Solubility Studies of the Ca-CaO-CaCl2 System — **Source link**

K.M. Axler, G.L. DePoorter

Related papers:

- Direct electrochemical reduction of titanium dioxide to titanium in molten calcium chloride

- A new concept for producing Ti sponge: Calciothermic reduction

- CaCl2-rich region of the CaCl2-CaF2-CaO system

- Calciothermic reduction of titanium oxide and in-situ electrolysis in molten CaCl2

- Calciothermic reduction of titanium oxide in molten CaCl2

SOLUBILITY STUDIES OF THE
Ca-CaO-CaCl$_2$ SYSTEM

by

Keith M. Axler

ProQuest Number: 10783658

ProQuest 10783658

A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science (Materials Science).

Golden, Colorado
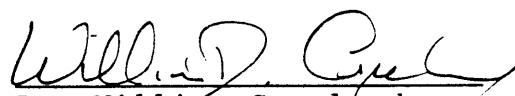
Date _11-9-90_

Signed: _Keith M. Axler_
Keith Martin Axler

Approved: _Gerald L. DePoorter_
Dr. G.L. DePoorter
Thesis Advisor

Golden, Colorado
Date _10 November 1990_

William D. Copeland
Dr. William Copeland
Professor and Coordinator,
Materials Science Program

ABSTRACT

The solubility of Ca metal has been measured in solutions comprised of varying amounts of CaO in $CaCl_2$. The investigation has included solubility determinations at 850 and 900°C. The experimental work involved quenching specimens of selected compositions from elevated temperatures to preserve the high-temperature phase distribution. The reacted specimens were analyzed for dissolved Ca and for CaO composition. Data are presented which establish the effects of CaO composition on the solubility of Ca. Relevant thermodynamic parameters were determined from the solubility data. Additionally, the significance of this work to pyrochemical processing involving the $Ca-CaO-CaCl_2$ system is discussed.

TABLE OF CONTENTS

PAGE

TABLE OF CONTENTS
(continued)

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGMENTS

Chapter 1

INTRODUCTION

The work described herein has been conducted to provide data in support of process optimization studies relating to the pyrochemical processing of PuO_2. The process currently in use for the conversion of PuO_2 to Pu metal is direct oxide reduction (DOR). Modern DOR has evolved from the original technique used to obtain plutonium metal from the oxide during the Manhattan project. This involved an oxidation/reduction reaction of PuO_2 with Ca metal. A simplified reaction scheme is presented in Equation 1.

$$PuO_2 + 2Ca^\circ \rightarrow Pu^\circ + 2CaO \qquad (1)$$
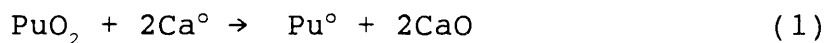
In early developmental work (1), reductions were performed at $1000^\circ C-1050^\circ C$. The metal product was recovered as a metallic dispersion. The lack of an integral product phase was attributed to the CaO distribution in the final system. For a period of time thereafter, the metal was produced via bomb reduction (2) of PuF_4. This process produced an integral metal product; however, radiation exposure problems are associated with the neutron multiplication involving F. This phenomena is due to the $\alpha \rightarrow n$ reaction in which F absorbs

α radiation and subsequently produces neutrons and gamma radiation.

Later, experiments by Jenkins, et al. (3) were conducted to refine the technique for direct reduction of the oxide with Ca. A salt solution phase of $CaCl_2$ was provided to dissolve the CaO generated during the reaction. Those researchers first demonstrated Ca reduction of PuO_2 within a molten $CaCl_2$ matrix. The work reported by these researchers was for small scale studies (approximately 60 gm PuO_2). The $CaCl_2$ provided a solvent for the CaO product species. In that work, integral products were not obtained and the Pu remained finely divided.

In further developments, scientists at Livermore (4) demonstrated that large scale (>1000 gm) PuO_2 reductions conducted within a $CaCl_2$ flux could provide an integral Pu metal product phase. This technique was further developed at Los Alamos (5).

A DOR reaction cell is shown in Figure 1. In the current DOR process, commercially obtained anhydrous $CaCl_2$ pellets are pretreated by melting and sparging with an argon/chlorine gas mixture in a dehydration process. The treated salt is then cast into cylinders which reduces surface area and provides for convenient handling. These cast salt charges are then stored under vacuum to prevent any moisture pick up. All further operations are conducted within dried air glove boxes.
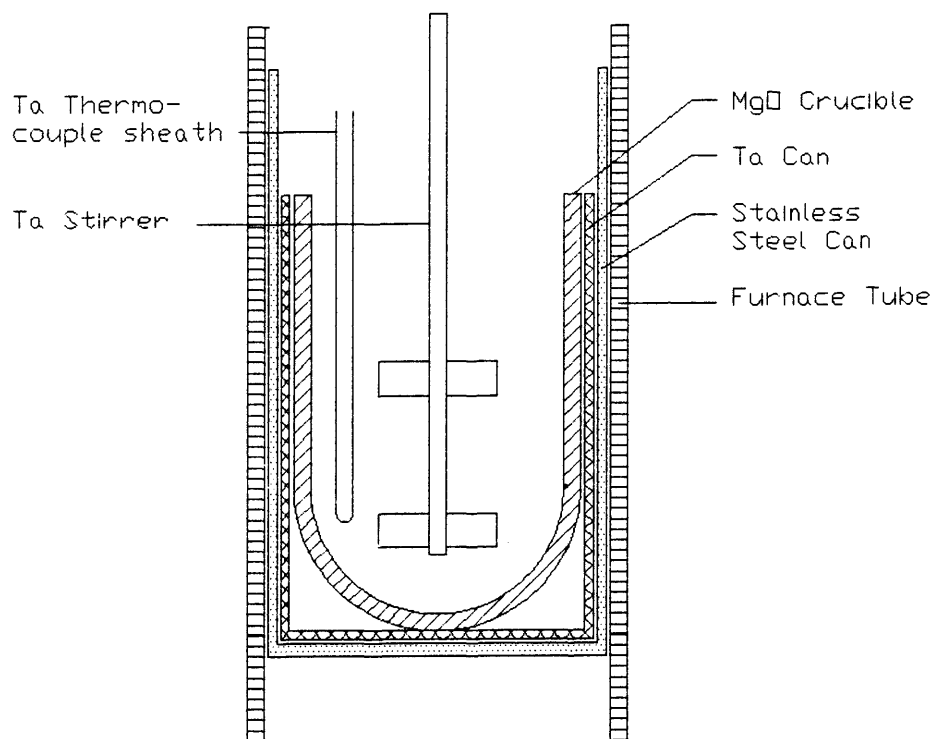
Figure 1. DOR reaction apparatus.

The hot salt charges are maintained above 100°C while moved into the glove boxes. This helps to minimize the absorption of water from the air during handling.

Due to their high thermodynamic stability, MgO crucibles are used for containment in DOR processing. The salt, PuO_2 feed, and Ca metal are reacted in a resistively heated furnace under positive argon pressure. A thermocouple sheath extends into the crucible from a fitting in the top flange of the furnace. Once the system is above the melting point of the salt charge, a stirrer is lowered into the melt. The stirring promotes the reduction of the oxide feed. A temperature excursion occurs which is associated with the exothermic heat of reaction. The system is controlled at approximately 850°C with continued stirring.

After reaction, the stirrer and thermocouple are raised out of the melt so they are not frozen into place upon solidification of the salt. Then the system is held at temperature for the plutonium product to coalesce. Once the system is cooled, the MgO crucible is removed, broken open, and the product button is separated from the salt phase. If the metal coalesces completely, there is a discrete phase disengagement at the salt/metal interface.

It should be mentioned that the DOR process is not a purification step. PuO_2 is an extremely stable oxide from a

standpoint of chemical thermodynamics; other metal oxides which are introduced as impurities in either the feed or the salt are generally reduced to metal by reaction with Ca. Purification is conducted via subsequent electrorefining of the DOR product metal.

As the DOR reaction proceeds within the salt solution phase, Pu metal is generated via reduction of the oxide by dissolved Ca. The Pu precipitates and forms a metal product phase below the salt. The subsequently produced CaO remains within the salt phase and decreases the solubility of Ca.

Since the reduction of PuO_2 proceeds within the salt solution phase, the amount of dissolved Ca influences the reaction kinetics. The effect of CaO concentrations within the molten salt phase needs to be characterized for further DOR process optimization. Results presented herein address this issue.

