**Development of a Solid
Absorption Process for
Removal of Sulfur from
Fuel Gas
First Quarterly Technical
Report**

MASTER

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May 1980

**Prepared for
the U.S. Department of Energy
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Battelle
Pacific Northwest Laboratories

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DEVELOPMENT OF A SOLID
ABSORPTION PROCESS FOR
REMOVAL OF SULFUR FROM
FUEL GAS
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CONTRACT DE-AC01-79ET11028
DEVELOPMENT OF A SOLID ABSORPTION PROCESS FOR
REMOVAL OF SULFUR FROM FUEL GAS

G. E. Stegen and K. M. Olson

I. OBJECTIVE AND SCOPE OF WORK

The objective of this project is to develop and demonstrate at bench scale a process for removing sulfur from reducing gases at high temperature ($>700^{\circ}\text{C}$). The process will use molten salts contained within the pores of a solid ceramic support material. It is expected that sufficient data will be obtained to allow scaleup and preliminary evaluation of the process.

II. SUMMARY

This report covers technical progress on development of the Solid Supported Molten Salt (SSMS) Process during August through October of 1979. This work is being performed under sponsorship of the U.S. Department of Energy, Division of Fossil Fuel Processing.

Much of the work during this quarter involved the set up and initial operation of experimental equipment. Equipment set up and operated during the quarter includes an apparatus for following gas/solid reactions at temperatures up to 900°C using a gravimetric technique, an aging chamber for exposing samples to various gas atmospheres at elevated temperature, equipment for impregnating porous ceramic samples with molten salts, and equipment for measuring crush strength at elevated temperature.

Data obtained so far indicate that the porous ceramic materials tested (Al_2O_3 , ZrO_2 , MgO , and $\text{Li}_2\text{O}\cdot\text{Al}_2\text{O}_3$) are readily wet by the molten salt and their open pore volume can be almost completely filled with salt by soaking in a salt bath for a relatively short period of time (vacuum is required in some cases to remove trapped gases). Materials tests and literature information both indicate that Al_2O_3 will not be an acceptable ceramic support material. Lithium aluminate ($\text{Li}_2\text{O}\cdot\text{Al}_2\text{O}_3$) presently appears to be the most promising candidate support material, MgO and ZrO_2 also remain as possibilities. A number

of porous lithium aluminate samples have been fabricated in house; testing of these is just getting underway.

III. INTRODUCTION

On August 1, 1979, Battelle Pacific Northwest Laboratories began a project to develop the Solid Supported Molten Salt (SSMS) Process for removing sulfur compounds from fuel gases at elevated temperature ($>700^{\circ}\text{C}$). This process is based on the use of molten mixtures of alkali metal carbonates and calcium carbonate as the active reactants for removing sulfur compounds. The sulfur removal capacity of the molten salt mixture may be regenerated by stripping with CO_2 and steam, usually at a reduced temperature. In this process, the molten salt mixture is contained within the pores of a porous ceramic substrate material. The absorbent material may be used in a packed bed, moving bed, or fluidized bed absorber.

The primary application for the Solid Supported Molten Salt process is expected to be in desulfurizing fuel gases produced by gasification of coal. It would be used most advantageously in applications where it is desirable to reduce or eliminate any cooling of the gas between the gasifier outlet and the gas user. Examples of such applications include gas turbines, high temperature fuel cells, boilers, and furnaces which operate in relatively close proximity to a coal gasifier. In these applications, reduction or elimination of the gas cooling requirements will generally improve thermal efficiency by retaining the sensible heat in the gas and may result in simplification of the process by elimination of gas cooling (and in some cases reheating) equipment and by elimination of process condensates and the equipment required for their handling and treatment.

Funding for the current two year development effort has been provided by the U.S. Department of Energy. The objectives of the present program are to obtain process and materials data sufficient to demonstrate feasibility of the process at bench scale and to allow preliminary economic analysis. Process data to be obtained include sorbent sulfur capacity, reaction kinetics and other operating characteristics. Various candidate materials will be purchased or fabricated and tested for suitability as porous ceramic substrate materials.

Process Chemistry

The calcium carbonate contained in the molten salt mixture is the primary reactant for removing sulfur compounds (primarily H_2S and COS) from the gas. Hydrogen sulfide is removed from the gas by the following reaction

This reaction is favored by higher temperatures and may be reversed by lowering the temperature and increasing the CO_2 and H_2O partial pressure. The alkali metal carbonates will also react with H_2S , however, the equilibrium is less favorable so that the reaction with calcium carbonate will predominate if it is present in the melt. The equilibrium constant for reaction (1) based on mole fractions is given by

$$K_1 = \frac{[\text{CaS}]}{[\text{CaCO}_3]} \cdot \frac{[\text{CO}_2][\text{H}_2\text{O}]}{[\text{H}_2\text{S}]} P \quad (2)$$

Where P is the total pressure in atmospheres and $[]$ denotes the mole fraction of a component in the liquid or gas phase.

