

Effect of Temperature and Cycle Time on Reduction

The effect of furnace temperature upon metal recovery was investigated. Metal yields at 1100°C, 1150°C and 1200°C for cycles of ½ to 8 hours under vacuum were determined as indicated by the Table 2 data and graphically represented in Figure 16. These tests were conducted with the basic charge proportions of 6 mols CaO:4 mols Al, (double the stoichiometric aluminum requirement).

TABLE 2

Effect of Temperature and Cycle Time on Reduction

(A) Calcium Yield

Hours under Vacuum	Calcium Recovery, Percent		
	1200°C	1150°C	1100°C
½	8.0	8.6	8.4
1	14.5	13.3*	8.6
2	25.0	16.7**	14.7
3	34.9	22.3	19.6
5	47.5	--	--
8	45.0	34.7	--

(B) Aluminum Efficiency

Hours under Vacuum	Aluminum Efficiency, Percent		
	1200°C	1150°C	1100°C
½	7.7	8.3	8.1
1	14.0	12.9*	8.4
2	24.3	16.2**	14.3
3	34.0	21.6	19.0
5	46.1	--	--
8	43.7	34.3	--

* 1 hour 10 min. under vacuum
** 1 hour 45 min. under vacuum

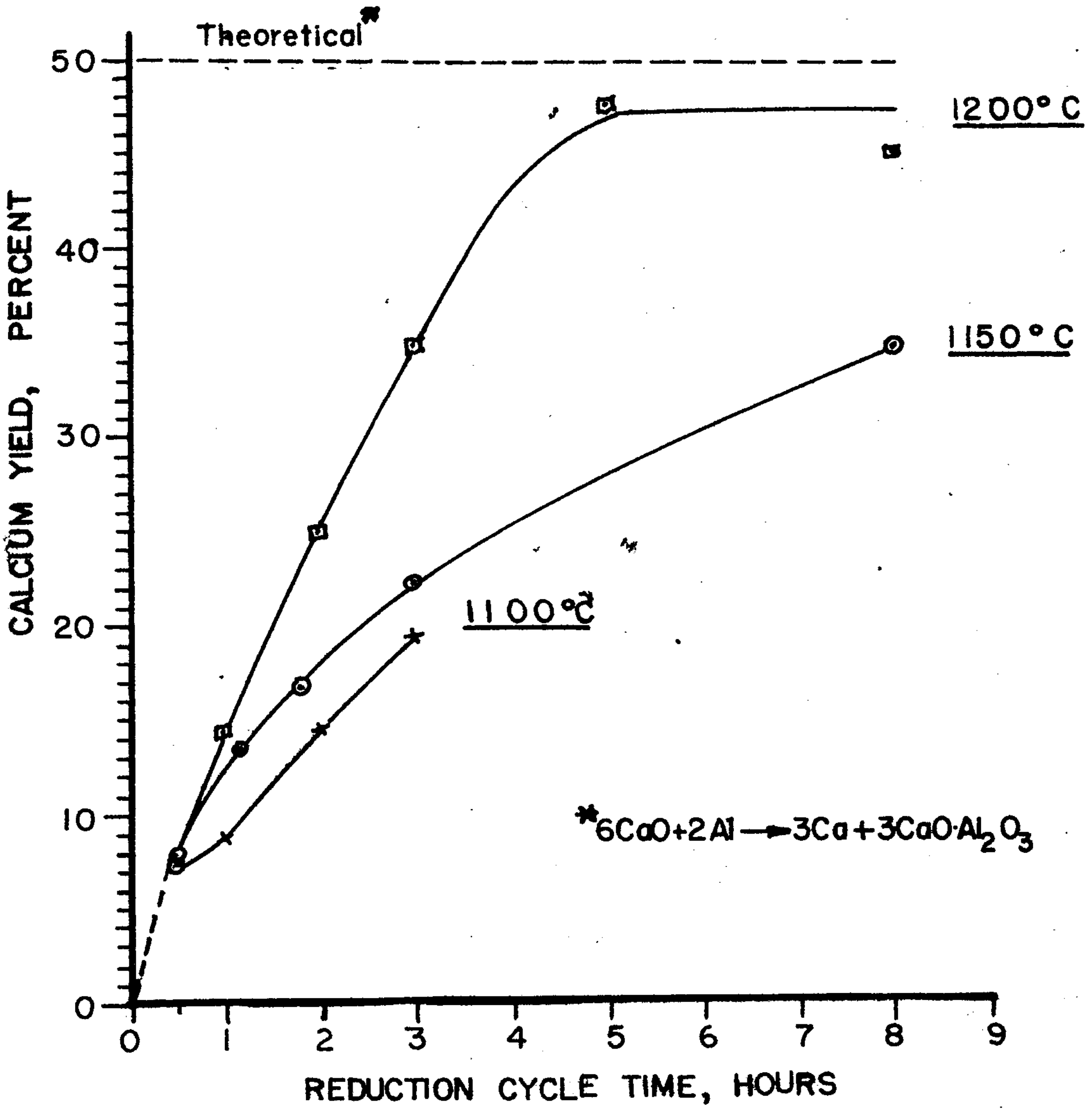
The calcium yield curve, on Figure 16, so nearly coincides with the aluminum efficiency data for this 6:4 blend ratio that a separate aluminum efficiency curve was not plotted for these Table 2 data.

These data show that the maximum economic reduction temperature was desirable. However, the choice of this temperature would be a function of the reduction retort life at these furnace temperatures.

The 1200°C maximum temperature approaches the 1225°C

FIGURE· 16

EFFECT OF TEMPERATURE ON CALCIUM RECOVERY



*$6CaO + 2Al \rightarrow 3Ca + 3CaO \cdot Al_2O_3$

recommended(9) maximum temperature usable in the alloy retorts of the Pidgeon or ferrosilicon process magnesium plants, and slightly above the 1170°C -- 1200°C range reportedly(5) used in the New England Lime Company retorts when used for calcium metal production.