Chapter 2

DISCUSSION OF PREVIOUS WORK

2.1 Ca-CaCl$_2$ System

The solubility of Ca in CaCl$_2$ has been well estab-
lished (6,7,8).   In the published work on the Ca-CaCl$_2$
system, Sharma (9) obtained solubility data by removing
aliquots from the melt in Ta draw tubes. The sample thieves
were lowered into the melt at selected temperatures and
allowed to equilibrate with the temperature of the melt. By
pressurizing the system, aliquots were driven into the sample
thieves. Then, the samples were removed from the melt and the
removed aliquots were allowed to cool in place. The total Ca
retrieved in the sample thief was assumed to be dissolved at
the elevated temperature. A Ta frit was installed at the
bottom of the sample thief to obviate the problem of Ca
condensation within the tube and to avoid removing Ca from the
immiscible upper phase when lowering the tubes into the melt.
Temperatures from 800°C to 940°C were included in this
investigation.   Solubilities for Ca in CaCl$_2$ reportedly
increases from 2.142 to 3.598 mole % over this temperature
range.

Dworkin, et al. (6) determined the solubility of Ca in
CaCl$_2$ using a technique which measured the specific conduc-

tivity of the melt. They determined the Ca solubility in $CaCl_2$ to be 2.95 mole % at 855°C. In that study, a molybdenum crucible was used to contain the molten salt system.

Peterson and Hinkelbein (7) published the results of a study conducted on specimens encapsulated in stainless steel cells and quenched in a water bath. In that investigation, the samples were intermittently shaken while held at the selected temperature for 2 hours, then allowed to equilibrate by soaking for 1 additional hour. The authors mentioned that soak times of 24 hours did not change the observed compositions. They reported values of 3.8 and 4.2 mole % Ca in $CaCl_2$ at 900°C and 950°C, respectively. Details on Ca determinations on reacted specimens were not included in that work.

An early work by Cubicciotti and Thurmond (9) involved a reported value of Ca solubility in $CaCl_2$ to be 16 mole % at 900°C. The experimental approach taken in that work involved quenching reacted specimens in a water bath. Fe crucibles were used for sample containment. The determination of Ca within the reacted salt phase was determined by difference based on chloride measurements. Considerable discrepancy exists between the data of these researchers and the trends observed in a review of the entire published data.

Staffanson (10) reported a solubility of 3.3 mole % Ca in $CaCl_2$ at 763°C. That value is slightly higher than values reported in the more recent studies.

Solubility data from previous researchers are summarized in Table 1.

2.2 CaO-CaCl₂ System

The $CaCl_2$ system has been studied extensively, and a compilation has been provided by Perry and MacDonald (11). In that publication, binary phase diagrams are presented which reflect the results of individual past studies as well as that of the authors. In recent discussions, Perry (12) mentioned that the early work by Wenz, et al. (13) presented an accurate phase diagram in which a phase of invariant stoichiometry at 20 mole % CaO was omitted. That phase diagram has been provided in Figure 2. That compound had originally appeared in the diagram presented by Neumann, et al. (14).

Table 1. Solubility Data for Ca-CaCl$_2$

Mole % Ca	Mole % CaCl$_2$	T°C	Reference
4.2	95.8	950	Peterson & Hinkelbein (7)
3.589	96.411	940	Sharma (8)
3.466	96.534	925	Sharma (8)
3.257	96.743	900	Sharma (8)
16.0	84.0	900	Cubiciotti & Thurmond (9)
3.8	96.2	900	Peterson & Hinkelbein (7)
2.95	97.05	855	Dworkin, et al. (6)
2.748	97.252	850	Sharma (8)
2.45	97.55	830	Sharma (8)
2.7	97.3	800	Shaw and Perry (15)
2.142	97.858	800	Sharma (8)
2.2	97.8	785	Dworkin, et al. (6)
3.3	96.7	763	Staffanson (10)
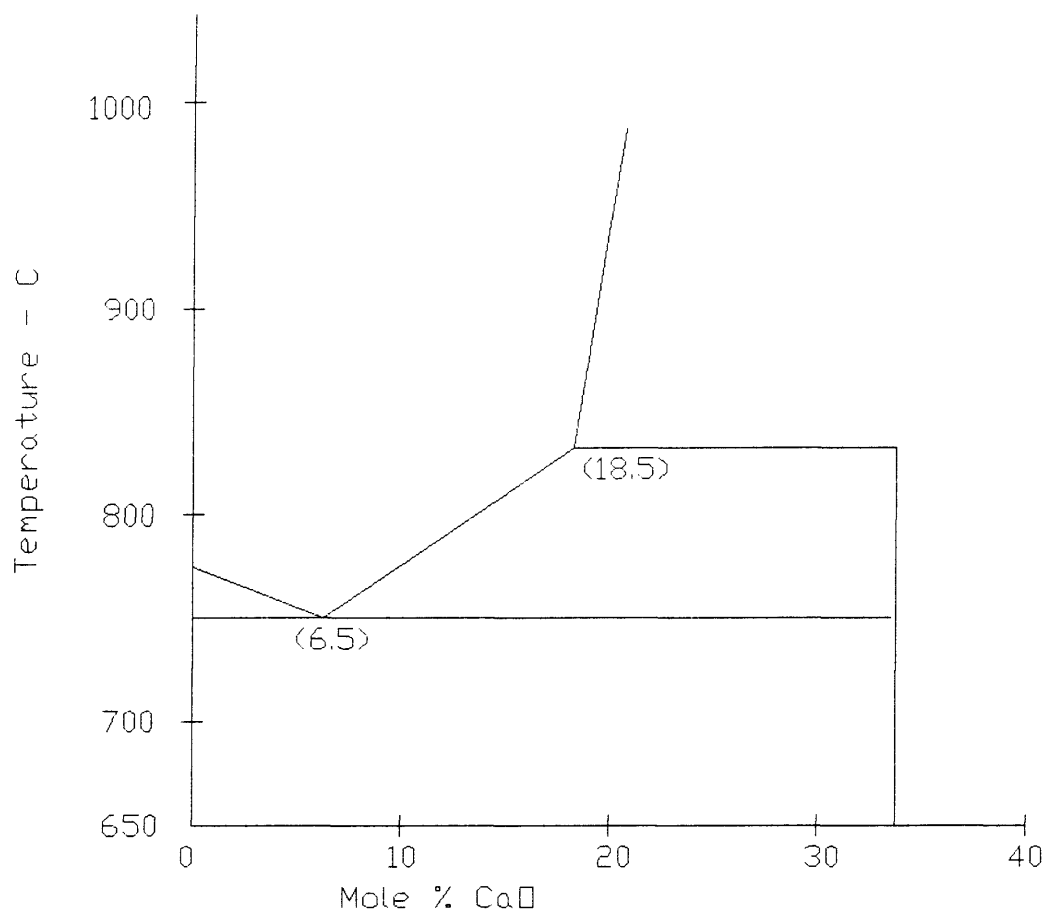
Figure 2. CaO-CaCl$_2$ binary phase diagram as published
by Wentz et al.

2.3 Ca-CaO-CaCl$_2$ System

The effects of CaO content on the solubility of Ca within the molten salt system has not been characterized until the recent work by Perry and Shaw (15). These researchers have established the solubility of Ca in CaO-CaCl$_2$ solutions at 800°C. Measurements of the Ca solubility in CaCl$_2$ as a function of CaO content were conducted at 800°C. In that study, aliquots were removed from the melt by application of silica glass tubes. In that work, a value of 2.7 mole % Ca in pure CaCl$_2$ was obtained. That study established Ca solubilities in solutions up to 9.1 mole % CaO where the solubility of Ca was suppressed to 0.4 mole %.

Chapter 3

PREPARATION OF MATERIALS/EXPERIMENTATION

3.1 Preparation of Materials

Extreme measures were required to produce quality specimens for this investigation due to the high reactivity of Ca metal and the hygroscopic nature of $CaCl_2$. All operations were conducted under an argon atmosphere and all starting materials were of the highest purity available.