Experimentally determined values for K_1 , are shown in Figure 1. Also shown are the thermodynamic K for reaction (1) and experimental values of K_2 for the reaction of H_2S with the alkali carbonate eutectic. The value of K_2 was calculated using the relationship

$$K_2 = \frac{[\text{M}_x\text{S}]}{[\text{M}_x\text{CO}_3]} \cdot \frac{[\text{CO}_2][\text{H}_2\text{O}]}{[\text{H}_2\text{S}]} P$$

Where M_xCO_3 denotes the eutectic mixture of sodium, lithium and potassium carbonates. When calcium is present, the primary role of the alkali carbonates is to act as a solvent for the calcium carbonate. Sodium, Potassium and Lithium carbonates form a eutectic melting at 394°C .⁽¹⁾ The eutectic composition corresponds to approximately 1/3 by weight of each of the carbonates. This mixture forms a clear liquid which is stable at temperatures required for the Solid

FIGURE 1. Reaction of H₂S with the Molten Alkali Carbonate Eutectic; with and without Calcium Carbonate Addition⁽¹⁾

Supported Molten Salt process i.e. 500-850°C. At concentrations up to at least 22% by weight calcium carbonate is soluble in the alkali carbonate eutectic and has little effect on the melting point.

IV. TECHNICAL PROGRESS

The overall project is broken down into two phases. In the first phase, basic process and materials data will be developed. In the second phase a bench scale system with about 25 cfm capacity will be built and tested.

During the first three months of work on this project, progress was made on several of the phase I tasks as follows.

Task 1-2 Support Material Selection and Procurement (K. M. Olson)

The objective of this task is to identify and obtain (if available) highly porous ceramic materials which may serve as suitable substrates for holding melts containing Na_2CO_3 , K_2CO_3 , Li_2CO_3 , CaCO_3 , and CaS . The material must be stable in neutral and reducing atmospheres and must resist attack by the melt at temperatures between 500°C and 800°C, and preferably up to 900°C. The material must be producible in tonnage quantities at a reasonable price.

The first step in the search for such a ceramic was to look at stable, high melting oxides. It was assumed that stable oxides would be superior to other refractory materials such as carbides, nitrides, refractory metals, and intermetallics. Also avoided were materials containing silica which is rapidly attacked by the salt and those containing iron which interferes with the process chemistry. A number of stable oxides are given in Table 1 in order of free energy of formation.

Al_2O_3 was an obvious first choice. It has a high melting point and is stable and inexpensive. In addition there is a large established technology for its fabrication in tonnage quantities with good control of physical properties such as porosity and pore size.

Porous Al_2O_3 samples were obtained from United Catalysts Inc. and Harshaw Chemical and tested in the molten salt. The information obtained from these tests, together with information gained from the literature⁽⁸⁾ and elsewhere^(9,10)

TABLE 1. Pertinent Properties of Some Stable High Temperature Oxides

Oxides	$\Delta G_f(298K)(2)$ Kcal/MoleO ₂	Melting(3) Point, °C	Crystal System	Linear Expansion Coefficient, 0-1000°C (cm/cm °C×10 ⁶)	Density
2 (CaO)	-288.68	2580	cubic(4)	--	3.32(4)
2 (MgO)	-272.2	2800	cubic(4)	13.5(5)	3.57(4)
LiAlO ₂ 1/2 (Li ₂ O·Al ₂ O ₃)	-269.51	1625	α-hexagonal(6) β-monoclinic(6) γ-tetragonal(7)	12.4(6)	3.40(8) 2.61(8) 2.615(8)
2 Li ₂ O	-268.6	1700	cubic (spinel)(4)	--	2.013(4)
1/2 (CaO·Al ₂ O ₃)	-263.95	1600	--	--	2.98(4)
1/2 (MgO·Al ₂ O ₃) (spinel)	-261.73	2135	cubic(4)	7.6(5)	3.59(4)
2/3 Al ₂ O ₃	-252.13	2050	α-hexagonal(4) γ-cubic (defect spinel)(4)	8.8(5)	3.98(4) 3.65(4)
ZrO ₂	-258.2	2715	monoclinic (LT)(4) tetragonal (HT)(4) cubic (stabilized)(4)	10.0(5)	5.56(4) 6.10(4) 5.5-5.9(4)

indicates that the molten salt mixture reacts with Al_2O_3 to form aluminates, i.e. $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3$, $\text{K}_2\text{O}\cdot\text{Al}_2\text{O}_3$, $\text{Li}_2\text{O}\cdot\text{Al}_2\text{O}_3$ and $\text{CaO}\cdot\text{Al}_2\text{O}_3$. Thus, it appears that Al_2O_3 can be eliminated as a candidate material. Other materials listed in Table 1 which can be eliminated include CaO and Li_2O which are soluble in the salt when CO_2 is present. Thermodynamic data indicate that $\text{CaO}\cdot\text{Al}_2\text{O}_3$ will be converted to $\text{Li}_2\text{O}\cdot\text{Al}_2\text{O}_3$ in the presence of lithium carbonate at high temperature. This then leaves MgO , ZrO_2 , $\text{MgO}\cdot\text{Al}_2\text{O}_3$, and $\text{Li}_2\text{O}\cdot\text{Al}_2\text{O}_3$ as candidate materials. (There are also other possibilities such as zirconates about which less is known). Lithium aluminate ($\text{Li}_2\text{O}\cdot\text{Al}_2\text{O}_3$) currently appears to be the most promising candidate material.