---

(5) Loomis, page 3

(9) Pierce, W. M.; Waring, R. K.; Fetterolf, L. D.; and Mahler, G. T., <u>Metals Technology</u>, T.P.1707, August 1944

DISCUSSION

Vacuum Retort

Attempts at aluminum and silicon reduction of magnesium and calcium oxides by Matignon failed during World War I, for lack of heat resisting steels and vacuum pumps$^{(10)}$. The success of the alloy retorts introduced for magnesium production in World War II does not imply that all problems have since been solved. Two alloy steel retorts, one a 29% Cr-20% Ni (FA 20) and one a 35% Ni-20% Cr (International Nickel Company "Incoloy"), were used in the accumulation of these data. One ordinary steel pipe retort was also used in an attempted emergency substitution. Observations on the working lives of only one retort of each of three different steels offer only a limited basis for comparison of construction materials. However, based on the following data it was clearly evident that the use of anything but alloy steel for any extensive high temperature vacuum work in this furnace was a waste of time and materials. All three materials were standard pipe sizes; heavier walled sections would have afforded longer service time from even the ordinary steel retort:

---

(10) Kroll, W. J., Metal Industry(London), 73, October,1948

Retort Material	Hours above 1100°C[(a)]	Heating Cycles[(b)]
1) FA 20 (29Cr-20Ni)	70	9
2) Incoloy (35Ni-20Cr)	120	5
3) Carbon steel pipe	10	3

(a) Life of retort in hours of vacuum tightness
(b) Number of times retort was heated from room temperature to 1100°C or better

The FA-20, 29%Cr-20%Ni, alloy was used solely because it was the highest Cr-Ni alloy pipe section available at the initial construction of this experimental furnace. The Figure 17 photograph shows the corrosion failure that occurred in this alloy section. The areas of highest corrosion were directly opposite the bottom "Globar" furnace heating elements. Although no contact occurred between the heating elements and the retort, some local overheating is evident. The 4½" length of the corroded area is worth noting as it attests to the length of the high temperature zone in the retort.

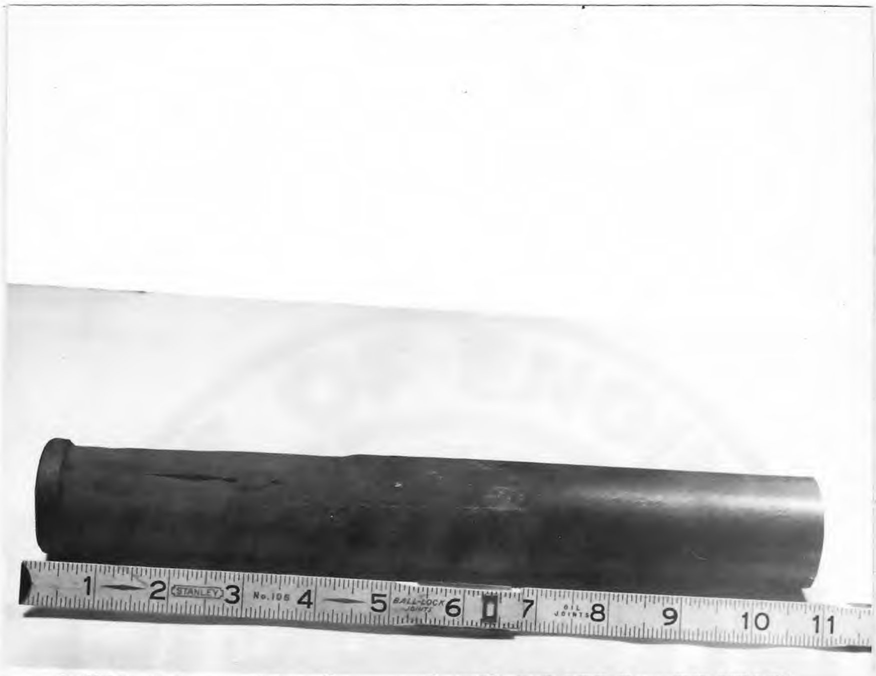
The 35% Ni-20% Cr alloy was used because it approached the 35Ni-15Cr alloy used for vacuum retorts for the 1170°C service in the Pidgeon magnesium process plants. The retort of this alloy failed in this experimental furnace when a refactory support failed and allowed it to drop in contact with the bottom two "Globar" electric resistance heating elements in the retort furnace. The general appearance and measured corrosion rate of the undamaged part of the retort indicated that this failure occurred within one half of the expected life under these conditions. The photograph, Figure 16, of the damaged retort section shows the localized failure of the 35Ni-20Cr alloy retort.

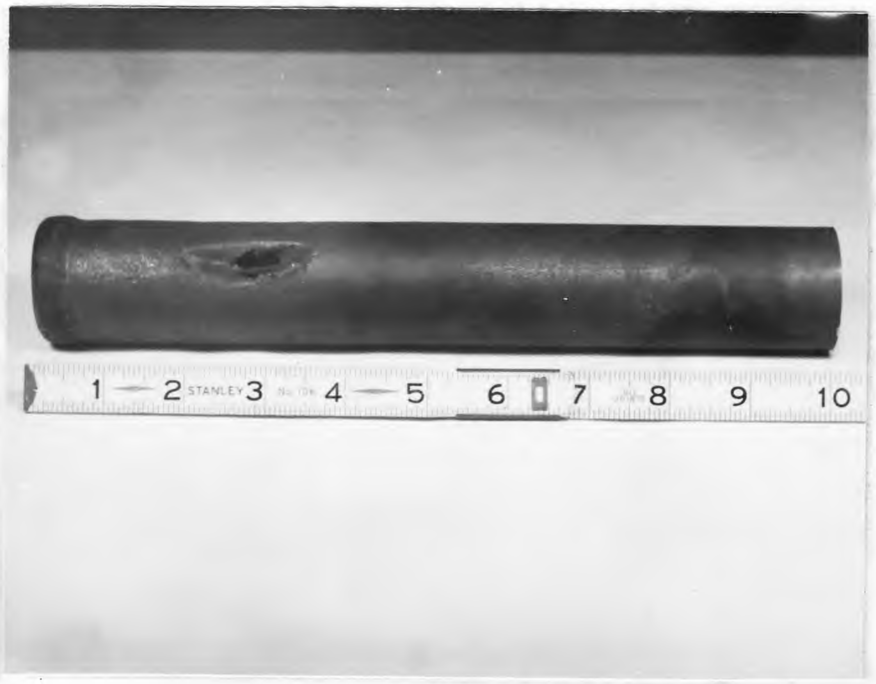
It should be noted that the retort furnace was always heated at the maximum power input rate. The retorts were thereby heated from room temperature to 1100 to 1200°C within 4 to 5 hours. The retort was cooled to room temperature after each series of test runs.

