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Glass and Ceramic Materials for the Immobilization of Megacurie- Amounts of Pure Cesium-137

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ABSTRACT

Megacurie-amounts of radioactive cesium (^{137}Cs and ^{134}Cs) can be satisfactorily incorporated in a variety of ceramic forms including glass, glass-ceramics, cesium-loaded zeolites, and the mineral pollucite. Glasses which contain up to 45 mass percent Cs_2O can be prepared having leach rates in distilled water at 25°C in the range 2×10^{-5} to 3×10^{-3} g $\text{Cs}/\text{cm}^2/\text{day}$. Attempts to produce glass ceramics containing pollucite failed to yield a glass that crystallized but did yield several satisfactory glasses. Leach rates of fully loaded zeolites containing 23 mass percent Cs_2O decreased from 10^{-4} g $\text{Cs}/\text{cm}^2/\text{day}$ to 3×10^{-6} g $\text{Cs}/\text{cm}^2/\text{day}$ as the firing temperature was increased from 500 to 1100°C . Aqueous solutions of cesium chloride mixed with bentonite clay react when dried and fired at 750 to 1000°C to form pollucite. A 79% yield was found at 1000°C .

GLASS AND CERAMIC MATERIALS FOR THE IMMOBILIZATION OF MEGACURIE-AMOUNTS OF PURE CESIUM-137

INTRODUCTION

Nuclear wastes from the reprocessing of reactor fuels at Hanford are reworked to separate the principal heat-generating isotopes, ^{137}Cs and ^{90}Sr . These isotopes are currently being doubly encapsulated as cesium chloride and strontium fluoride for interim storage in a water-cooled storage basin using materials and techniques of high reliability. Neither of these compounds, however, is very compatible with materials suggested in plans for ultimate final storage of nuclear wastes. By the end of the campaign at Hanford there will be megacurie quantities of these isotopes in storage. This paper describes additional research which has been done to further enhance the high integrity system presently in use and converting cesium chloride either to materials which are more suitable for final storage or to materials which are readily incorporated into those found in proposed plans for final storage.

SUMMARY AND CONCLUSIONS

Reprocessing of nuclear fuels at Hanford has generated megacurie-amounts of isotopically enriched ^{137}Cs chloride. In this investigation we have looked at various alternate products to replace CsCl for interim storage and which can be used to convert CsCl to a form more acceptable to proposed final storage criteria. Four materials were investigated and the results are summarized below.

Glasses made from cesium carbonate and/or cesium carbonate solutions mixed with typical glass-forming components (e.g., SiO_2 , B_2O_3 , etc.) had leach rates in distilled water which were 2×10^{-5} to 3×10^{-3} g Cs/cm²/day and contained 30 to 45 mass percent Cs_2O . With densities about 3.5×10^3 kg/m³ these glasses offer the highest cesium storage densities of the products studied and require the least complicated processing method. However, the leach rates for the glasses with ~45 mass percent Cs_2O are high relative to the other products studied.

Glass-ceramic materials offer the advantage of immobilizing the cesium as pollucite ($\text{CsAlSi}_2\text{O}_6$) which is a very insoluble mineral and then surrounding these crystals with a stable and nonleachable glass. Attempts to produce such materials yielded several acceptable glasses which would not crystallize to glass-ceramics. While excellent pollucite glass-ceramics have been made^[1] they require methods which would be too exotic for use in the nuclear industry. Also, the cesium storage density (~0.7 kg/m³) is so low that it would require double the storage volume of glass and about four times the storage volume of CsCl. Clearly, this is unacceptable.

Cesium can be loaded onto zeolites (AW-500[®] and Zeolon 900[®]) such that the product, fired to 1100°C, contains 23 mass percent Cs_2O . These products have excellent leach rates which vary from 1×10^{-4} g Cs/cm²/day to 3×10^{-6} g Cs/cm²/day as the temperature at which the products are fired is increased from 500 to 1100°C. While the leach rates are excellent and good long-term physical stability can be expected, the cesium storage density is the lowest of the products studied. A low storage density remains even if the bulk density could be increased to near

the theoretical limit.

Cesium chloride can be converted directly to pollucite by mixing a 3M CsCl solution with bentonite clay, drying and firing to 1000°C. By 750°C the reaction is complete according to X-ray analysis. Addition of NaOH to make the starting solution 1.5M NaOH and 3M CsCl and precalcining the bentonite lowers the temperature for complete reaction to 600 to 650°C. Chemical analysis of these products shows little or no vaporization of cesium during the firing process. If this product can be sintered to near theoretical density, it becomes competitive with glass. On this basis it has a slightly lower cesium storage density (1.2×10^3 kg Cs/m³ of product) than glass (1.4 - 1.5×10^3 kg Cs/m³ glass) but potentially a much lower leach rate ($<1 \times 10^{-7}$ g Cs/cm²/day as opposed to 2×10^{-5} to 3×10^{-3} g Cs/cm²/day for glass).