3.1.1 Encapsulation Cells

The materials to be quenched from elevated temperatures had to be encapsulated within leak-tight, refractory containers which could withstand the thermal shock associated with the quenching operation. The material best suited for this application is Ta. Although a literature search on the Ca-Ta system did not reveal any published phase diagram work, Ta has historically provided service for high temperature operations involving containment of molten salts and reactive metals (16). Ta cans were produced by machinists at Los Alamos specializing in rare-metal fabrication to provide the best possible containment cell. The cans were designed to provide sufficient volume for the unreacted materials while minimizing the void volume over the
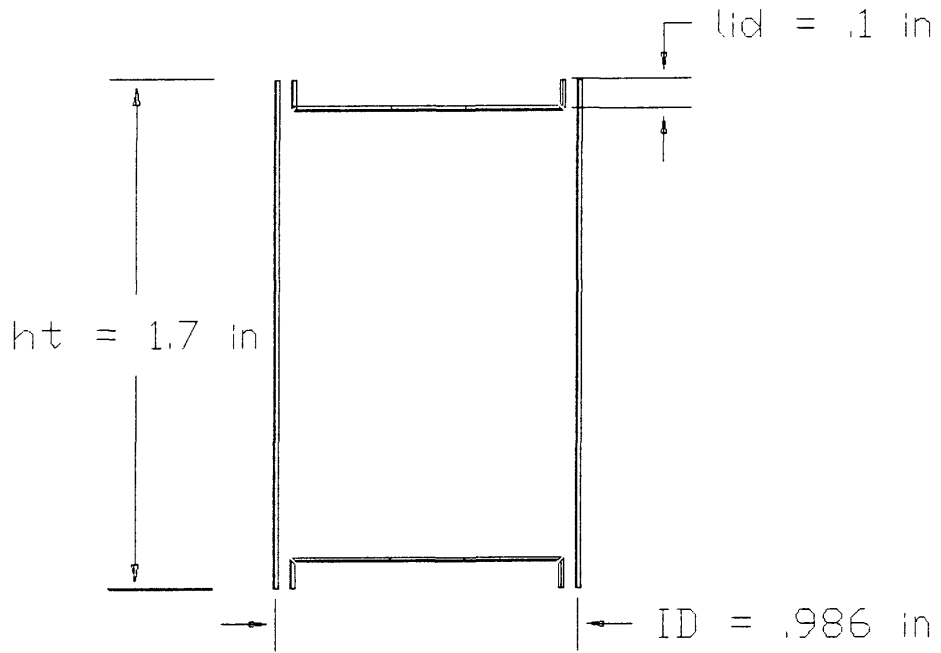
Figure 3.   Tantalum encapsulation cell.

molten system. The optimum cell dimensions were based on the
volume of the reactants in the forms selected for this
investigation, i.e., dendritic Ca and beads of $CaCl_2$. A
drawing of the encapsulation cells is shown in Figure 3 which
gives the exact dimensions used in fabrication.

Sections of Ta tubing and the lids fabricated from Ta
sheet appear in Figure 4. A photograph appears in Figure 5
which shows the Ta encapsulation cells produced for this
investigation. The surface conditions of the cans before and
after the reaction are apparent. A slight staining of the
outer surface was observed after the heat treatment and
quenching.

Prior to encapsulating the reactants, efforts were taken
to develop a technique which would ensure that welding the
lids onto the cans would not elevate the Ta surface
temperature to the point where the contained Ca metal could
vaporize significantly. A large steel collet was provided
which made a snug fit around the can and provided a heat sink.
Omega temperature indicating markers (Omega Engineering Inc.)
were used to obtain thermal profiles of the Ta cans while the
bottoms were welded on. These indicators provided
confirmation of temperatures on the outer wall from 52°C to
427°C in approximately 14° increments. Even with the use of
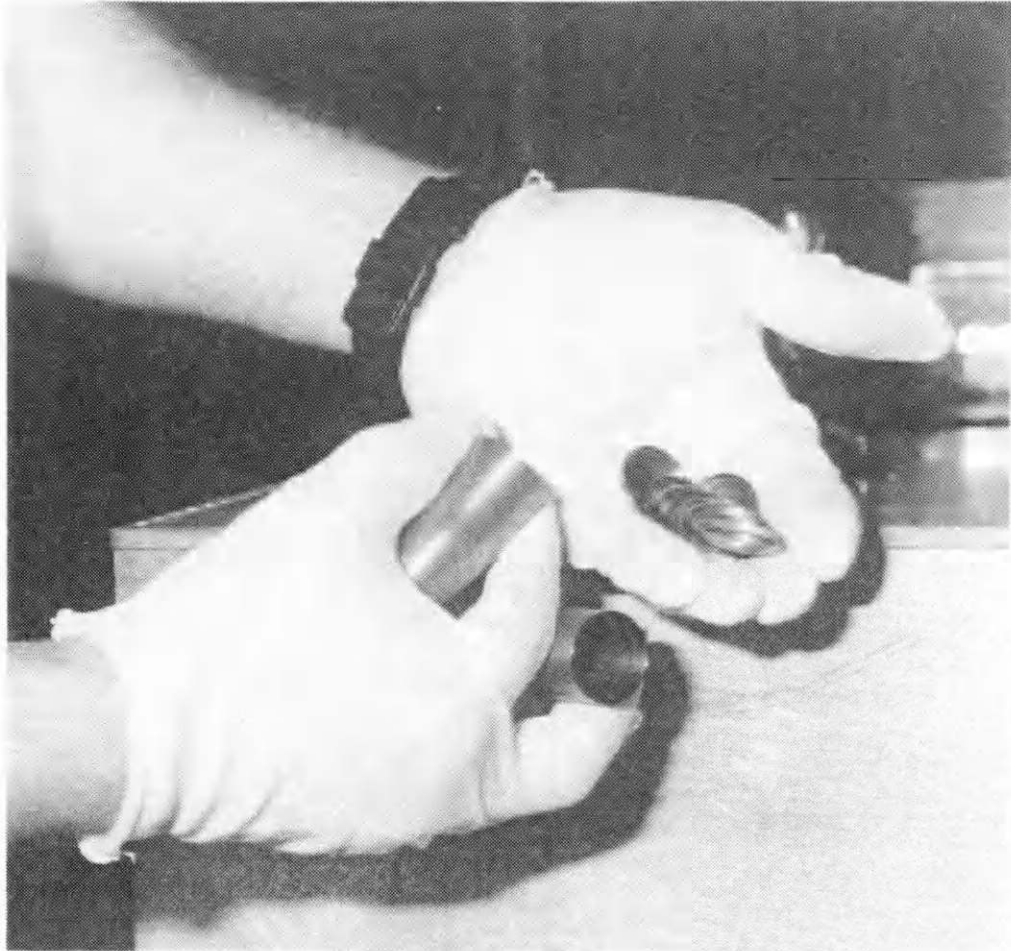
Figure 4. Ta components used to fabricate the
encapsulation cells.

Figure 5.   Ta encapsulation cans.   The can on the left has
            been subjected to quenching and has a darkened
            appearance.

the collet as a heat sink, conventional TIG welding techniques were unsatisfactory as the cell walls were exposed to temperatures in excess of 427°C. during the welding operation.

A successful approach to sealing the cells involved using an Nd-Yag laser welder. The laser welding technique maintained temperatures below 150°C at a distance of 0.8 cm below the weldment. The parameters for the welding operation are provided in Appendix A.

The surfaces to be welded were machine polished and cleaned with acetone in an ultrasonic generator. The welding was conducted under positive argon pressure. All weldments were examined via helium leak detection to verify that each was leak-tight.

3.1.2 Preparation of Reactants

The Ta cans, with one end sealed and leak checked were sent to APL Engineered Materials for the selected $CaO/CaCl_2$ compositions to be melted into place. Previous researchers have used APL materials in their phase investigations of the $Ca/CaCl_2$ and $Ca/CaO/CaCl_2$ systems (12,17). APL conducted this operation using a furnace contained within a glove box held at <10ppm oxygen and <10ppm moisture to conduct the pretreatments. Virtually identical equipment is maintained within the chemistry and metallurgy research

building at Los Alamos for plutonium related phase investigations. However, use of these facilities would cause plutonium contamination of the otherwise nonradioactive materials and induce considerably greater difficulty of handling.

The materials used were "ultra-dry" (manufacturers specification) 99.995% pure $CaCl_2$ and 99.99% pure CaO. Since the dissolution of CaO in $CaCl_2$ is reportedly slow (18), a preparation of CaO produced by decomposition of the oxalate was used. This procedure for generation of CaO provides a product with greater surface area than the conventional method which involves preparing CaO from the carbonate. By using the higher surface area CaO, dissolution was enhanced. The analysis data are provided in Appendix B.

The $CaCl_2$/CaO preparations were melted into the Ta cans during a pretreatment at 900°C in the glove box furnace. The pretreatment increased the void volume within the cells which allowed space for addition of the Ca dendrites. Before they were removed from the inert glove box, each Ta can was hermetically sealed within a mylar bag.

The Ca metal used in this investigation was 99.995% pure Ca dendrites provided by Aesar and preserved, under argon, within glass ampules until the loading procedure was conducted. The purity of the Ca metal was also verified by the

Figure 6. Ca and CaCl$_2$ sealed within glass ampules.

analytical services at Los Alamos (see Appendix B). A

photograph of the Ca and $CaCl_2$ used in this investigation

appears in Figure 6.