The retort was centrally located between the three "Globar" heating elements, and clamped by an outside bracket, to hold it for even heating and to prevent breakage of the "Globar" by movement of the retort during the retort charging or discharging operation. The retort was supported in the extreme hot end by an insulating fire brick pier cut for this purpose. It was the shrinkage of this supporting pier that allowed the Incoloy retort to be lowered against the bottom "Globar" elements.

Both the Incoloy and the FA-20 alloy retorts were welded with Inconel rod, and capped with an Inconel plate welded to seal the hot end of the retort. The Inconel welds were less corroded than the FA 20 tube and about equally corroded with the Incoloy tube. Arc welds were used; only two weld patches were required to repair the

RETORT FAILURES





alloy retorts.

The ordinary steel pipe failures all occurred in the hot end weld. The ordinary steel welds had so many vacuum leaks that two different caps were successively welded and then cut off before a vacuum tight weld was obtained with a third cap. The arc welds with ordinary steel held a vacuum for only 6 hours. The third and last weld, a gas weld, held for about 24 hours. The failures were through slag inclusions in the weld metal which either failed to hold a vacuum when first tested or which were exposed as the weld metal scaled away when heated to 1100°C - 1200°C.

The quality of a vacuum tight weld is determined by the skill of the individual welder to build a weld that is free of flux inclusions all the way through. The diligent use of the chipping hammer is as important as the proper use of the welding machine in the production of a vacuum tight weld for high temperature service.

Vacuum leaks were located in the cold retort by applying a soap solution to the suspected area while maintaining about a 100 pound air pressure in the retort. Soap bubbles formed where the air leak occurred. When such leaks were repaired the weld metal was ground through the slag inclusion to solid metal before the weld patch was applied. Weld repairs built on solid base alloy did not leak.

All pipe connections were sealed with a Glyptal lacquer. All rubber to metal connections were sealed with a vacuum grease "Celvacene" (Distillation Products Company).

The cold, outside end of the retort which held the water cooled condenser was sealed to the condenser pipe with Glyptal. The stopper and the retort opening were cleaned of dust and coated with Celvacene to insure a vacuum tight seal. The stopper was held in the retort by both the vacuum and the CBG screw connector. The vacuum was usually enough, with the CBG fitting being used to insure a tight seal in occassional doubtful cases and for pressure testing of the retort. The retort extended 6 inches outside of the refractory furnace wall so that the alloy retort was never hot enough to damage the rubber stopper. Some difference was noted in the temperature of the cold end of the retorts between that of the alloy retort as compared with the ordinary steel retort. Where the cold end of the alloy retort, at the rubber stopper, was perhaps 150°F with the low thermal conductivity alloy, this temperature was in the order of 220° when the more conductive ordinary steel retort was used. This temperature difference of the retort in contact with the rubber stopper was sufficiently higher with the ordinary steel retort to cause a noticeable softening and marking of the stopper by the hot retort that did not occur with the alloy retort.

Vacuum System

Two mechanical vacuum pumps with a combined pumping capacity of 110 liters per minute of free air were connected to the retort. This pump capacity enabled a pump-down to 40 microns pressure within an average time of 8 minutes, with pump-down times ranging from as short as 2 minutes to as long as 25 minutes. Excluding vacuum leak conditions the rate of pump down was slowest when pumping down a retort for the first time after a furnace shut down. It was concluded that this was explained by the initial outgassing of the retort and by water vapor in the pump oil. Part of this could be corrected by changing the vacuum oil or by running the pumps one or two hours before test use. The pump-down rate and ultimate vacuums improved with each successive test run in an uninterrupted series of runs. This condition was used to advantage, when possible, to obtain the minimum pump down time for the test runs of shortest cycle time. The purpose of timing the vacuum cycle from 40 microns pressure rather than from the initial "vacuum-on" time was to minimize the detrimental effect of very slow pump down on the very short cycles. Since the pressure measured in the vacuum line is different from the pressure existing at the evaporating or subliming surface of the charge, the choice of starting vacuum was rather arbitrary. The 40 micron pressure gave better correlations between cycle times than when cycle times were measured from the initial "vacuum-on" indicating that this pressure was nearer the evaporation pressure than the initial time and therefore more nearly measured the time in which calcium was evaporated and sublimed from the reduction charge. The fact that metal was produced in subsequent runs at pressures as high as 70 microns indicated that a higher starting pressure could have been used, however, the pump down time between these pressures was not significant in these tests. The point of starting pressure is only of interest to those who may use this or similar equipment to continue or compare these tests.

Vacuum Reactions

The reduction residue retained the shape and size of the original briquettes charged. The spent briquettes were generally dark grey in color, and were considerably stronger and harder than the original briquettes. Attempts to dry polish the spent briquettes for microscopic examination failed when the briquette cut the grinding compound off of the backing. If left exposed to the atmosphere the briquettes would pick up moisture and crack; wet polishing of the spent briquettes was unsuccessful for the same reason.

Some indication of the completeness of the reaction was given by the temperature rise of the spent briquettes upon discharge from the retort. In the case of the long cycle there was only a slight if noticeable temperature rise. The spent briquettes of the long cycles appeared as shown above the 8 hour row in Figure 19. However, as the cycle time was shortened the temperature rise increased. The maximum temperature rise was a brilliant calcium flare in the case of the ½ hour and 1 hour cycle briquettes. A heavy oxide coating or "growth" was left on these briquettes as may be seen in the photograph, Figure 19.