There has been a considerable amount of work done on development of lithium aluminate ceramics, primarily in two areas. First the molten carbonate fuel cell, which is presently under development, uses porous lithium aluminate to hold molten mixtures of lithium and potassium carbonate at the cell operating temperature of about 650°C . Much of the information on these materials is proprietary to General Electric and United Technologies. However, Argonne National Laboratory (ANL) has published a large amount of information on work it has done in the past three years on this material.⁽⁸⁾ The ANL reports indicate that lithium aluminate is stable to molten lithium and potassium carbonates for long periods - the goal for the ceramic tiles used in fuel cells is a 40,000 hr life. The properties desired for the ceramics used in molten carbonate fuel cell tiles are similar to those needed for the Solid Supported Molten Salt Process. The major differences include: Larger pore diameters are desirable and higher operating temperatures are required for the SSMS Process, and the salt used in the SSMS Process contains additional components (sodium, calcium and sulfur) which could have some effect on the ceramic.

In addition to the work related to the molten carbonate fuel cell, work was performed on development of lithium aluminate ceramics as part of the Hanford Coproduct Program (the co-products being plutonium and tritium). The work was performed during the mid-1960's, however, the reports have only recently been declassified.⁽⁶⁾ As part of this program, lithium aluminate was evaluated as a material for tritium breeding blankets in fusion reactors. It was produced by reacting lithium carbonate and alumina powders at $750\text{--}800^\circ\text{C}$ for 24 hours. This left 3% residual lithium carbonate, a mixture of α and γ lithium

aluminate and the compound $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3$ slightly substoichiometric in Li_2O . This material was ball milled, pressed into pellets at 40,000 PSI using lithium stearate as a binder and calcium carbonate as a sintering aid. The pellets were then fired at 1200°C for 24 hours or 1375°C for 14 hours. The final pellet densities were about 80% theoretical. They found the vapor pressure of lithium oxide over lithium aluminate to be negligible below 1200°C .

Argonne has experimented with several methods of producing lithium aluminate. It may be produced by either of the following reactions

The product of the above reaction is milled, pressed into the desired shape and sintered. ANL has supplied us with two discs which they produced. These samples were made from commercial lithium aluminate powder which was first ball milled to 100%-325 mesh, cold pressed and sintered at 1100°C for 2 hours. These samples are presently being evaluated.

Lithium aluminate is not available commercially as a porous ceramic. It is however, available as a powder. Since porous ceramics are not available for purchase we have initiated a (fairly limited) in-house effort to fabricate a number of samples for testing and evaluation. Several different techniques are being tried (see task 1-3).

A consideration of the thermodynamics of the aluminate formation reactions shows why Al_2O_3 is subject to attack by the salt and why lithium aluminate is a preferred material. The free energy change for a number of the important reactions is given in Table 2. Free energy of formation data is given for reference in Table 3. Reactions 1, 2, and 3 (Table 2) show that lithium aluminate formation is very favorable at high temperatures. Reactions 4 and 5 indicate

TABLE 2. Thermodynamics of Aluminate Formation

Reaction	$\Delta G(\text{Kcal/gmole})$		
	298°K (a)	800°K (a)	1100°K (b)
(1) $\text{Li}_2\text{CO}_3 + \text{Al}_2\text{O}_3 \rightarrow \text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 + \text{CO}_2$	+15.55	-7.06	-15.06
(2) $2\text{LiOH} + \text{Al}_2\text{O}_3 \rightarrow \text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3$	-5.7	-22.80	-27.82
(3) $\text{Li}_2\text{O} + \text{Al}_2\text{O}_3 \rightarrow \text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3$	-26.43	-28.70	-29.95
(4) $\text{Na}_2\text{CO}_3 + \text{Al}_2\text{O}_3 \rightarrow \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$	+23.19	+2.81	-5.34
(5) $\text{CaCO}_3 + \text{Al}_2\text{O}_3 \rightarrow \text{CaO} \cdot \text{Al}_2\text{O}_3 + \text{CO}_2$	+25.6	+4.8	-3.8
(6) $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 + \text{Li}_2\text{CO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3$	-7.63	-9.88	-9.71
(7) $\text{CaO} \cdot \text{Al}_2\text{O}_3 + \text{Li}_2\text{CO}_3 \rightarrow \text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 + \text{CaCO}_3$	10.05	-11.89	-11.26

Notes:

(a) carbonates and hydroxides as solids.

(b) Li_2CO_3 , LiOH , Na_2CO_3 as liquids, CaCO_3 and Li_2O as solids

that sodium and calcium aluminate formation becomes somewhat favorable at high temperatures but reactions 6 and 7 indicate that they will be mostly converted to lithium aluminate when lithium carbonate is present.

TASK 1 3 Support Material Fabrication and Durability Testing

The purpose of this task is to develop methods for fabricating porous ceramic materials and to assess the suitability of materials for use in the Solid Supported Molten Salt Process.