Using the cesium storage density as the primary consideration, both cesium glasses and pollucite would be selected as candidates for final or interim storage. Which of these two would be selected depends in large part upon how easily pollucite, formed from bentonite and aqueous cesium chloride, can be sintered to near theoretical density. If densification is feasible, then pollucite should be selected because of overall stability and low leach rate (it is a natural mineral which has been around for millennia).

Stability of these materials with respect to the changes that occur as ^{137}Cs decays to ^{137}Ba suggests product criteria which have not been adequately defined. Langlet^[2] addressed the problem and indicated that pollucite might have structural stability problems due to stresses caused by the decay of ^{137}Cs after 30 years of

storage (one half-life). A glass product may also have a similar problem.

EXPERIMENTAL

MATERIALS

All chemicals used in this work were analytical grade except for Cs_2CO_3 (99.9%) and sand (99.7% SiO_2). Bentonite clays were obtained from Federal Bentonite Company, Cleveland, Ohio (Wyo-Bond[®], 200 mesh) and Georgia Kaolin, Elizabeth, New Jersey (MC-101[®], 200 mesh). These clays were either used as received or calcined at 750°C for 24 hr prior to use. While both clays behaved similarly, only the Wyo-Bond results are reported here. Zeolites were obtained from the Norton Company, Worcester, Massachusetts (Zeolon 900[®]) and Linde Division of Union Carbide Corporation, Tarrytown, New York (AW-500[®]).

PROCEDURES

Glass

Most glasses were made by mixing typical glass forming components [e.g., SiO_2 (sand), B_2O_3 , etc.] with a 1.3M Cs_2CO_3 solution, since that is how the Encapsulation facility receives the cesium. Dry mixing of the glass components was also used and gave similar results. These mixtures were melted in Pt-5% Au crucibles at temperatures up to 1500°C. Visually acceptable glasses were leached in distilled water at ambient temperatures and the leachate analyzed on a Varian Techron AA-6 atomic absorption spectrometer. Viscosities of three glass melts were determined by Battelle Pacific Northwest Laboratories, Richland, Washington.

Glass-Ceramics

Similar techniques were used in preparing glass-ceramic materials. After a good glass melt was obtained the sample was air-quenched and then heat-treated at temperatures up to 1000°C. Any crystalline material was analyzed by X-ray diffraction. If no crystallization occurred after initial heat treatment, the glass was crushed and remelted with 5 mass percent TiO_2 or ZrO_2 .

Zeolites

Columns containing approximately 50 ml of zeolite were washed and classified with water. A 0.1M Cs_2CO_3 was adjusted to pH ~7 using 10M HCl. Fifteen column volumes of this solution were passed through the column at the rate of one column volume per hour. After washing with water the loaded zeolites were dried and fired at 500°, 800°, and 1100°C on a schedule of four hours at each temperature. Samples were taken at each temperature for composition analysis and leach studies. Cesium analyses were done by fusing the loaded zeolite with lithium metaborate for 15 min at 1000°C. The fused material was dissolved in 10% HCl, diluted with distilled water, and analyzed by atomic absorption.

CsCl-Bentonite

Bentonite clay either as-received or precalcined was mixed with a 3M CsCl solution, dried and fired at 500°, 600°, 650°, 750°, and 1000°C for 2 hr at each temperature. This preparative scheme simulated the use of current Encapsulation feed with pH adjustment or the use of solutions of CsCl dissolved from loaded capsules. The rate of reaction was increased by mixing a solution which was 1.5M NaOH and

3M CsCl with either as-received or precalcined bentonite.^[3] Compositional analyses were done in the same fashion as the zeolites described above. Differential thermal analyses (DTA) and thermal gravimetric analyses (TGA) on samples dried at 110°C were obtained using a Mettler Vacuum Thermo-analyzer with an air atmosphere.

RESULTS AND DISCUSSION

GLASS

Glasses with the compositional ranges shown in Table I (see Tables A-I and A-II for more detailed compositions) were generally colorless with the exception of those containing zinc, which were pink-to-purple.