In the first tests of this vacuum reduction system the briquettes were pushed against each other into the retort, with the last briquettes in blocking and covering those first in the retort. It was noted that the two briquettes furtherest in the retort exhibited the highest temperature rise, or would even flare when the front, exposed two did not. When the briquettes were charged flat, in the position as shown in Figure 9, the temperature rise was about equal in all four briquettes. It was therefore concluded that the pressure in the back end of the retort must have been higher than that in the front of the charge so that the evaporation of the calcium proceded at a slower rate in this portion of the charge. The color of the flare indicated that the calcium had formed, but had not been

SPENT BRIQUETTE RESIDUE

Fig. 19 - Spent Briquette Residue

removed. When the briquettes were charged flat the charge was more open, and a greater surface area of the briquette charge was exposed for evaporation of the calcium.

The calcium yields from the ½ hour cycle tests were all about the same for all temperatures and charges tested. This might be explained by the pressure and temperature in the retort at this stage of the cycle. If the pressure was sufficiently high that the calcium could be removed only by evaporation then the rate was controlled by the surface area of the charge. Since the charge was composed of four equal sized briquettes in each case, the surface area was equal and the evaporation rate could have been the controlling factor rather than the charge composition, or the slight temperature differentials that existed during this time.

The calcium was assumed to be removed from the charge by sublimation when lower pressures were established for the longer reduction times.

Effect of Charge Impurities on Metal Quality

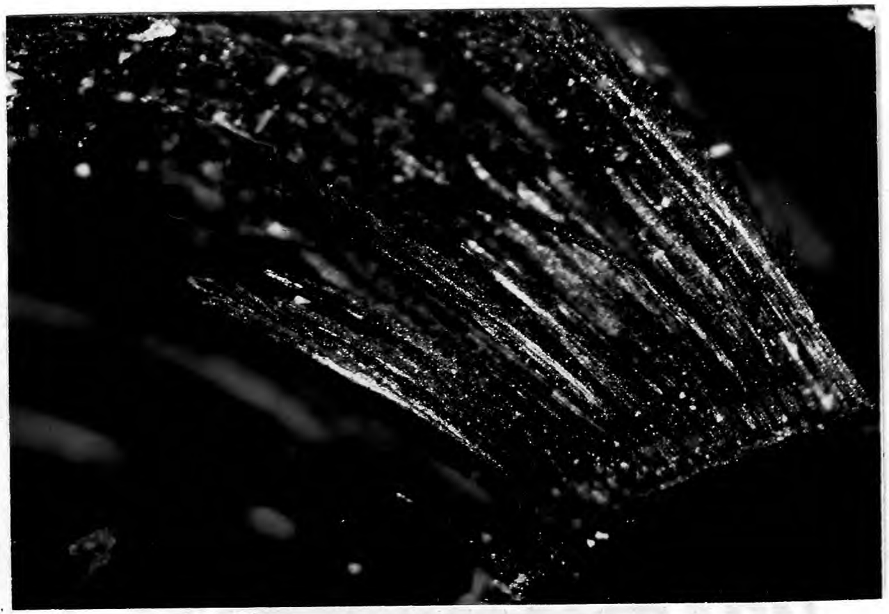
In this process only two charge materials are required, calcium oxide and aluminum. Impurities in either of these materials will lead to contamination of the calcium metal product. Since, however, the calcium is sublimed out of the charge after the thermal reduction occurs, the metal is purified of materials of low vapor pressures at these temperatures. The metal will be contaminated by the more volatile metals such as magnesium, zinc, sodium, manganese which may be present in both the aluminum reducing agent or present as reducible compounds in the calcine. However, the end use determines whether these elements are to be considered co-products or contaminants.

In any case sodium and potassium which may be produced from the calcine are objectionable as a fire hazard. These latter two alkali metals will readily burn when exposed to the air upon opening the retort and so ignite the crystalline calcium deposit. A similar sodium problem occurred in the Pidgeon or ferrosilicon process for magnesium production. In the magnesium process the sodium was collected in a special baffled condenser in the cold end of the condenser section. In a similar fashion a small flange or baffle was added to the condenser in this laboratory furnace, see Figure 8, which acted to separate the sodium from the calcium. This was satisfactory when a dense deposit was formed. However, when large loose crystals were formed during the longer cycle, the sodium seemed to collect between the large crystals even at the hot end of the condenser, and the metal was lost by fire when removal was attempted. Half size charges which produced dense crystalline deposits were used in the longer cycles to reduce the size of the metal deposit and avert fire loss.

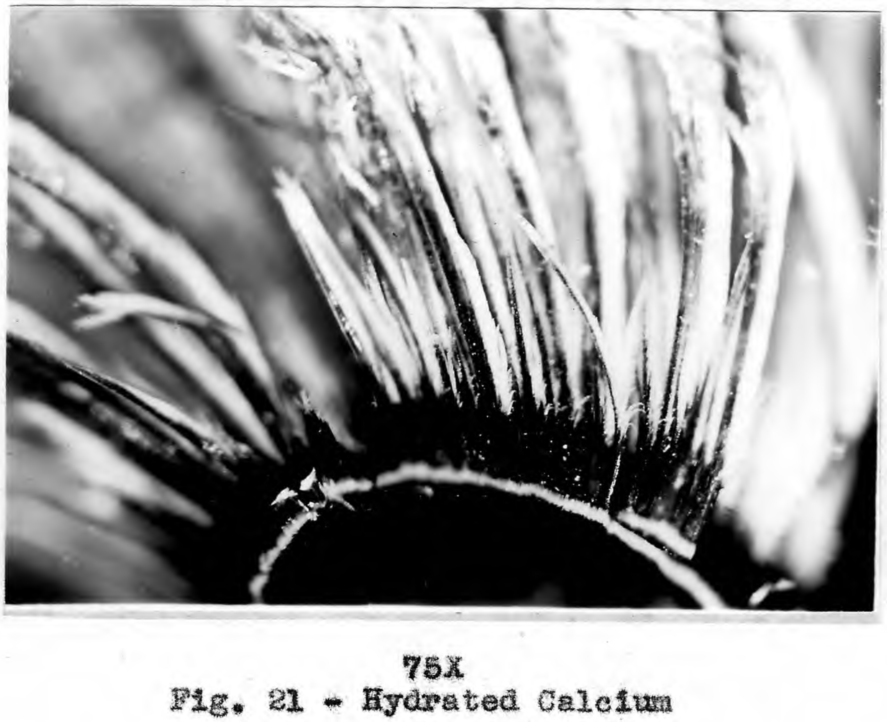
Hotter condenser temperatures, which caused dense metal formation in the Pidgeon Magnesium process retort may have also caused a dense, sodium free calcium metal deposit on this condenser system.