Work during this quarter included set up of materials exposure and aging furnace, set up of equipment for measuring crush strengths at high temperature ($>650^\circ\text{C}$), testing of a number of commercially available ceramics, and fabrication of a number of lithium aluminate ceramics for testing.

Materials Exposure/Aging Tests

An aging chamber has been set up for exposing the ceramic samples to molten salt mixtures and synthetic fuel gas/regeneration gas atmospheres over extended periods. The chamber consists of a 2 1/2 inch O.D. quartz tube inside an

TABLE 3. Free Energy of Formation of Some Pertinent Compounds

Oxide	$-\Delta G_f(298K)$	$-\Delta G_f(800K)$	$-\Delta G_f(1100K)$	Oxide	$-\Delta G_f(298K)$	$-\Delta G_f(800K)$	$-\Delta G_f(1100K)$
$\alpha\text{Al}_2\text{O}_3(\text{c})$	378.078	340.481	317.396	$\text{Li}_2\text{CO}_3(\text{c})$	270.598	236.225	216.706
$\gamma\text{Al}_2\text{O}_3(\text{c})$	373.790	336.697	314.122	$\text{Li}_2\text{CO}_3(\text{l})$	264.232	234.312	217.755
$\text{CO}_2(\text{g})$	94.265	94.556	94.658	$\text{Li}_2\text{O}(\text{c})$	134.348	118.120	108.198
$\text{CaCO}_3(\text{c})$	269.68 ^(b)	238.9 ^(a)	224.17 ^(a)	$\text{LiOH}(\text{c})$	104.858	85.943	74.961
$\text{CaCO}_3(\text{l})$	--	--	--	$\text{LiOH}(\text{l})$	102.683	86.334	77.521
$\text{CaO}(\text{c})$	144.247	131.845	124.507	$\text{Li}_2\text{O}\cdot\text{Al}_2\text{O}_3(\text{c})$	538.858	487.300	455.548
$\text{CaS}(\text{c})$	112.297	110.341	103.493	$\text{MgO}(\text{c})$	135.985	123.064	115.003
$\text{CaO}\cdot\text{Al}_2\text{O}_3(\text{c})$	527.89 ^(b)	480.0 ^(a)	450.7 ^(a)	$\text{MgCO}_3(\text{c})$	245.742	212.664	--
$\text{H}_2\text{O}(\text{g})$	54.636	48.646	44.712	$\text{MgO}\cdot\text{Al}_2\text{O}_3$	521.358	471.169	440.194
$\text{H}_2\text{S}(\text{g})$	7.955	12.162	8.688	$\text{Na}_2\text{CO}_3(\text{c})$	250.496	216.743	197.813
$\text{K}_2\text{CO}_3(\text{c})$	254.444	219.255	197.413	$\text{Na}_2\text{CO}_3(\text{l})$	246.625	214.886	197.664
$\text{K}_2\text{O}(\text{c})$	76.986	59.914	48.606	$\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3(\text{c})$	511.122	457.998	425.746
$\text{K}_2\text{O}\cdot\text{Al}_2\text{O}_3$	Not Available			$\text{K}_2\text{CO}_3(\text{l})$	250.822	217.413	196.996

*Unless otherwise indicated, all data from Reference 11.

(a) Data from Reference 2.

(b) Data calculated from information in References 2 and 12.

(c) Crystal, (g) gas, (l) liquid.

electric tube furnace. An alumina tube is used as a liner for the quartz tube since quartz is rapidly and severely attacked by the molten salt. A cover gas continuously flows through the chamber. In the present arrangement mixtures of CO_2 , CO , H_2 , N_2 , H_2S , and steam can be supplied to the aging chamber in virtually any proportion. The steam is supplied by saturating the gas stream at a measured temperature. The other gases are metered in using rotameters. Two sets of samples have been exposed in the aging chamber to date. Prior to placing the samples in the aging furnace they are soaked in the molten salt mixture (see task 1-4), cooled, and weighed. Measures which may be used to evaluate attack on the samples include weight loss, physical appearance, crush strength, hardness and reactivity. The results of the tests completed to date are given in Table 4. Also shown in Table 4 are similar data from two samples (GR1 and GR2) which were aged in the gravimetric reaction test apparatus (see Task 1-5). The weight loss data reported for test AG-1 are somewhat on the high side. When the samples were removed from the furnace it was found that a small amount of salt had seeped out and was lost. Although the amount lost appeared to be small it certainly contributed to the weight loss. In test AG-2 the samples were placed in weighted alumina boats so that salt loss could be accounted for.