3.1.3 Specimen Encapsulation Procedure

The mylar bags containing the $CaO/CaCl_2$

preparations from APL were opened under positive argon

pressure at the laser welding facility at Los Alamos where the

Ca metal was added and the cans were sealed without exposing

the materials to air. All samples were comprised of 20 gm

total $CaO/CaCl_2$ with 2 gms of Ca added to each. The

consistent sample sizes provided uniform thermal masses which

ensured that the quenching rates would be consistent

throughout the experimental matrix. The large excess of Ca

was provided so that the maximum solubility could be achieved

in each specimen. This was verified by the presence of a Ca

metal phase present in each encapsulation cell after reaction.

The lids were machine polished, cleaned, and welded onto

the Ta cells under an atmosphere of argon pressure. Each

final weldment was examined by optical microscopy and, as was

proven in the subsequent reactions, all were leak-tight.

3.2 Experimental Apparatus/Procedures

The encapsulated samples were reacted by heating to the selected temperatures under positive argon pressure, and then quenched by immersion into a bath of Dow 550 fluid maintained at ambient temperature. After quenching the encapsulations were opened under an argon atmosphere and analyzed for dissolved Ca. Additionally, all samples were submitted for post mortem examination by chemical analysis to determine the exact composition of each system.

3.2.1 Furnace Details

A schematic diagram of the furnace arrangement is provided in Figure 7. A Lindberg furnace, Model 55035, was equipped with an LFE programmable controller (The Mark IV Co., LFE Instruments Division). An LFE limit controller was installed to protect against an accidental temperature excursion. Control was accomplished via a stainless steel sheathed K-type thermocouple laced onto the encapsulation cans with Ta wire. A quartz furnace tube was fitted for service with positive argon pressure. A Ta basket was fabricated which held the encapsulations in the heat zone.
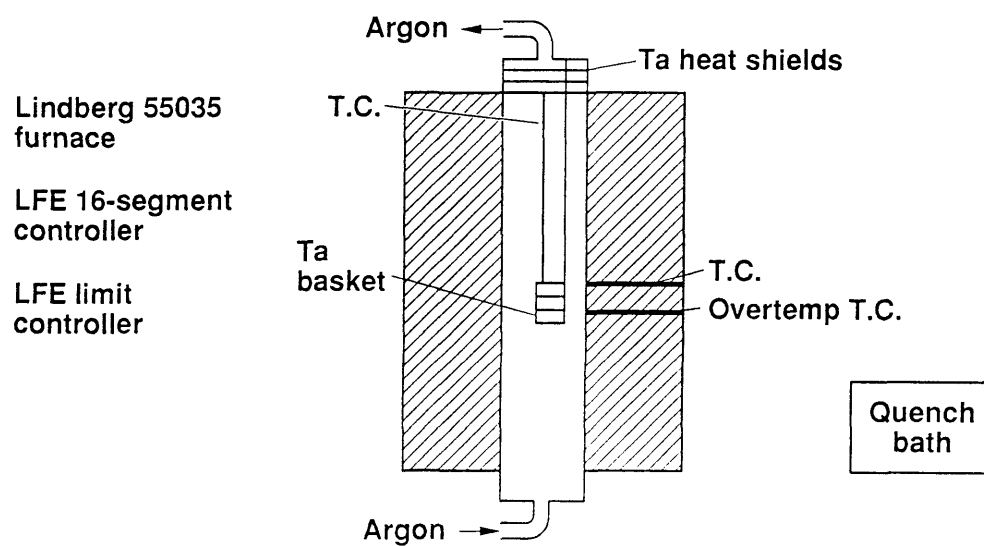
Figure 7. Schematic representation of furnace and hardware.

3.2.2 Reaction Conditions

The encapsulated specimens were placed into the Ta basket in intimate contact with the thermocouple. Argon was passed through the furnace for a minimum of 20 minutes prior to heating. Sample temperature measurements and furnace control were both accomplished via the thermocouple contacting the sample. By using a 2 hour ramp time, there were no problems with temperature excursions typically encountered when controlling off the sample thermocouple.

A soak time of 24 hours was used for reacting the samples in this study. The selection of soak time was based on a review of previous experimental work on this and other analogous systems. Additionally, a study was conducted to verify that equilibrium was established in the reacted samples. Two specimens of identical composition were prepared; one was equilibrated by soaking for 24 hours at 850°C, the other was held for 24 hours at 900°C then for 24 hours at 850°C. These samples produced virtually identical final compositions. Details are provided in Chapter 4.

3.3 Quenching Operation

After quiescent heating for the prescribed time at the selected temperature, the Ta basket was lowered from the heat zone into the quench bath. This operation was completed in

under 3 sec. A similar technique has been previously demonstrated by Axler, et al. (19) to successfully preserve high-temperature phase distributions.

The quench bath was a one liter container of Dow 550 Fluid, a liquid designed expressly for high-temperature heat transfer. The bath was held at room temperature and during the quenching operation was stirred at approximately 800 rpm with a magnetic stirrer.

3.4 Determinations for Dissolved Ca

After quenching, the reacted specimens were transferred to an argon atmosphere and the encapsulations were opened using a standard tubing cutter. Specimens for analysis were removed from the central region of the solidified salt phase to avoid removing any excess Ca which had wet the interior walls of the cell. (The Ta cans and the Ta furnace basket were saved for recycling.)

The removed aliquots were weighed to a four decimal place value on a Mettler electronic balance which was calibrated immediately prior to this operation. Each weighed salt sample was then wrapped in mylar and placed into a water chamber on a custom made gas evolution measurement apparatus. A schematic diagram is presented in Figure 8.

Spring
hooks

Ground
glass
seat

Stopcock
vent

Sample
chamber

Hempel gas
burrette

Receiver
Tube

3-way
stopcock
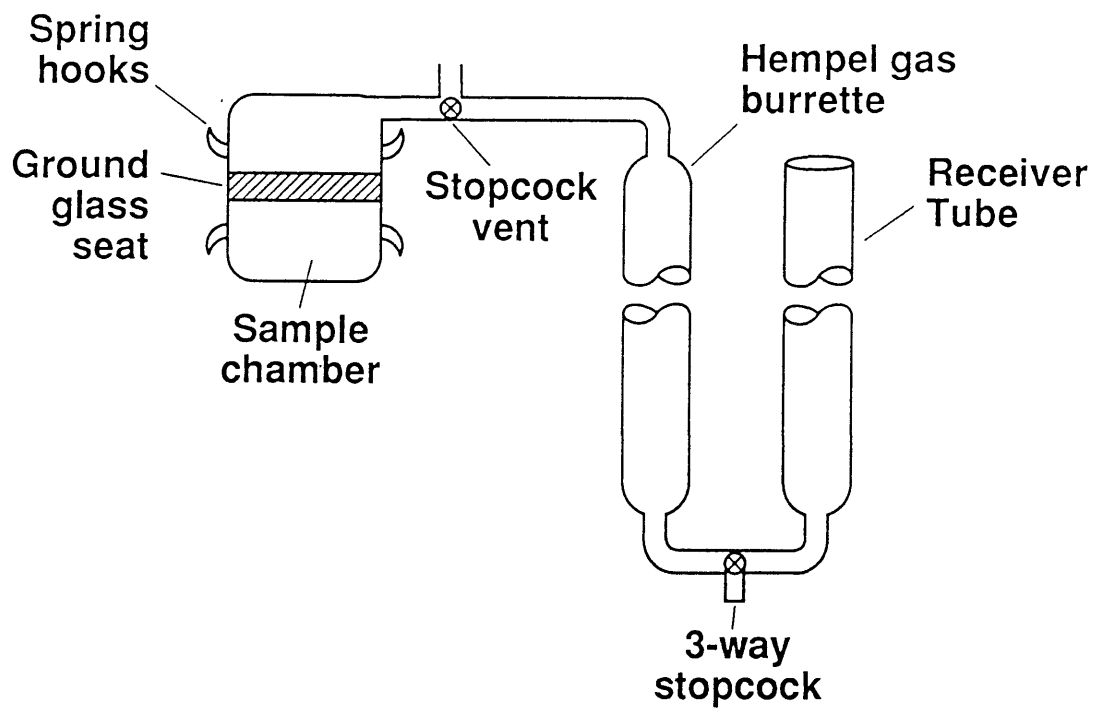
Figure 8. Schematic representation of the hydrogen
measurement apparatus.

A photograph of the assembled apparatus appears in Figure 9 and a close-up view of the reaction chamber is shown in Figure 10.

In the reaction chamber, the mylar envelopes were opened by spinning the water with a magnetic stirrer.