The principal metallic impurity in this calcium metal was magnesium. The exact quantity of magnesium found in the calcium metal varied at different locations in the condenser deposit. Spectrographic analysis of metal samples indicated that the metal deposited within the first three hours of reduction cycle was highest in magnesium content, in the order of 10-50 percent. Analysis of the crystalline deposits of an eight hour run indicated decreasing amounts of magnesium were deposited as the cycle time was increased. Photomicrographs of the unetched crystals did not reveal any distinctive stratification but indicated a continuous crystal growth perpendicular to the surface of the condenser, as shown in the 100X photomicrograph, Figure 20. However, when these crystals were exposed to the air a selective oxidation and hydration of the calcium metal occurred. The same Figure 20 crystals when viewed after three quarters of an hour exposure to the air were photographed at 75X for Figure 21. By visual inspection it appears that the first film deposited on the condenser

PHOTOMICROGRAPHS



100X
Fig. 20 - Crystalline Calcium



75X
Fig. 21 - Hydrated Calcium

PHOTOMICROGRAPHS

10X
Fig. 22 - Hydrated Calcium Crystals

10X
Fig. 23 - Hydrated Calcium Crystals

is calcium metal, followed by the dark, uneffected strata which would contain the magnesium metal. The dark strata is then followed by a white calcium rich deposit that was indicated by the spectrographic analysis. The group of crystals shown in Figures 20, thru 23 was about 1/16 inch long; Figure 22, at 10X, shows the proportion of this stratification of the whole crystal growth. Inspection of exposed crystals from other test runs indicated that Figures 20, 21 and 23 were typical, however, some exceptions were found in which a presumed magnesium rich strata preceded and/or replaced the thin calcium strata shown here.

The average magnesium content of the calcium would vary with the composition of the calcine and aluminum used. In these tests the aluminum contained 0.041-0.043 percent by weight of magnesium metal. In the longer cycles, of maximum calcium recovery a 100% recovery of this amount of magnesium would account for 0.1-0.2% of one percent magnesium in the producible calcium metal. The calcine which contained 1.41% MgO could yield about 1.3% average magnesium content in the maximum, long cycle calcium metal. In the ½ to 3 hour cycles a 100% recovery of the magnesium from the calcine and aluminum would account for 6-8 percent of the total metal recovered within those cycles. These short cycles are of interest only in the experimental plotting of short cycle yield curves such as shown in Figures 14, 15 and 16. Commercial production would be on the longer cycles for high calcium yield which would minimize the magnesium contamination. Spectrographs did indicate, however, that the magnesium contamination would vary in quantity throughout the calcium deposit, being highest in the initial metal deposited on the condenser and least in the last calcium metal collected. The purity of the calcium metal analyzed would therefore also depend upon the location of the sample on the condenser deposit. Loomis(5) reported that the magnesium content of the calcium metal produced in the New England Lime Company retort product ranged from a few hundredths of one percent to over 2% at selected points.

Dominion Magnesium Ltd. patent(11) on this thermal reduction process specifies a CaO containing no more than 1% of MgO and the New England Lime Company calcine was reported(5) to contain only 0.65% MgO. Adherence to either of these specifications could limit the average magnesium contamination from the calcine to less than 1% of the metal recovered.

A high MgO content of the calcine not only contri-

---

(5) Loomis, page 3
(11) Dominion Magnesium Ltd., Brit. 602,062 May 16, 1946

butes contaminating magnesium to the calcium but reduces the calcium yield as well. The extreme case would be the dolomitic calcine containing 40.32% MgO and 56.08% CaO which was used for magnesium production by the ferrosilicon process as shown in equation (1), below. A similar reaction was postulated for the aluminum reduction of a dolomitic calcine, as shown in equation (2). This latter equation indicates that each 1% MgO could nullify approximately 1.4% CaO for calcium metal production. The reaction of the MgO free calcine is shown in equation (3) for comparison.

$$\begin{array}{lllll}
(1) & 2\ MgO{\cdot}CaO + Si & \longrightarrow & 2\ Mg + 2\ CaO{\cdot}SiO_2 \\
(2) & 3\ MgO{\cdot}CaO + 2\ Al & \longrightarrow & 3\ Mg + 3\ CaO{\cdot}Al_2O_3 \\
(3) & 6\ CaO + 2\ Al & \longrightarrow & 3\ Ca + 3\ CaO{\cdot}Al_2O_3
\end{array}$$

The best way to produce a magnesium free calcium is to start with a magnesium free calcine. Second to exclusion, some low magnesium content metal can be obtained by selecting sections of the calcium that are of lowest magnesium content. From this it might be concluded that some segregation of metals could be accomplished by controlling the condenser temperature similar to that used to condense sodium in a cold, baffled condenser section. A Dominion Magnesium Ltd. patent(11) indicated that the calcium vapor condenses in a zone maintained at 750°-680°C and that the

---

(11) Dominion Magnesium Ltd. patent, page 51

magnesium vapor condenses in a zone maintained at 350°-275°C.

Betcherman and Pidgeon(12) in their studies of the distillation of calcium and magnesium cited the fact that the most efficient separation of any two metals should result from a process carried out at the lowest possible temperature since the ratio of the vapor pressures increase with decreasing temperature. This relation could be used to advantage in purifying the calcium by redistillation. This also partially explains the high magnesium content of the first metal, Figure 21, that was produced when the briquette charge was rising to retort temperature.