The results of the aging and gravimetric tests show that the porous alumina ceramics tested readily react with the molten salt mixture at temperatures of interest for the Solid Supported Molten Salt Process. The thermodynamic data and other available information indicate that the loss in weight is caused by formation of aluminates following the reaction

If this reaction goes to completion, the weight of CO_2 lost will amount to 44% of the initial salt weight. If only the Li_2CO_3 reacts, the weight loss amounts to about 15% of the initial salt weight. Two of the aged samples (GR-1 and 1-AG-4) were analyzed to determine how much of the original carbonate remained. It was found that less than 10% of the original carbonate remained after

TABLE 4. Data From Pellet Aging Tests

Material Type	Material Designation	Sample Number	Initial Ceramic Weight	Initial Salt Weight	Weight Loss	% Loss on Salt Weight	Temperature range °C	Aging Time	Atmosphere	Test Number
Alumina	UC-1	1-AG-1	2.5828	0.8747	0.4749	54.3	625-870	267 hr	CO ₂ +H ₂ O	AG-1
Alumina	UC-1	1-AG-2	2.5534	1.0976	0.5602	51.0	625-870	267 hr	CO ₂ +H ₂ O	AG-1
Alumina	UC-1	1-AG-3	2.449	0.7461	0.3982	53.4	625-870	267 hr	CO ₂ +H ₂ O	AG-1
Alumina	HA-1	1-AG-4	1.8135	1.584	0.835	52.7	625-870	267 hr	CO ₂ +H ₂ O	AG-1
Alumina	UC-1	2-AG-3	2.7811	1.0894	0.3054	28.0	726-776	144 hr	CO ₂ +H ₂ O	AG-2
Alumina	UC-1	2-AG-4	2.7070	1.006	0.2897	28.8	776-776	144 hr	CO ₂ +H ₂ O	AG-2
Alumina	HA-1	2-AG-5	0.571	0.476	0.076	15.9	726-776	144 hr	CO ₂ +H ₂ O	AG-2
Alumina	HA-1	2-AG-6	0.5612	0.5570	0.0682	12.24	726-776	144 hr	CO ₂ +H ₂ O	AG-2
MgO	AP-2	2-AG-7	0.256	0.160	0.0068	4.3	726-776	144 hr	CO ₂ +H ₂ O	AG-2
ZrO ₂	AP-3	2-AG-8	0.0802	.0264	.0003	1.11	776-776	144 hr	CO ₂ +H ₂ O	AG-2
Alumina	UC-1	GR-1	2.4810	.934	0.35	37.5	590-780	260 hr	CO ₂ +0-25% H ₂ O +0-90% H ₂	GR-1
ZrO ₂	AP-3	GR-2	.644	0.212	.0892	42.1	590-830	376 hr	CO ₂ +0-50% H ₂ O +0-70% H ₂ +0-1780 ppm H ₂ S	GR-2

aging. The residue which remained after leaching one of the aged samples with dilute HCL was examined by x-ray diffraction and found to be approximately 75% lithium aluminate and 25% alumina.

Lithium Aluminate Sample Fabrication

Lithium aluminate samples have been fabricated using several techniques. As of the end of October approximately fifty samples had been prepared. Testing of these samples is just beginning. The following procedures have been used to fabricate the samples.

- Lithium Aluminate Powder: Commercially available lithium aluminate powder is pressed into pellets and sintered at temperatures between 700°C and 1500°C.
- Lithium Carbonate and Alumina Powders, Dry: the dry powders are ground or milled together and pressed into pellets. The pellets are then sintered at temperatures between 700°C and 900°C, usually for 12 to 24 hrs.
- Lithium Carbonate and/or Lithium Hydroxide and Alumina Powder, Wet: The lithium compounds are dissolved in water and the alumina powder added. The mixture is stirred as the water is evaporated off. When most of the water has been evaporated, the mixture is pressed into pellets, dried and sintered at temperatures between 750°C and 950°C.

Pellets produced from lithium aluminate powders showed no volume change and crumbled easily when fired at temperatures of 1000°C or less for 20 hrs. Pellets fired at 1250°C and 1500°C for 20 hours showed 12% and 28% volumetric shrinkage respectively, weigh loss was 2 to 3% and 10-12% respectively. The high weight loss at 1500°C was probably caused by decomposition of the aluminate and sublimation of Li_2O .

The behavior of pellets produced by reaction of lithium carbonate or hydroxide with alumina is quite different from those produced using lithium aluminate powders. Pellets which appear to be fairly strong (quantitative strength tests have not yet been made) have been produced at reaction (sintering) temperatures as low as 750°C. There is little additional change in weight or density as the reaction temperature is increased from 750°C to 900°C. The volume of the pellets increases substantially as they react. Volume increases

of up to 30% were measured with lithium carbonate as the reactant. Lithium hydroxide produced a somewhat smaller increase - up to 18.2%. Additional discussion and experimental data on the lithium aluminate samples are included next section (Task 1-4).

The preliminary results from the lithium aluminate fabrication tests indicate that a highly porous lithium aluminate can be produced which will accommodate a relatively high loading of molten salt. The suitability of this material for use in the Solid Supported Molten Salt Process remains to be determined.

Task 1-4 - Development of Techniques for Impregnating the Porous Solid Substrate with Molten Salt Mixtures

The objective of this task is to develop techniques for loading the pores of the ceramic substrate with salt, to evaluate the salt loading capacity of various samples, and to provide loaded samples for use in other tasks.

Tests made during the quarter have shown that with some materials, the pores can be virtually filled with the molten salt mixture by simply soaking the sample in a molten salt bath for a relatively short period of time, (2 to 20 min). With other samples it is necessary to remove trapped gases from the pores by applying a vacuum.