The salt was dissolved and the Ca, present as dissolved metal, reacted with the water to evolve H_2 gas. The simplified reaction is given in Equation 2.

$$Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2 \qquad (2)$$
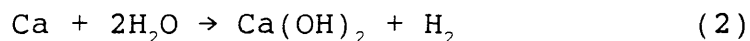
The subsequently-produced H_2 volume was measured in a calibrated column. By determining the H_2 mole numbers, the amount of Ca metal dissolved in the salt was established. This method for determining dissolved Ca has been previously demonstrated by other researchers (9,12) to provide accurate determinations of dissolved Ca. Additionally, the apparatus assembled for use in this study was tested by obtaining measurements of evolved H_2 from a series of more than 30 pure Ca samples. These tests were conducted on sample sizes which were calculated to be within the order of magnitude of the amounts of Ca present as dissolved metal within the actual specimen matrix. The tests refined the measurement procedure to a point where 1% errors were typical.
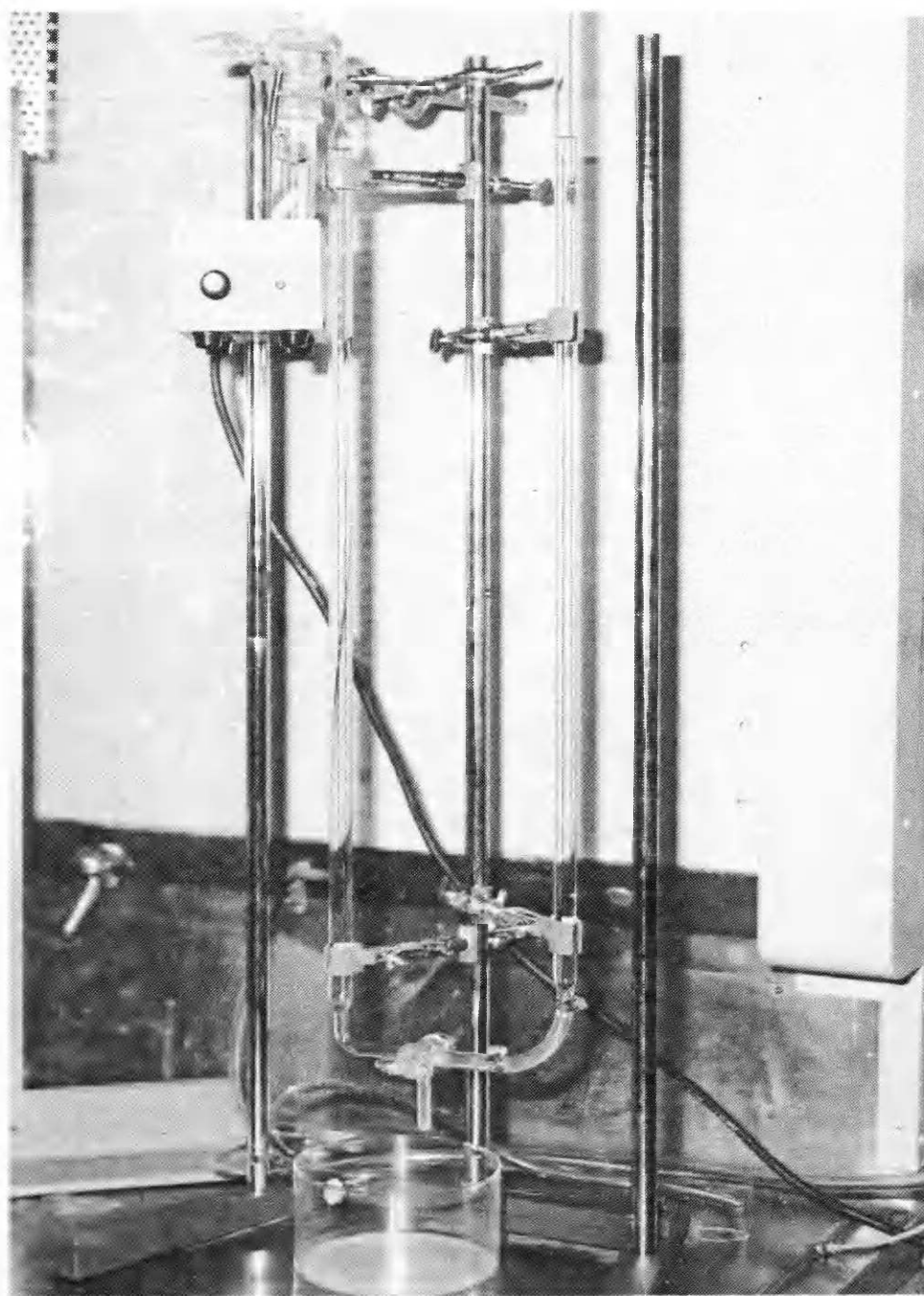
Figure 9.   Hydrogen measurement apparatus.
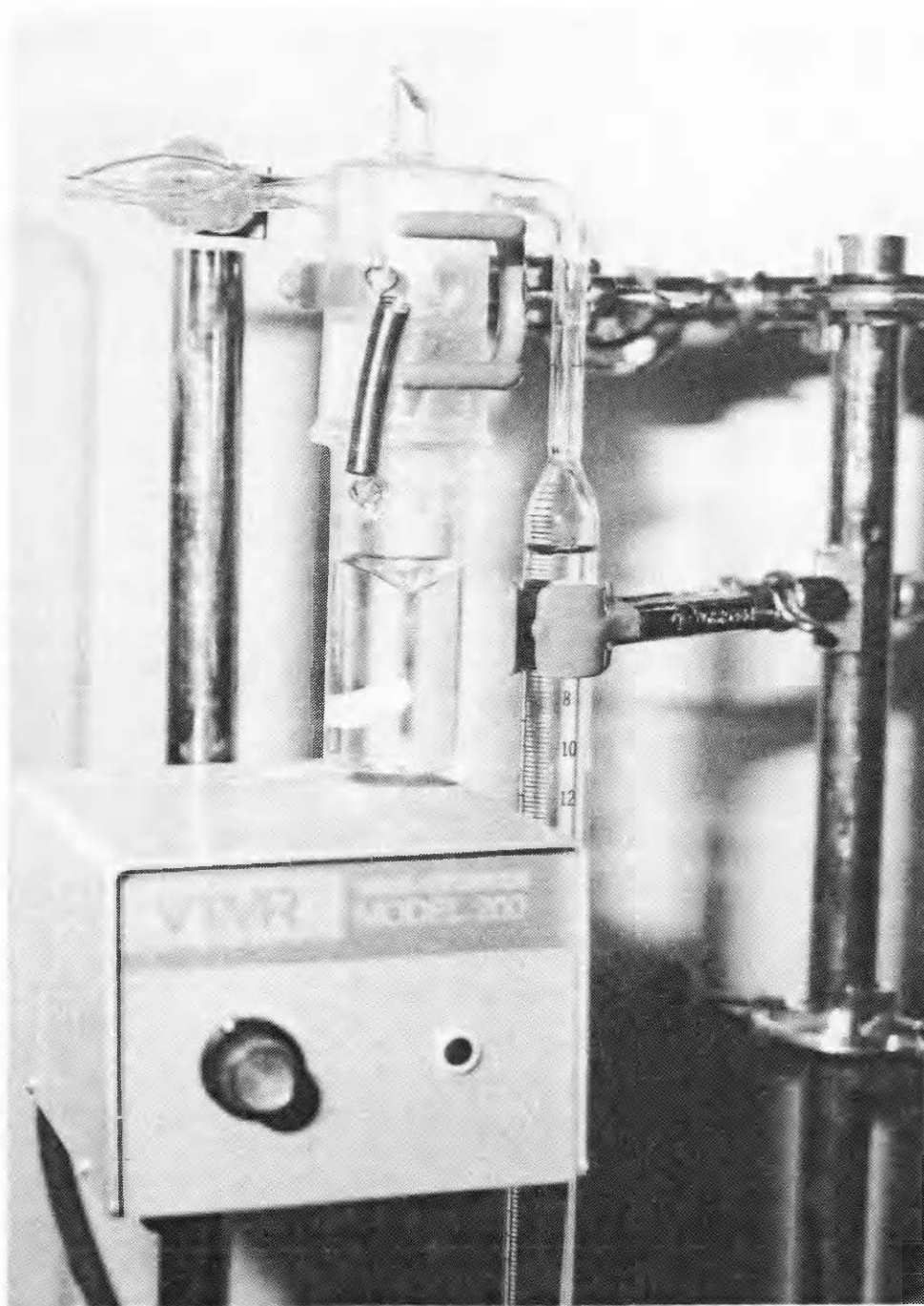
Figure 10. Reaction chamber on hydrogen measurement apparatus.