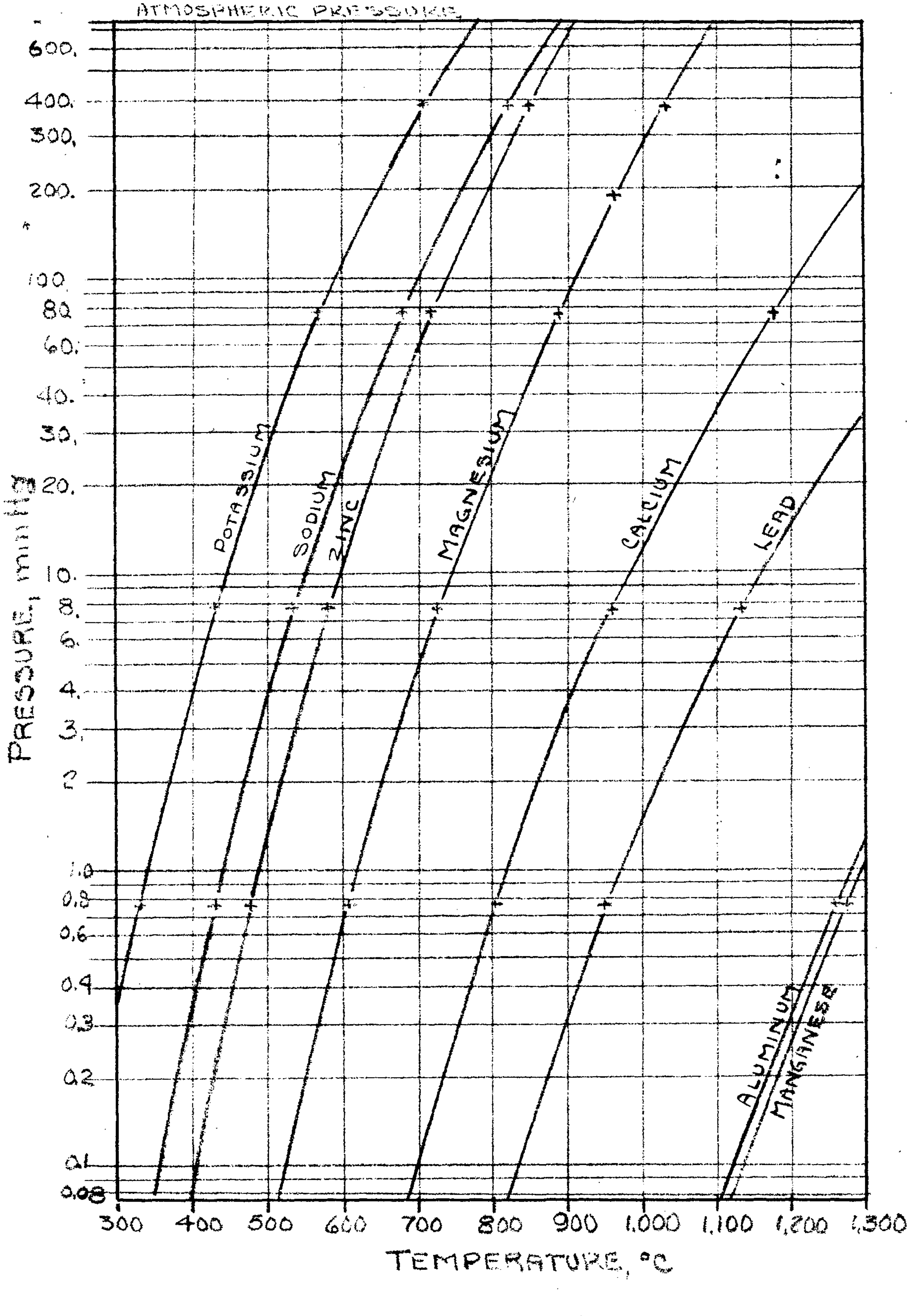
The vapor pressure curves of the major contaminants found in the calcium metal are shown in Figure 24. The increase in the ratios of the vapor pressures of the various potential contaminants are roughly evident in the comparison of the pressure ratios at decreasing temperatures.

---

(12) Betcherman, I. and Pidgeon, L. M., *Trans. Can. Inst. Min. & Met.*, *58*, p167-187, 1951

FIGURE 24

VAPOR PRESSURE DATA(13)



(13) Kelly, K.; U.S.B.M. Bulletin 383, (1935)

APPENDIX

APPENDIX A

RAW MATERIALS

APPENDIX A

RAW MATERIALS

(1) Calcine

Supplier: Merck Company Analytical grade

Particle Size: Minus 100 mesh

Analysis*:

CaO	94.09%	by weight
MgO	1.41	"
R_2O_3	0.49	"
Loss on ignition	2.87	"
Acid insoluble	1.02	"

Bulk Density:
Loose, 0.81 g/cc
Packed, 1.25 g/cc

(2) Aluminum

Supplier: Fischer Scientific

Manufacturer: Aluminum Company of America

Particle Size: (a) 8-20 mesh, (b) 20-30 mesh

Analysis:

Al	99.5% by weight
Mg	0.041*(8-20 mesh)
Mg	0.043*(20-30 mesh)

Bulk Density:

	8-20 mesh	20-30 mesh
Loose:	0.323 g/cc	0.546 g/cc
Packed:	0.402 g/cc	0.612 g/cc

---

* Analysis by International Testing Laboratories

APPENDIX B

PRODUCT ANALYSIS

APPENDIX B

PRODUCT ANALYSIS

The chemical analysis of the calcium metal produced by this process varies with the raw materials, the location of the sample in the total product and the cycle time of the reduction from which the sample was produced. Metal analyzing over 98 percent calcium has been produced by this process.

Spectrographs of 3 calcium metal products of 1200°C Runs 44 and 45 were prepared to identify and roughly locate the principle contaminants. Run 44 produced a calcium yield of about 10 percent of the calcium in the charge; Run 45 produced a calcium yield about 40 percent of the calcium in the retort charge. The magnesium content of the Run 44 metal was about 2½ times as great as that produced in Run 45, and about 50 times as great as that in the last metal recovered in Run 45. This is summarized as follows:

Sample Run* Number	Calcium Yield	Relative Proportion of Mg in Product	Remarks
44	10%	5	Cross section of deposit
45	40%	2	Cross section of deposit
45	40%	0.1	Filing, last metal deposited

*See Table 3 for test run data

This indicates that the first metal deposited was highest in magnesium, and that the last metal deposited was lowest in magnesium content.