The procedure used in these tests is as follows. Calcium, sodium, lithium and potassium carbonate powders^(a) are weighted and mixed at the desired composition. The mixture is placed in an alumina vessel and brought up to a temperature of 650-725°C. At this temperatures the mixture is a clear liquid with an appearance similar to water. To prevent decomposition of the carbonates, CO₂ is continuously bubbled through the solution. Samples to be impregnated are first dried and weighed and are then suspended approximately an inch above the liquid which allows them to warm up to near the bath temperature. The samples are then dipped in the bath for a measured period of time. In some cases a vacuum is drawn on the bath while the samples are soaking. This

(a) In some cases lithium hydroxide has been used in place of lithium carbonate. This is converted to the carbonate after melting by bubbling CO₂ through the mixture.

removes trapped gases from the pores. When the samples are finished soaking they are removed and placed in a porous ceramic cup located in another furnace. Most of the surface liquid drains off and soaks into the porous cup (which is essentially being used as a blotter). The samples are then removed, cooled in a dessicator and weighed.

An analogous test has been run on a number of samples using boiling water rather than molten salt. The samples are boiled for 15-20 min, and surface water drained or blotted off. The volume of water retained in the pores and hence the open pore volume is then determined by the increase in weight.

The results of the boiling water and molten salt soaking tests are given in Table 5 for the commercially obtained samples. For the porous alumina samples shown, the water pickup in the boiling water test ranged from 0.15 to 0.4 cm³ per gram of ceramic while the weight increase on soaking the ceramic in the salt bath ranged from 0.3 to 0.94 gram of salt per gram of ceramic. In most cases the ratio of salt pickup to water pickup weights is a little above 2/1, which is in line with the ratio of their densities. This indicates that the salt is filling essentially all the pores accessible to the boiling water. Using vacuum (28" to 30" Hg) to remove residual trapped gases from the pores had little if any effect on the samples tested, again indicating that essentially all of the open pores were filled by soaking in the molten salt bath. The higher than normal salt loadings shown for the high (30%) calcium carbonate tests resulted from excess surface salt. This mixture is more viscous and has a higher melting point than the 20% and 22.7% mixtures used in the other tests and did not drain off the samples very well.

The single sample of MgO tested so far showed a lower than expected ratio of salt pickup to water pickup. It appears that this was caused by a higher than expected water pickup which may have resulted from reaction of the MgO with water. If the salt pickup is compared with the void volume based on percent of theoretical density it appears to be about right i.e. the void volume is calculated as 0.2 cm³/g and the ratio of salt pickup to void volume is 2.31 g/cm³. The ratio of the salt pickup to water pickup weights for the ZrO₂ sample is about as expected, indicating that the pores are filled by soaking without vacuum.

TABLE 5. Results of Boiling Water and Molten Salt Soaking Tests on Commercial Ceramics

Material	Designation	Density		Water Pickup		Salt Soak Test		Salt Mix	Salt Soak Description		
		g/cc	%	cc/cc*	cc/g	Salt* Cer.	Salt H ₂ O		Temp	Time	Comments
Alumina	UC-1	2.07	52.4	0.39	0.19	0.46	2.42	A	600°C	30 sec	
Alumina	UC-1	2.11	53.4	0.401	0.19	0.489	2.57	A	596°C	2 min	
Alumina	UC-1	2.14	54.0	0.41	0.19	0.42	2.57	A	598°C	10 min	
Alumina	UC-1	2.11	53	0.40	0.19	0.346	1.82	B	680°C	3 min	
Alumina	UC-1	2.11	53	0.40	0.19	0.387	2.04	B	662°C	4 min	
Alumina	UC-1	2.11	53	0.40	0.19	0.372	1.96	B	655°C	3 min	
Alumina	UC-1	2.11	53	0.40	0.19	0.430	2.26	B	690°C	3 min	
Alumina	HA-1	1.435	36	0.552	0.385	0.496	1.38	A	594°C	30 sec	
Alumina	HA-1	1.435	36	0.552	0.385	0.777	2.02	A	595°C	5 min	
Alumina	UC-1	2.11	53	0.400	0.19	0.305	1.60	B	711°C	3 min	
Alumina	UC-1	2.11	53	0.400	0.19	0.406	2.14	B	718°C	3 min	
Alumina	HA-1	1.43	36	0.552	0.385	0.804	2.09	B	725°C	5 min	
Alumina	HA-1	1.43	36	0.552	0.385	0.815	2.12	B	725°C	13 min	
Alumina	HA-1	1.43	36	0.552	0.385	0.874	2.27	B	723°C	10 min	
Alumina	UC-1	2.11	53	0.358	0.1699	0.393	2.31	B	657-714°C	3 hrs	Vacuum
Alumina	UC-1	2.11	53	0.376	0.178	0.403	2.27	B	714°C	3 min	
Alumina	UC-1	2.11	53	0.437	0.207	0.434	2.10	B	709°C	3 min	
Alumina	UC-1	2.11	53	0.428	0.203	0.465	2.29	B	708°C	7 min	Vacuum
Alumina	UC-1	2.11	53	0.371	0.176	0.426	2.42	B	708°C	7 min	Vacuum
Alumina	UC-1	2.11	53	0.459	0.218	0.478	2.19	B	708°C	8.3 min	Vacuum
Alumina	UC-1	2.11	53	0.325	0.154	0.367	2.38	C	707°C	3 min	high CaCO ₃
Alumina	UC-1	2.11	53	0.409	0.194	0.474	2.45	C	709°C	3 min	high CaCO ₃
Alumina	UC-1	2.11	53	0.335	0.159	0.392	2.46	C	714°C	3 min	high CaCO ₃
Alumina	HA-1	1.435	36	0.567	0.395	0.834	2.11	B	709°C	13 min	
Alumina	HA-1	1.435	36	0.549	0.383	0.992	2.59	C	708°C	10 min	high CaCO ₃
Alumina	AP-1	--	--	--	0.360	0.942	2.61	B	710°C		
MgO	AP-2	1.818	51	0.873	0.480	0.625	1.30	B	710°C	10 min	
ZrO ₂	AP-3	2.976	54	0.440	0.148	0.330	2.23	B	708°C	10 min	