3.5 CaO Determinations

Data from alkalinity determinations on the reacted salts were obtained to establish the exact CaO composition. This procedure was conducted on three sections removed from each reacted specimen. The sections were dissolved in an excess of water then titrated back to pH 7. Through the moles of HCl consumed in the titration, the moles of both species (Ca and CaO) contributing to the alkalinity were determined. Having established the mole numbers of Ca via H_2 evolution, the CaO composition in the reacted specimens was calculated by difference. The data are reported as mole % CaO and mole % Ca. The associated calculations appear in Appendix C.

3.6 Determination for $CaCl_2$

The sections removed from the reacted specimens which were used for H_2 evolution analysis were submitted, as dissolved material, for chloride analysis. The technique used was an argentometric titration. This provided values for $CaCl_2$ within the samples (see Appendix C.). By obtaining values for chloride, the $CaCl_2$ composition was verified in the reacted samples. By using the results of the chloride determinations in concert with the alkalinity data and H_2 evolution measurements, a mass balance confirmation was available.

Preparations of known compositions of $CaCl_2$ and Ca metal were dissolved in water and submitted for chemical analysis to provide a verification of the analytical support received in this study. The chloride determinations on these 4 spiked samples were all within <0.3 % of the known values. Additionally, analysis for Ca by ICP was also requested as it was initially believed the $CaCl_2$ compositions could be obtained through the Ca/Cl ratios after the Ca mole numbers were accounted for in the CaO and dissolved Ca determinations. However, Ca analysis data on the spiked samples were found to contain +/- 4.5 % error. The Ca error was considered unreasonable and $CaCl_2$ compositions were satisfactorily determined via the chloride values.

Chapter 4

EXPERIMENTAL RESULTS

4.1 Ca Solubility Data

This investigation has extended the available data on Ca solubility in the Ca-CaO-CaCl$_2$ system. In this work, the solubility of Ca in CaCl$_2$ has also been experimentally confirmed at 850°C and 900°C.

Data for Ca solubility in the CaO-CaCl$_2$ system as a function of CaO content at 850°C and 900°C are provided in Tables 2 and 3.

4.2 Comparison of Data with Previously Reported Values

In this work, the solubility of Ca in pure CaCl$_2$ was determined in an effort to confirm the viability of the experimental technique prior to extending the investigation into a previously uncharacterized region of the Ca-CaO-CaCl$_2$ system. In this study, measurements of 2.7 mole % and 2.8 mole % were obtained for the solubility of Ca in pure CaCl$_2$ at 850°C. This shows excellent agreement with the value of 2.748 mole % reported by Sharma (8). As mentioned previously, that work involved the removal of aliquots from the melt via sample thieves.

Table 2. $Ca-CaO-CaCl_2$ Solubility Data for 850°C

Ca MOLE %	CaO MOLE %	$CaCl_2$ MOLE %
2.8	0.0	97.2
2.7	0.0	97.3
2.3	0.5	97.2
2.4	0.7	96.9
2.0	1.2	96.8
2.0	1.1	96.9
1.8	3.4	94.8
1.8	3.4	94.8

Table 3. Ca-CaO-CaCl$_2$ Solubility Data for 900°C

Ca MOLE %	CaO MOLE %	CaCl$_2$ MOLE %
3.7	0.1	96.2
3.2	1.4	95.4
3.2	1.4	95.4
2.9	4.0	93.1
2.7	4.6	92.7
1.9	5.9	92.2
1.9	6.0	92.1

In a recent conversation, Sharma (16) expressed concern that the data from that previous work might reflect a slight error inherent in the sampling technique. When the salt aliquots were removed, there was no way to verify that Ca inclusions were not taken up into the tubes from the excess Ca which was present as a second liquid phase above the salt. However, good agreement with the current work indicates that the previous data were valid.

The data for Ca solubility in pure $CaCl_2$ obtained in this work does not agree as well with the values reported by Dworkin, et al. (6). They reported a value of 2.95 mole % Ca for the solubility in pure $CaCl_2$ at 850°C.

Solubility data for Ca in Ca-CaO-$CaCl_2$ at 900°C obtained in this work appear in Table 3. In this study, a 900°C specimen of pure $CaCl_2$ was not obtained. The samples which were prepared without CaO had been found to contain small amounts of CaO in the post mortem chemical analyses. This is assumed to be due to Ca reacting with Ta oxide present on the cell walls during the heat treatments. Upon visual examination, some Ta cells were found to have oxidized slightly during the pretreatments of the CaO-$CaCl_2$ preparations. These were included in the matrix, as the post mortem examinations would determine the final compositions of

the reacted specimens, and the CaO content would not be
assumed from the preparations.

The specimen produced with the lowest amount of CaO,
0.1 mole % CaO, had a Ca solubility of 3.7 mole %. It can be
assumed that a slightly higher value would have been obtained
if the CaO was not present. This assumption is based on the
Ca solubility suppression observed throughout this study as a
function of CaO content. Sharma (8) reported a solubility of
3.26 Ca in $CaCl_2$ at 900°C. Peterson and Hinkelbein (7)
reported a value of 3.8 mole % Ca in $CaCl_2$ at 900°C.

4.3 Discussion of Results Within the Previously Uncharacterized Region

To determine if the specimens were truly representative
of the high-temperature phase distributions a test was
conducted by approaching equilibrium from two directions for
two identical samples. One specimen was heated at 900°C for
24 hours and then held at 850°C for an additional 24 hours
prior to quenching; the other received the standard 24 hours
soak at 850°C. The specimen which was equilibrated after the
higher temperature treatment had a final composition of
2.0 mole % Ca dissolved in a 1.1 mole % CaO solution. The
sample receiving the treatment at 850°C had a final
composition of 2.0 mole % Ca in 1.2 mole % CaO. By achieving

agreement between specimens which were allowed to equilibrate via two different approaches to 850°C, confirmation of equilibrium was established over the region of low CaO content.

At the higher CaO compositions, the experimental values at 850°C were not consistent. Several specimens were prepared at >4 mole % CaO, and might have comprised even greater CaO concentrations by reducing the Ta oxide on the inner cell walls as discussed earlier. As with the complete matrix of specimens, three portions were removed from each and individually analyzed for alkalinity to obtain CaO compositions. The alkalinity determinations for the CaO compositions in these samples indicated nonuniformity. By the detection of varying amounts of CaO within portions of the same reacted specimens, complete CaO dissolution was not achieved in these specimens, and equilibrium was not indicated.

The kinetic limitation on CaO dissolution might have been at least partially overcome with stirring, or through the use of more finely ground CaO in the initial compositions.

The kinetic limitations to CaO dissolution have been previously observed by Perry and MacDonald (11). In that work, specimens of 28 mole % CaO reportedly were allowed several days to dissolve in $CaCl_2$ at 927°C. In this work,

difficulties were encountered with the dissolution of much lower amounts of CaO at 850°C. This illustrates the strong temperature dependence on the dissolution rate over a temperature range significant to DOR processing.

Chapter 5

THERMODYNAMIC ANALYSIS

The equilibrium data at 850°C and 900°C from this work have been combined with the 800°C data of Perry and Shaw (8) in an effort to determine the partial molar heats and entropies of solution for Ca for a selected range of Ca-CaO-CaCl$_2$ compositions. These partial molar quantities are expressed within Equations 3 and 4.

$$\frac{\Delta \overline{H}_{ca}}{R} = -\left(\frac{\partial \ln X_{ca(sat)}}{\partial \left(\frac{1}{T} \right)} \right) \left(\frac{\partial \ln a_{Ca}}{\partial \ln X_{Ca}} \right) \tag{3}$$

$$\frac{\Delta \overline{S}_{ca}}{R} = \left(\frac{\partial \ln X_{ca(sat)}}{\partial \ln T} \right) \left(\frac{\partial \ln a_{ca}}{\partial \ln X_{ca}} \right) \tag{4}$$

The assumption is made that Henry's law applies ($a_{Ca} = KX_{Ca}$). For this assumption,

$$\frac{\partial \ln a_{ca}}{\partial \ln X_{ca}} = 1.$$

For these calculations, this term is taken to be unity. The technique applied to calculate these partial molar

quantities has been described by Hildebrand, et al. (20).
Plots of Ca solubility against CaO concentration were produced
from the data at the three temperatures. The data were curve-
fit using polynomial regression analysis. The equations
obtained were then used to calculate Ca concentrations at CaO
mole fractions of 0.01, 0.02, and 0.03. The range of CaO
concentrations for which the partial molar quantities were
calculated was limited by the narrow range of concentrations
measured at 850°C.