Standards were not available to determine exact percentages of the magnesium content, but relative quantities, as shown above, could be roughly determined. These spectrographs indicate that the dark band shown on the Figure 21 photomicrograph to be principally magnesium. The white, hydrated crystal sections shown in Figure 21 were indicated to be the calcium rich sections of the deposit.

APPENDIX C

EXPERIMENTAL DATA

APPENDIX C

KEY TO TABLE 3

Column Headings

(1) Run Number
Test run number assigned in chronological order in which tests were conducted and recorded.

(2) Temperature, °C
Nominal furnace temperature measured in maximum temperature zone of retort.

(3) Blend
CaO and Al blended in the ratio of 6 mols of CaO to indicated number of mols of Al.

(4) Cycle Time
(A) Reduction cycle time measured from 40 microns Hg.
(B) Reduction cycle time measured from the time the retort was closed for vacuum pump-down.

(5) Charge Weight, grams
Weight of briquetted retort charge.

(6) Calcium Weight, grams
Weight of metal produced from charge (5)

(7) Calcium Yield, percent
Weight of metal produced expressed as percent of the weight of calcium contained in the reduction charge (5).

(8) Aluminum Yield, percent
Weight of metal produced expressed as percent of calcium metal theoretically producible with the aluminum in the charge; one mol of aluminum could, theoretically liberate 3 mols of calcium metal.

(9) Ultimate Vacuum
Ultimate pressure in mm Hg attained by end of each run is indicated by the McCleod gage reading.

Footnotes to Table 3

*The "Globar" heating elements were found to be in contact with the retort causing local overheating and fusion of the briquette charge.

**Temperature consistently on the high side.

TABLE 3

EXPERIMENTAL DATA

(1)	(2)	(3)	(4)		(5)	(6)	(7)	(8)	(9)	(10)
Run No.	Temp. °C	Blend	Cycle Time (A)	(B)	Charge Weight Grams	Calcium Weight Grams	Calcium Yield, %	Aluminum Efficiency, %	Ultimate Vacuum (Microns)	Remarks
Equipment Test Runs:										
1	1150	6:6	1-45	2-3	21.1529	3.0016	30.8	9.8	13	3 briq. charge.
2	1150	6:6	1-43	2-0	42.6510	Melted			20	5 briq. charge.
3	1150	6:6	-	1-55	42.8257	0.1255	0.6	0.4	50	Vacuum leak.
4	1150	6:6	-	1-15	41.0711	Nil			70	Vacuum leak.
5	1150	6:6	-	2-10	21.3530	Nil			50	Vacuum leak.
6	1150	6:6	-	1-50	21.3890	Burned during removal from condenser.			55	New pump installed.
7	1150	6:6	-	2-5	21.3900	" " " "			60	Retort vacuum leak.
8	1150	6:4	1-40	2-10	19.5293	Burned after removal from condenser.			22	2 briq. charge.
28	1100	6:2	-	0-18	33.9016	Nil			Nil	Retort vacuum leak.
Process Tests										
9	1150	6:4	1-45	2-25	39.0430	3.3520	16.7	16.2	35	Cond. baffle at 1-1/2".
10	1150	6:4	1-10	1-30	39.0910	2.6750	13.25	12.9	35	
11	1150	6:4	3-10	3-25	39.6233	Burned after collection			17	
12	1150	6:4	0-30	0-43	39.394	1.7423	8.6	8.3	25	
13	1150	6:4	3-0	3-5	39.0864	4.4849	22.3	21.6	20	
14	1150	6:4	2-0	2-5	39.2723	Burned after collection			25	
36	1150	6:4	8-0	8-7	38.9514	7.07	34.9	34.25	22	Sparks.
15	1100	6:4	1-0	1-10	39.0169	1.7262	8.6	8.35	30	Residue flared.
16	1100	6:4	0-30	0-40	39.8758	1.7178	8.36	8.1	22	Residue flared.
17	1100	6:4	2-0	2-5	39.1370	2.9610	14.7	14.3	17	Residue flared.
18	1100	6:4	3-0	3-23	39.6242	3.9946	19.6	19.0	22	Residue temperature rise.
37	1100	6:4	8-0	8-5	39.2555	3.108	Incomplete product collect		19	Metal on retort shield.
27	1200	6:2	-	0-6	34.5199	0.436	2.2	4.2	50	Retort failure.
48	1200	6:2	1-0	0-40	34.6338	Nil				Retort failure.
24	1200	6:2	1-0	1-5	34.5924	1.431	7.1	13.8	25	
26	1200	6:2	2-0	2-5	34.6044	1.6606	8.3	16.1	23	
29	1200	6:2	3-0	3-5	34.4513	3.0883	Incomplete		18	Spilled sample jar.
44	1200	6:2	3-0	3-5	34.5926	2.1710	Incomplete		22	Part burned.
35	1200	6:2	8-0	8-10	34.5870	6.4384	31.9	62.1	5	
42	1200	6:2	8-45	9-5	34.6103	7.092	35.2	68.3	20	
22	1200	6:4	0-30	0-33	39.1613	1.6030	7.95	7.7	22	Residue flared.
20	1200	6:4	1-0	1-5	39.2011	2.9167	14.5	14.0	21	Residue flared.
23	1200	6:4	1-0	1-3	39.2216	2.4343	12.0	11.7	25	
39	1200	6:4	1-0	1-8	39.1822	3.5030	17.4	16.8	17	Coarse Al in charge.
21	1200	6:4	2-0	2-5	39.1853	5.0419	25.	24.3	17	
45	1200*	6:4	2-40	2-43	39.1607	7.7032	38.2	37.1	22	Alloy retort failure.
19	1200	6:4	3-0	3-10	39.0655	7.0228	35.	33.9	20	Sparks.
46	1200	6:4	4-0	4-20	39.2309	Nil - Briquette fused in retort			26	Vacuum leak.
33	1200**	6:4	5-0	5-15	39.1447	9.5727	47.5	46.1	5	
31	1200	6:4	6-0	6-5	39.2094	Burned after collection			8	
38	1200	6:4	8-0	8-10	39.1746	Burned after collection			14	
41	1200	6:4	8-0	8-15	39.2600	Burned after collection			10	
43	1200	6:4	8-0	8-25	19.6059	4.541	45.	43.7	5	
40	1200	6:4	11-0	11-10	76.	Burned after collection			15	
47	1200	6:6	0-30	0-42	43.8175	1.9143	9.5	6.1	40	
25	1200	6:6	1-0	1-4	43.7969	4.5473	22.5	14.7	20	
30	1200	6:6	3-0	3-2	43.8272	4.2586	45.9	29.7	13	
32	1200	6:6	3-0	3-6	43.8274	Burned during removal from retort			8	
34	1200	6:6	3-0	3-6	43.7510	7.94	39.5	25.6	15	