TABLE I
COMPOSITIONAL RANGES FOR GLASSES

<u>Component</u>	<u>Mass Percent</u>
Cs ₂ O	30-45
SiO ₂	18-42
B ₂ O	0-15
Na ₂ O	0-8
Li ₂ O	0-10
TiO	<5
Al ₂ O ₃	<11
Frit*	50-70

*See Table A-II for the zinc-borosilicate frit composition.

In the early stages of the project, melting temperatures were kept low because of the Encapsulation Facility's cesium chloride melter was to be used with its operating temperature limit of 900°C. This restriction was relaxed as the project proceeded.

Glasses which appeared to be single phase melts were

leach-tested. Leach rates from these glasses ranged from 2×10^{-5} to 3×10^{-3} g Cs/cm²/day. The lowest leach rate (Table A-III) was found for a glass containing lithium as a fluxing agent. This low leach rate was probably due in part to the mixed alkali effect.^[4,5] By comparison with other glasses these leach rates are not good. However, for interim storage and in comparison with CsCl, these leach rates are acceptable.

Six samples were made to test the effect of Al₂O₃ addition to the glass composition. The amount of Al₂O₃ ranged from 0 to 11 mass percent. Before the expected lowering of the cesium leach rate became evident the melting temperature increased beyond the capability of our furnaces. However, some indication of a lowering of the leach rate was noted in a sample containing 3.5 mass percent Al₂O₃.

Three glass melts which, upon visual examination, seemed to have viscosities low enough to be compatible with the Encapsulation Facility equipment were sent to Battelle-Northwest laboratories for viscosity measurements. These data are summarized in Figure 1 (also Table A-IV). At 900°C none of these glass melts had a viscosity low enough to be acceptable for use in present Encapsulation Facility equipment.

As viscosity was of primary importance and no glasses were found with a viscosity of about 100 poises at temperatures of 900°C or less, this aspect of the project was given decreased emphases. For glasses with high cesium content relatively low leach rates were obtained. Cesium storage densities were also high (1.4×10^3 to 1.5×10^3 kg Cs/m³ of glass).