Plots of $Rln(X_{Ca(sat)})$ vs. 1/T were produced corresponding
to each selected CaO concentration in the solution. The
coefficients (slopes) from a linear fit of the data provided
the partial molar enthalpy of solution for Ca. The plots of
$Rln(X_{Ca(sat)})$ vs. ln(T) for each CaO concentration provided the
partial molar entropies of solution for Ca. This information
could be utilized in thermodynamic modeling of the Ca-CaO-
$CaCl_2$ system. The tabulated results for the calculated
partial molar quantities are provided in Table 4.

Table 4. Partial Molar Quantities for Ca in Ca-CaO-CaCl$_2$
Solution as a Function of CaO Concentration

X CaO Mole Fraction	$\Delta \bar{H}_{Ca}$ cal/mole	$\Delta \bar{S}_{Ca}$ cal/(mole°K)
0.01	11,300	10.1
0.02	14,700	13.1
0.03	18,400	16.3

Chapter 6

CONCLUSIONS/RECOMMENDATIONS FOR FURTHER WORK

The solubility of Ca in pure $CaCl_2$ increases from 2.14 to 3.6 mole percent from 800°C to 900°C according to Sharma (5). This strong temperature dependency over a range of interest to DOR processing has been confirmed within this work.

It is insufficient to consider only equilibrium values for Ca solubility in $CaCl_2$ for a description of Ca compositions in the DOR salt system. The additional complexity arises from compositional changes occurring as the reaction proceeds in the DOR system. Combining the data in this investigation along with that of Perry and Shaw (15), a description of the Ca solubility in the $Ca-CaO-CaCl_2$ system is provided for a range of temperatures from 800°C to 900°C. It is important that the available data be considered as descriptive of equilibrium conditions. For application to DOR processing, kinetic limitations on CaO dissolution cannot be ignored. It has been demonstrated that due to the CaO dissolution kinetics, the effective Ca content within the DOR salt system cannot be assumed implicitly from equilibrium solubility data. The kinetic constraints on CaO dissolution are overcome considerably when the temperature increases from 850°C to 900°C. Within the DOR system, temperature increases,

either by control or through excursions associated with the exothermic heat of reaction, would invoke greater Ca solubility. However, the increased temperature would perhaps more rapidly accelerate the dissolution of available CaO. Therefore the effective Ca content within the salt may not increase significantly. In fact it can be argued that in a balance of the two competing factors, over the time of the process, the effective amount of solubilized Ca may be decreased by the increased CaO dissolution with increasing temperature.

The density (21) of $CaCl_2$ is 2.15 gm/cc, and the density of CaO is 3.25-3.38 gm/cc. This suggests that insoluble CaO within the DOR system will reside near the salt-metal interface. This may contribute to insufficient coalescence of the Pu metal product and subsequently reduce the process efficiency.

The data presented in this study show that in the low CaO range of the $CaO-CaCl_2$ system, Ca solubility is considerably increased through a temperature range of 850°C-900°C. However, over the time intervals associated with DOR processing, the dissolution rate of CaO remains a major factor in predicting the amount of Ca in solution. Within the time provided for DOR reaction these kinetic factors remain important considerations. Temperature increases over the

characterized ranges may actually reduce reaction efficiency by the accelerated CaO dissolution rate.

As mentioned previously, the recovery of integral product metal is directly related to the efficiency of CaO dissolution in the salt solution phase. CaO dissolution efficiency has a dramatic temperature dependence. However, if satisfactory metal coalescence is achieved at the lower temperatures, it appears that no justification exists to increase temperatures on the basis of enhancing the CaO dissolution.

The kinetic limitations on the CaO solubility indicate that further characterization of the equilibrium behavior would provide limited value to current processing development. It is recommended that a parametric study be conducted to elucidate the dissolution rates for both Ca and CaO within the salt system. Additionally, studies to characterize the relative contributions of dissolved and undissolved Ca to the reduction of PuO_2 would provide further insight into the DOR process.

REFERENCES

1. J. G. Reavis, J. A. Leary, and K. A. Walsh, "Nonaqueous Dissolution of Massive Plutonium" U.S. Patent 3,049, 423, August 1962.

2. R. D. Baker, "Preparation of Plutonium Metal by the Bomb Method", Los Alamos Scientific Laboratory Report LA-473, 1946.

3. I. L. Jenkins et al., in Extractive and Physical Metallurgy of Plutonium and Its Alloys, W. D. Wilkinson (ed.), Interscience, N.Y., 1960.

4. W .Z. Wade and T. Wolf, "The Production of Plutonium Metal by the Direct Reduction of the Oxide", University of California Report UCRL-50483, 1968.

5. L. J. Mullins, D. C. Christensen, and B. R. Babcock, "Fused Salt Processing of Impure Plutonium Dioxide to High-Purity Metal", Los Alamos Scientific Laboratory Report LA-9154-MS, 1982.

6. A.S. Dworkin et al., Discussions of the Faraday Society, 32, 188, 1961.

7. D. T. Peterson and J. A. Hinkelbein, J. Phys. Chem., 63, 1360, 1959.

8. R.A. Sharma, J. Phys. Chem.,74, 3897, 1970.

9. D. D. Cubicciotti and C. D. Thurmond, J, Amer., Chem., Soc., 71, 2149, 1949.

10. L. I. Staffanson, The Physical Chemistry of Metals in Their Molten Halides, Ph.D. Thesis, London Univ., 1959.

11. G. S. Perry and L. G. MacDonald, J. Nuc. Mat., 130, 234, 1985.

12. G. S. Perry, Atomic Weapons Establishment, U.K., informal communication, 1990.

13. D. A. Wenz, I. Johnson, and R. D. Wolson, J. Chem. Eng. Data, 14, 250, 1969.

14. B. Neumann, C. Kroger, and J. Juttner, Z. Electrochem. Angew. Phys. Chem., $\underline{41}$, 725, 1935.

15. G. S. Perry and S. J. Shaw, "Solubility of Calcium in $CaO-CaCl_2$", AWE Report O-16/90, 1990.

16. J. L. Long, "Molten Salt Extraction of Americium from Plutonium 0.5 wt.% Neptunium Alloy", Rockwell International Rocky Flats Plant Report CD67-3086, May, 1967.

17. R. A. Sharma, General Motors Research Laboratory, informal communication, 1990.

18. G. S. Perry and L. G. MacDonald, J. Nuc. Mat., $\underline{130}$, 234, 1989.

19. K. M. Axler, E. M. Foltyn, R. I. Sheldon, and W. B. Hutchinson, J. Nuc. Mat., $\underline{161}$, 131, 1989.

20. J. H. Hildebrand, J. M. Prausnitz, and R. L.Scott, Regular and Related Solutions, Van Nostrand Reinhold Co., N.Y., 1970.

21. R. C. Weast and D.R. Lide (Ed.s), Handbook of Chemistry and Physics, CRC Press, Boca Raton, FL., 1989.

APPENDICES

APPENDIX A.   Nd-Yag Laser Welding Parameters Used in the Fabrication of the Ta Encapsulation Cells

Wavelength: 1060 nm. (I.R.)

Power: 375 watts

Pulse Time: 5 milliseconds

Pulse Rate: 16/sec.

Travel Rate: 12"/min.

Spot Width: 0.040"

APPENDIX B.   Analytical Data on Reactants

406 NORTH BUSEY AVENUE • URBANA, ILLINOIS 61801-2598
TEL. (217) 356-1347 • TELEX 206718 • CABLE ANPHYSLAB

MATERIAL: CaO , 99.99%   NOTE: Elements not reported less than
BATCH NUMBER: Typical Analysis   0.02 ppma (µmol/mol) of sample.

Spark Source Mass Spectrographic Analysis ppm by weight.

ANALYSIS ppm		ANALYSIS ppm		ANALYSIS ppm	
Li	0.04	As		Sm	
Be		Sc		Eu	
B	0.2	Br		Gd	
F		Rb		Tb	
Na	0.7	Sr	48	Dy	
Mg	2	Y		Ho	
Al	0.1	Zr		Er	
Si	5	Nb		Tm	
P	0.3	Mo		Yb	
S	1	Ru		Lu	
Cl	0.5	Rh		Hf	
K	0.02	Pd		Ta	
Ca	Major	Ag		W	
Sc		Cd		Re	
Ti		In		Os	
V		Sn		Ir	
Cr	<1	Sb		Pt	
Mn		Te		Au	
Fe	<0.9	I		Hg	
Co		Cs		Tl	
Ni	< 8	Ba	0.2	Pb	
Cu		La		Bi	
Zn		Ce		Th	
Ga		Pr		U	
Ge		Nd			

APPENDIX B.   Analytical Data on Reactants (continued)

406 NORTH BUSEY AVENUE • URBANA, ILLINOIS 61801-2508
TEL. (217) 356-1347 • TELEX 206718 • CABLE ANPHYSLAB

CERTIFICATE OF ANALYSIS

MATERIAL: CaO   Calcium Oxide   99.99%

BATCH NUMBER: Typical Analysis

MAJOR COMPONENT ANALYSIS: Percent by weight.