Notes:

% Density = Density of Sample ÷ Theoretical Density of base material X100%

Water Pickup cc/cc = volume of water uptake ÷ volume of sample

Water Pickup cc/g = volume of water uptake ÷ dry sample weight

Salt/Cer. = weight increase from soaking in salt bath ÷ initial dry weight

Salt/H₂O = weight increase in salt soaking test ÷ weight increase in water pickup test

*In most cases the water pickup, density, and salt pickup were not determined on the same sample. Typical numbers for similar samples were used in calculating ratios.

Salt Mix (by weight) (A), Na₂CO₃ = 26.7%, K₂CO₃ = 26.7%, Li₂CO₃ = 26.7%, CaCO₃ = 20%
 (B), Na₂CO₃ = 29.7%, K₂CO₃ = 30.7%, Li₂CO₃ = 16.8%, CaCO₃ = 22.7%
 (C), Na₂CO₃ = 26.7%, K₂CO₃ = 27.6%, Li₂CO₃ = 15.1%, CaCO₃ = 30.6%

Boiling water and salt soaking tests have also been carried out on the initial set of lithium aluminate samples which were fabricated in-house. The results of these tests are given in Table 6. The weight increase during the boiling water soak ranged from 31.7 to 43.5% of the ceramic weight. This indicates an open pore volume of 41.9 to 51.5% of the sample volume. The percent void volume indicated by the sample density measurements varies between 42.1% and 55% and agrees with that determined by the water pickup test within a few percent. The salt soaking tests showed that a high salt loading could be obtained: 49% to 84% of the initial ceramic weight. However, the weight increase during the salt soaking tests is less than expected from the water pickup and density measurements. When vacuum was not used, the salt pickup was only 1.24 to 1.82 times the water pickup. By using vacuum this was increased substantially to between 1.75 and 2.15. This indicates that a portion of the pore volume is less accessible to the molten salt mixture than to boiling water.

Task 1-5 - Determination of Sorption Capacity, Regeneration Efficiency and Absorption and Regeneration Reaction Kinetics using Gravimetric Tests.

During this quarter experimental equipment was assembled for following the weight of sorbent pellets as they react with various gases at high temperature. The experimental thermal balance assembly is shown in Figure 2. The sample is suspended from a balance using a platinum wire and hangs inside the heated reaction tube. The reactant gases are metered with rotameters and flow first to an evaporator where steam is added. From the evaporator the gases flow into the bottom of the reaction tube where they are preheated prior to contacting the sample. Purge gas (CO_2 or N_2) flows into the glass bell which surrounds the balance and out through the vent line near the top of the reaction tube. The balance, manufactured by Wm. Ainsworth & Sons Inc., is equipped with a mechanism which will automatically add or remove counterweights over a range of 390 mg, it has an electrical output and can usually be read to the nearest 0.05 mg.

As of the end of October, two samples have been tested in the thermal balance. The first sample tested (GR-1) was a porous alumina ring approximately 0.6" in diameter and 0.3" thick, which was saturated with a salt mixture consisting of 29.7% (wt.) Na_2CO_3 , 30.7% K_2CO_3 , 16.8% Li_2CO_3 , and 22.7% CaCO_3 .

TABLE 6. Lithium Aluminate Pellets: Data From Fabrication, Water Soak, and Salt Soak Tests