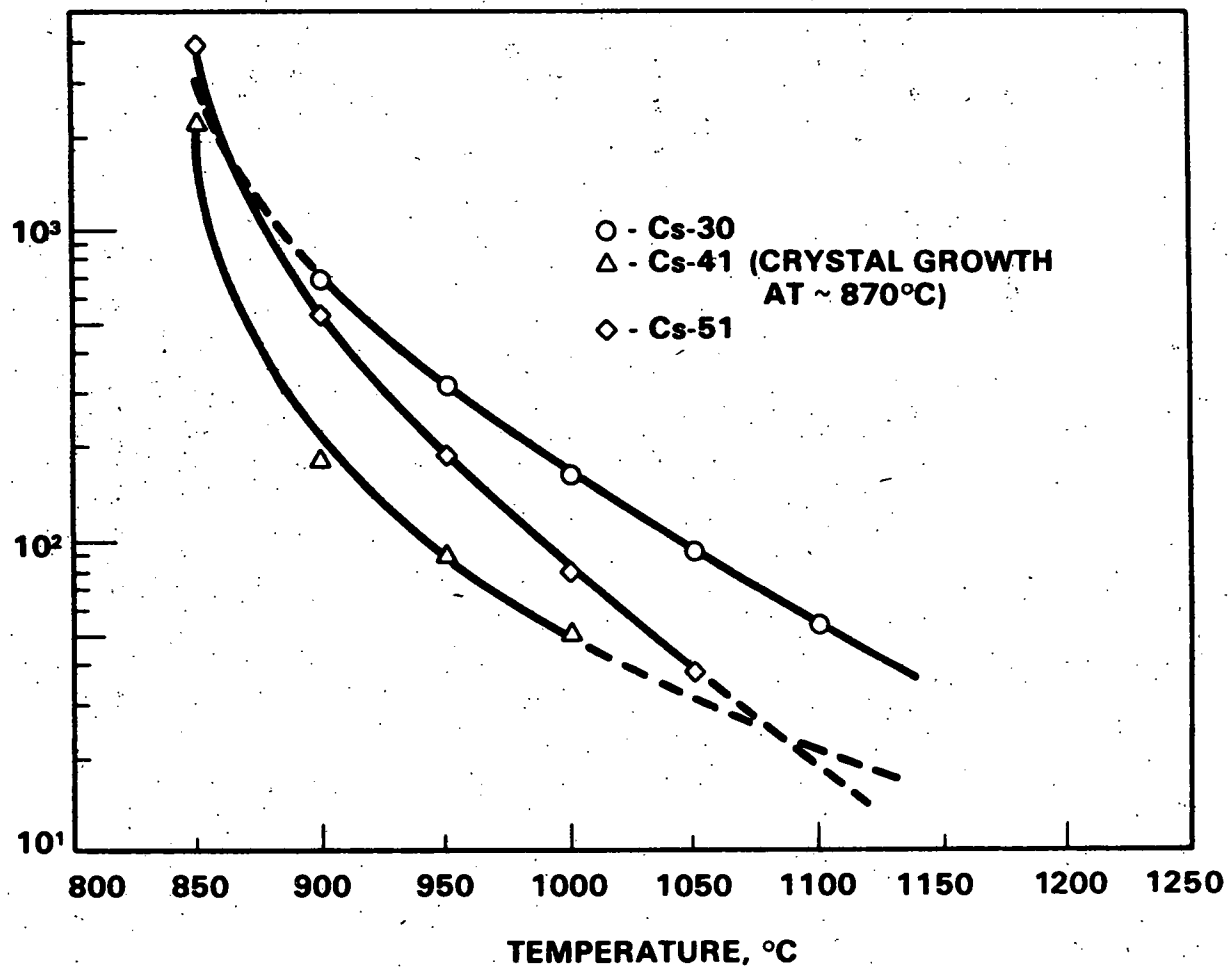


FIGURE 1
PLOT OF VISCOSITY (P) VERSUS TEMPERATURE (°C)
FOR CESIUM GLASSES

GLASS CERAMICS

While pollucite glass-ceramics offer great potential as materials for immobilizing radiocesium, attempts to produce one at temperatures less than 1500°C have thus far failed. Not all possibilities have been exhausted, however. Pollucite glass-ceramics are the subject of a rather extensive patent by Corning Glass Works.^[1] Unfortunately these compositions required the use of high temperatures (1850°-2000°C) and closed rhodium crucibles. Some of these glass ceramics did contain about 73 mass percent pollucite, assuming all of the reported Cs_2O was present as pollucite.

Attempts to make pollucite glass ceramics are summarized in Table II (see Table A-V for more detail). Some of these were patterned after the Corning patent, but with some of the Al_2O_3 or SiO_2 in excess of stoichiometric pollucite replaced with fluxing agents such as B_2O_3 and Na_2O . Even with the large addition of fluxes quite a few of the charges did not melt below 1500°C. Of those that did melt, crystallization could not be induced by heat treatment at temperatures up to 1000°C and the addition of 5 and 10% TiO_2 or ZrO_2 . If crystallized, these compositions should have yielded glass-ceramics with about 55 mass percent pollucite.

TABLE II
COMPOSITIONAL RANGES FOR GLASS-CERAMICS

<u>Component</u>	<u>Mass Percent</u>
Cs_2O	13-41
SiO_2	38-77
Al_2O_3	4-15
Na_2O	0-18
CaO	0-5
B_2O_3	0-15
Other oxides*	0-15

* BaO , P_2O_5 , ZrO_2 .

Most of the formulations that did not melt produced porous fused ceramics which contained pollucite.

While glass-ceramic densities are high ($\sim 3 \times 10^3 \text{ kg/m}^3$) they do not approach the cesium storage densities of glass. Cesium storage densities are about $0.7 \times 10^3 \text{ kg Cs/m}^3$ based on a density of 3.0 kg/m^3 and 60 mass percent pollucite in the product.

ZEOLITES

Table III summarizes the results of loading cesium on zeolites followed by firing. Cesium loadings were about the same for both AW-500 and Zeolon-900 at about 23% Cs_2O . The slight increase in cesium loading with increased firing temperature is due to loss of water and perhaps some other impurities. A general decrease in cesium leach rates (Table IV) is observed with increased firing temperature ($10^{-4} \text{ g Cs/cm}^2/\text{day}$ @ 500°C \rightarrow $3 \times 10^{-6} \text{ g Cs/cm}^2/\text{day}$ at 1100°C). This decrease probably indicates that the zeolitic cage in which the cesium is trapped collapses; therefore the cesium ion is more difficult to exchange from the fired zeolite.