COMPONENT   VALUE   METHOD

  Ca (theo.) = 71.47%
  Ca (found) = 71.35%   EDTA titration

TRACE ANALYSIS: ppm by weight.

COMPONENT   VALUE   METHOD

  74 trace element analysis -- see attached sheet .

APPENDIX B.   Analytical Data on Reactants (continued)

Analytical Chemistry Report

Sample No.: 72934   Date Reported: 13-AUG-90

Submitting Group: NMT- 6   Submitter: AXLER   Form B Code: S55G

Sample Identification: CACL2-APL   Date Submitted: 19-JUL-90

Sample Description: CACL2

Analyses Requested: O2   , CaO , ACOES, Rpt

Submitter's Comments:

ANALYTICAL RESULTS

Analytical Results	Analyst(s)	Notebook	Page(s)
CaO* = None detected	DMR	767	101

$$\supset_{,1^{\prime}} \! /\!\_$$

(*) % = g/100 g Sample and ppm = ug/g Sample
COMMENTS: *Initial pH = 5.6

APPENDIX B.   Analytical Data on Reactants (continued)

Analytical Chemistry Report

Sample No.: 72934   Date Reported: 9-AUG-90

Submitting Group: NMT- 6   Submitter: AXLER   Form B Code: S55G

Sample Identification: CACL2-APL   Date Submitted: 19-JUL-90

Sample Description: CACL2

Analyses Requested: O2   , CaO   , ACOES, Rpt

ANALYTICAL RESULTS
———— ————

Ag <10	Al 20	As <10	Au <10	B <10	Ba <10
Be <10	Bi <10	Ca <10	Cd <10	Ce <10	Co <10
Cr <10	Cs <10	Cu <10	Dy <10	Er <10	Eu <10
Fe <10	Ga <10	Gd <10	Ge <10	Hf <10	Hg <10
Ho <10	In NA	Ir <10	K NA	La <10	Li <10
Lu <10	Mg <10	Mn <10	Mo <10	Na <10	Nb <10
Nd <10	Ni <10	Os <10	P NA	Pb <10	Pd <10
Pr <10	Pt <10	Rb <10	Re <10	Rh <10	Ru <10
Sb <10	Sc <10	Se <10	Si 910	Sm <10	Sn <10
Sr 32	Ta <10	Tb <10	Te <10	Th <10	Ti <10
Tl <10	Tm <10	U <10	V <10	W 110	Y <10
Yb <10	Zn <10	Zr <10			

μeq

COMMENTS: Analyzed by ICP-AES and ICP-MS.
            Results in ppm unless otherwise noted.
            NA - not analyzed.

Result is based on sample as received and is expressed as
ug/g or ug/ml unless indicated otherwise. Result preceded by a
< symbol represents our present limit of detection.

QA Procedure:
Data Recorded in LA Notebook No.: 26651   Page(s): 121
Analyst(s):   CSB,PEC

APPENDIX B. Analytical Data on Reactants (continued)

Analytical Chemistry Report

Sample No.: 72801   Date Reported: 9-AUG-90

Submitting Group: NMT- 6   Submitter: AXLER   Form B Code: S55G

Sample Identification: CA-1   Date Submitted: 6-JUL-90

Sample Description: CA METAL

Analyses Requested: O   , Mg   , ACOES, Rpt

Submitter's Comments:
    NEED PURITY (CONCENTRATIONS OF TRACE METALS). ALSO,
    O2 ANALYSIS AND MG. PLEASE PLACE SAMPLE IN AR ATMOS-
    P

ANALYTICAL RESULTS

Ag <10	Al <10	As <10	Au <10	B <10	Ba <10
Be <10	Bi <10	Ca NA	Cd <10	Ce <10	Co <10
Cr <10	Cs <10	Cu <10	Dy <10	Er <10	Eu <10
Fe 13	Ga <10	Gd <10	Ge <10	Hf <10	Hg <10
Ho <10	In NA	Ir <10	K NA	La <10	Li <10
Lu <10	Mg 2	Mn <10	Mo <10	Na <10	Nb <10
Nd <10	Ni 18	Os <10	P NA	Pb <10	Pd <10
Pr <10	Pt <10	Rb <10	Re <10	Rh <10	Ru <10
Sb <10	Sc <10	Se <10	Si <10	Sm <10	Sn <10
Sr 20	Ta <10	Tb <10	Te <10	Th <10	Ti <10
Tl <10	Tm <10	U <10	V <10	W 90	Y <10
Yb <10	Zn <10	Zr <10			

COMMENTS: Analyzed by ICP-AES and ICP-MS.
             Results in ppm unless otherwise noted.
             NA - not analyzed.

APPENDIX C. Calculations of Ca and CaO Compositions Based on
H_2 Evolution Measurements and Alkalinity Determinations

Determination of $CaCl_2$ from chloride titration data.

Let   D = Sample wt. (gm)

      E = H_2 gas volume (ml)

      F = Displaced Height of gas

      (M) = E/167.85

where each ml. of gas displaces (1/167.85) M height.

      J = ambient pressure (mm Hg) corrected for temp.

      K = H_2 pressure in atms corrected for the displaced

   fluid suppressing the expansion of H_2.

      K = F*(2)*(1000ml/liter)*(9.80M/sec*sec)*

              (9.87E-6 atm/pascal)*(J/760mm Hg per atm)

         = H_2 pressure in atms.

NOTE: the factor of 2 is required as both the calibrated
column and the receiving tube, of the same internal
dimensions, contained displaced fluid.

      L = moles H_2= moles Ca

      L = (H_2 pressure)*(liters of gas)/[(gas const.)*(T(k))]

   L = K*(E/1000ml per liter)/[(0.082*temp.)

      M = grams Ca (dissolved)=L*40.08

          wt fraction Ca = D/M

APPENDIX C.   Alkalinity Determinations of Ca-CaO (continued)

Both Ca and CaO undergo hydrolysis in the presence of water to generate the hydroxide $Ca(OH)_2$. It is the hydrolysis of Ca which produces the H_2 gas as described previously - the hydrolysis reaction of CaO does not produce H_2. Due to the production of identical product species, the alkalinity determinations provided quantitative values of both Ca and CaO, the contribution of CaO to the measurements was established by difference from the Ca values previously obtained by H_2 evolution.

A 0.1N HCl solution is prepared and confirmed by standardization against a 0.1N solution of a known base. Aliquots from the reacted samples were dissolved in deionized/distilled water to an arbitrary volume. A pH electrode is standardized by calibration with buffered solutions of pH 7 and 10. The preweighed and dissolved samples were titrated to pH 7 and from the mole numbers of HCl consumed, the mole numbers of the alkali species can be calculated. The moles of HCl (moles hydronium ion) consumed in the neutralization reaction are calculated by the product of the volume consumed times the normality. This corresponds to twice the number of moles Ca(OH)2 as indicated in the following reaction:

$$4HCL + 2Ca(OH)_2 \rightarrow CaCl_2 + 4H_2O$$
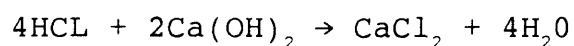
As mentioned, this represents the sum of the contributions of Ca and CaO into the system. The amount of moles in the sample size used for each determination was obtained from the H_2 evolution data and by difference, the mole numbers of CaO in each alkalinity sample were calculated.

APPENDIX C.   Calculation of $CaCl_2$ content by Argentometric
Titration (continued)

The specimens removed and examined for Ca by H_2 evolution
were each submitted for Cl analysis. This provided data on
the $CaCl_2$ composition of the exact specimen which provided the
Ca values.

A sample aliquot was transferred to a polyethylene beaker
and mixed with a non-ionic detergent, an HF solution and an
acetate buffer. Distilled water was used to dilute to an
arbitrary volume. The solution is titrated with a 0.1N silver
nitrate solution using a silver wire and a double junction
reference electrode. An auto-titrator was used in the
operation. The weight % Cl is calculated by the expressions
below:

Cl factor = (ml of 0.1N AgNO3) / (mg of Cl standard)

mg of Cl =

(ml of 0.1N AgNO3)*(Cl factor)*(sample vol.)/(aliquot vol.)

Wt. fraction Cl = (mg of Cl)/(mg of sample)

The wt fraction Cl provided for the calculation of the
$CaCl_2$ composition:

mole fraction $CaCl_2$ in sample = [(gm Cl)/(70.906)]/110.986

where 70.906 is the wt. Cl per mole $CaCl_2$ and 110.986 is the

molecular wt of $CaCl_2$.