APPENDIX C

SAMPLE DATA SHEET

RUN NO 39

April 25, 1953

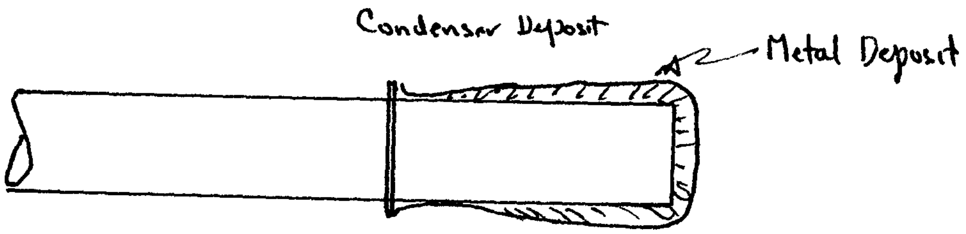
Charge: a) Blend: 6:4
b) Charge: 4 Briquettes (AC-1) & (AC-2), overall 1.34" Long x 1.02" Diameter
c) Weight: 39.1822 grams
d) Location: Charge @ 10½-14½"; Shield @ 9½"
e) Condenser: 1 liter/minute

Products: a) Metal: 3.5030 grams
b) Residue: 39.707 grams

Cycle: 1 hour

LOG

Time	Remarks	Furnace	Vacuum	Temperature
9:52 p.m.	Vacuum On	3.1	on	1181°C
:58		3.1	45_{m}	1199°C
10:00		(3.1)-(2.8)	32_{m}	1203°C
:05		(2.8)-(3.1)	22_{m}	1200°C
:15		(3.1)-(2.8)	19_{m}	1205°C
:25		(2.8)	17_{m}	1207°C
:30		(2.8)	17_{m}	1202°C
:40		(2.8)-(3.1)	17_{m}	1200°C
:45		(3.1)-(2.8)	17_{m}	1206°C
:50		(2.8)	17_{m}	1203°C
:55		(2.8)	17_{m}	1199°C
11:00	Vacuum Off			



APPENDIX D

VAPOR PRESSURE DATA

APPENDIX D

TABLE 4

VAPOR PRESSURE DATA

References: (13) Kelley, K., USBM Bulletin 383 (1935)
Data converted to $^\circ$C and mm Hg
(14) Metals Handbook, 1948, p28, converted vapor pressure data

$^\circ$C

Pressure, mm Hg	0.076	0.76	7.6	76.0	190.	380.0	760.0
Aluminum	1,110	1,263	1,461	1,713	1,837	1,940	2,056
Al_2O_3		2,122	2,351	2,628	2,757	2,864	2,977
Calcium	688	802	958	1,175	1,281	1,380	1,487
CaO	2,245	2,498					
Chromium	1,420	1,594	1,813	2,097	2,234	2,351	2,482
Copper	1,412	1,602	1,844	2,162	2,315	2,450	2,575
Iron	1,564	1,760	2,004	2,316	2,466	2,595	2,735
Lead	815	953	1,135	1,384	1,511	1,622	1,744
Magnesium	516	608	725	886	963	1,030	1,107
Manganese	1,115	1,269	1,476	1,750	1,890	2,019	2,151
Potassium	261	332	429	565	638	704	774
Sodium	349	429	534	679	754	819	892
Strontium			877	1,081	1,187	1,279	1,384
Zinc	399	477	579	717	784	842	907

APPENDIX E

REFERENCES

REFERENCES

(1) Mantell, C. L. and Hardy, C; *Calcium Metallurgy and Technology*, ACS Monograph 100, Reinhold Publishing Corp., 1945

(2) *Minerals Yearbook*, 1951, United States Dept. of Int.

(3) Ethyl Corporation, U. S. Patents 2,543,399, Nov. 12,1949; 2,543,406, 2,543,407, April 1, 1949; 2,561,862, Mar. 25, 1950

(4) Klagsbrunn, H. A., *Ind. & Engr. Chem.*, *37*, No. 7, July 1945, p608-615

(5) Loomis, C. C., *Trans. Electrochem. Soc.*, *89*, 1946, p207-216

(6) *Iron Age*, Vol. 171, May 21, 1953, p181

(7) Staub, P. H., *Chem. & Met. Engr.*, *52*, August 1945, p94-96

(8) Fujita, E., *Reports Gov't. Chem. Ind. Research Inst.*, Tokyo, February 1951

(9) Pierce, W. M.; Waring, R. K.; Fetterolf, L. D.; and Mahler, G. T., *Metals Technology*, T. P. 1707, August 1944

(10) Kroll, W. J., *Metal Industry* (London), *73*, October 1948

(11) Dominion Magnesium Ltd., Brit. Patent 602,062, May 16, 1946

(12) Betcherman, I. and Pidgeon, L. M., *Trans. Can. Inst. Min. & Met.*, *58*, 1951, p167-187

(13) Kelley, K., United States Bureau of Mines, Bulletin 383, 1935

(14) *Metals Handbook*, 1948 Edition, American Society for Metals, Vapor pressure data, page 28