Pellet Mix	Sintering Temp. (Max.)	Time at Max. Temp.	During Sintering		Density		Water Pickup		Salt Soak Test			Salt Soak Description		
			Wt. loss	Volume Change	g/cc	%	cc/cc	cc/g	Salt Cer.	Salt* H ₂ O	Salt* Mix	Temp.	Time	Comments
4	950°C	2 hr	10.5%	+2.9%	1.35	51.7%	0.491	0.364	0.578	1.5	D	693°C	20 min	
1	950°C	2 hr	10 %	+3.5%	1.41	54.0%	0.461	0.327	0.595	1.82	D	692°C	10 min	
4	900°C	2 hr	7.8%	--	1.49	57.3%	0.472	0.317	0.493	1.55	D	712°C	10 min	
1	900°C	2 hr	9.9%	--	1.51	57.9%	0.503	0.333	0.527	1.58	D	712°C	10 min	Boiled
4A	800°C	15 hr	24.0%	+26.3%	1.206	46.2%	0.510	0.423	0.526	1.24	D	709°C	10 min	Boiled
4A	800°C	15 hr	24.0%	+26.3%	1.206	46.2%	0.511	0.424	0.540	1.27	D	691°C	10 min	
4A	800°C	15 hr	24.0%	+26.8%	1.206	46.2%	0.510	0.424	0.839	1.88	D	712°C	24 min	Vacuum
4A	900°C	2 hr	24.7%	+27%	1.175	45%	0.511	0.435	Sample Fell Apart in Salt					Boiled
4A	900°C	2 hr	24.7%	+27%	1.175	45%	0.511	0.435	0.838	1.93	D	708°C	16 min	Vacuum
1A	750°C	64 hr	9.8%	+18%	1.404	53.8%	0.515	0.367	0.653	1.78	D	704°C	10 min	Boiled
1A	900°C	3 hr	9.8%*	+18.1%	1.40	53.6	0.472	0.337	No Salt Soak Test					
2A	750°C	64 hr	9.1%	--	1.47	56.3%	0.510	0.347	0.532	1.53	D	705°C	10 min	Boiled
2A	900°C	3 hr	10.6%	+18.2%	1.423	54.5%	0.488	0.343	No Salt Soak Test					
3A	900°C	3 hr	19%	+25.4%	1.28	49.0%	0.500	0.391	0.685	1.75	D	709°C	15 min	Vacuum
3A	900°C	3 hr	19%	+25.4%	1.28	49.0%	0.500	0.391	0.841	2.15	D	724°C	13 min	Vacuum
3A	900°C	3 hr	19%	+25.4%	1.28	49.0%	0.500	0.391	0.678	1.73	D	725°C	13 min	Vacuum

Notes:

Salt Mix D, Na₂CO₃ = 29.8%, K₂CO₃ = 30.8%, Li₂CO₃ = 16.6%, CaCO₃ = 22.8%

Pellet Mix 1 = LiOH + Al₂O₃ (coarse powder) wet mix

4 = LiOH + Al₂O₃ (coarse powder) + 1.3% Na₂CO₃ + 1.3% K₂CO₃, wet mix

1A = LiOH + Al₂O₃ (-325 Mesh) wet mix

2A = LiOH + Al₂O₃ (-325 Mesh) + 1.3% Na₂CO₃ + 1.3% K₂CO₃, wet mix

3A = LiOH + Al₂O₃ (-325 Mesh) wet mix

4A = Li₂CO₃ + Al₂O₃ dry mix

Boiled - These samples were boiled in water for approximately 30 min and dried prior to the salt soak tests

*In most cases the salt soak and water soak sets were not performed on the same sample, therefore the water pickup was estimated from the results for similar samples.

See also Table 5 notes

FIGURE 2. Thermal Balance Experimental Assembly

This sample showed a large, mostly irreversible, weight loss when exposed to temperatures of 1300°F to 1400°F in a CO₂ atmosphere.

The weight loss during the initial exposure for 12 hr at 1300 to 1400°F amounted to 33% of the initial weight of salt in the sample. Approximately 1/4 of this loss was regained when the temperature was reduced to 1120°F and the sample exposed to a steam CO₂ atmosphere for 65 hours. A second heating and cooling cycle resulted in additional weight loss. After 260 hr at temperatures of 1100 to 1440°F the total permanent weight loss amounted to 37.5% of the initial salt weight. After the sample was removed from the balance it was analyzed for residual CO₂ content by decomposing the carbonate with dilute HCl and measuring the CO₂ evolved. The weight of CO₂ evolved was 3.7 % of the initial salt weight. The CO₂ content of a similar sample which had been dipped in salt but not aged showed a CO₂ content of 34.5% of the initial salt weight. This indicates that most of the weight loss was caused by CO₂ loss which presumably resulted from aluminate formation. Analysis of the insoluble residue from the HCl digestion by X-ray diffraction showed that this material was 75% lithium aluminate and 25% alumina.

The second sample tested in the thermal balance (GR-2) consisted of nine 1/8" diameter by 1/8" long porous ZrO₂ (98%) + Al₂O₃ (2%) pellets, which were saturated with the same salt as sample GR-1. As the sample was heated initially from 1000°F to 1529°F in a CO₂ atmosphere it suffered a permanent weight loss equal to about 8% of the initial salt weight. After this the weight varied reversibly with temperature (still in a CO₂ atmosphere). The weight at 1529°F was lower than that at 1042°F by 3.5% of the initial salt weight. When the sample was exposed to a steam-CO₂ atmosphere for 26 hr at 1340 to 1440°F it suffered an additional permanent weight loss of 3.3%. Subsequent exposure to gases containing H₂ and in some cases H₂S in addition to CO₂ caused much larger and more rapid permanent weight loss. The total weight loss after 376 hours in the thermal balance was 42% of the initial salt weight. The reason for the loss in weight is being investigated.

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