TABLE III
CESIUM LOADING ON ZEOLITES

<u>Zeolite</u>	<u>Temperature, $^\circ\text{C}$</u>	<u>% Cs_2O</u>
AW-500	500	17.5
	800	25.5
	1100	23.0
Zeolon-900	500	19.2
	800	22.5
	1100	23.1

As a storage form, however, these products suffer from the major problem of low storage density. The as-fired

TABLE IV
CESIUM LEACH RATES FOR LOADED ZEOLITES

<u>Zeolite</u>	<u>Temperature (°C)</u>	<u>Leach Rate (10^{-4} g Cs/cm²/day)</u>	
		<u>99 hr</u>	
AW-500	500	1.2	
	800	0.76	
	1100	0.50	(24 hr)
		0.030	
Zeolon-900	500	1.42	
	800	0.92	
	1100	0.71	(24 hr)
		0.043	

products have bulk densities of about 1.0×10^3 to 1.2×10^3 kg/m³. Since cesium is about 25% of the mass, the cesium storage density is $\sim 0.25 \times 10^3$ kg/m³. This is to be compared with the glass densities of 3.5×10^3 kg/m³ or stored cesium densities of 1.4×10^3 to 1.5×10^3 kg/m³. Hot press sintering of the loaded zeolites may increase the density to 2×10^3 to 2.5×10^3 kg/m³, (0.5 to 0.62×10^3 kg/m³ cesium density), a value substantially lower than that of glass.

CESIUM CHLORIDE - BENTONITE CLAY REACTION

Differential Thermal Analysis (DTA), Thermal Gravitimetric Analysis (TGA) and X-ray powder diffraction were used to follow the reaction between CsCl and bentonite clay. X-Ray powder diffraction of the fired products (Table V) showed that this reaction was enhanced by the presence of NaOH and/or the use of uncalcined bentonite. Diffraction lines due to pollucite appeared in the powder pattern of a mixture of 3M CsCl + 1.5M NaOH + bentonite after firing to 600°C. The reaction was complete by 650°C. However, the addition of NaOH to the CsCl dilutes the cesium waste, thereby increasing storage volume. By reacting uncalcined

TABLE V
REACTION OF CsCl WITH BENTONITE CLAY
X-RAY RESULTS AND CESIUM CONTENTS

Sample	Firing Temperature, °C	Phases Present	Mass Percent Cs ₂ O
*Neutral- Calcined	500	CsCl	40.3
	600	CsCl	39.4
	650	CsCl	39.1
	750	CsCl	40.5
	1000	Pollucite	29.8
Neutral- Uncalcined	500	CsCl	28.9
	600	CsCl (weak)	31.2
	650	CsCl + unknown (all weak)	36.6
	750	Pollucite	35.2
	1000	Pollucite	35.5
Basic- Calcined	500	?	31.5
	600	CsCl, pollucite, CsAlSiO (?)	34.7
	650	Pollucite	28.8
	750	Pollucite	31.3
	1000	Pollucite	29.9
Basic- Uncalcined	500	CsCl, CsAlSiO ₄ (? weak)	29.8
	600	Unknown (weak)	31.9
	650	CsCl + unknown (all weak)	33.2
	750	CsCl + pollucite	30.3
	1000	Pollucite	30.7

*Neutral = 3M CsCl solution.

Basic = 3M CsCl and 1.5M NaOH solution.

Calcined or uncalcined refers to the bentonite.

bentonite with 3M CsCl the temperature at which the reaction yields pollucite was only raised by 50° to 100°C.

To further characterize these reactions and determine the mass losses DTA and TGA were run on the samples dried at 110°C. These analyses are summarized in Figures 2 and 3 along with the corresponding analyses for bentonite. All samples exhibited an endothermic reaction associated with water loss in the temperature range 50° to 150°C. A small endothermic peak in the range 450° to 475°C was due to the transformation of CsCl to β -CsCl and was observed in the samples prepared from calcined bentonite. This transition was not observable in the samples using uncalcined bentonite because a broad exotherm extending from about 150° to about 600°C masked its presence. This broad exotherm terminates in a weak endothermic peak which was due to a combination of water loss, as seen in bentonite clay, and the melting of CsCl (645°C). This water loss has been shifted to lower temperatures relative to bentonite clay due to the reaction between CsCl and the uncalcined bentonite. In the reaction between CsCl and calcined bentonite the endothermic peak was due solely to the melting of CsCl albeit shifted to *ca.* 600°C due to impurities. From the powder diffraction studies it was known that CsCl was completely consumed in the temperature range around 600°C by reaction with calcined bentonite in the presence of NaOH. Therefore, the absence of an endothermic peak in the DTA for this sample in the 600° to 650°C temperature range was not surprising. A final exothermic peak in the bentonite DTA was due to recrystallization. This same peak appeared in all of the samples prepared. However, it occurred at a slightly lower temperature for the reaction of 3M CsCl + 1.5M NaOH and calcined bentonite and in all cases was associated with a mass loss. While the exothermic recrystallization of the excess

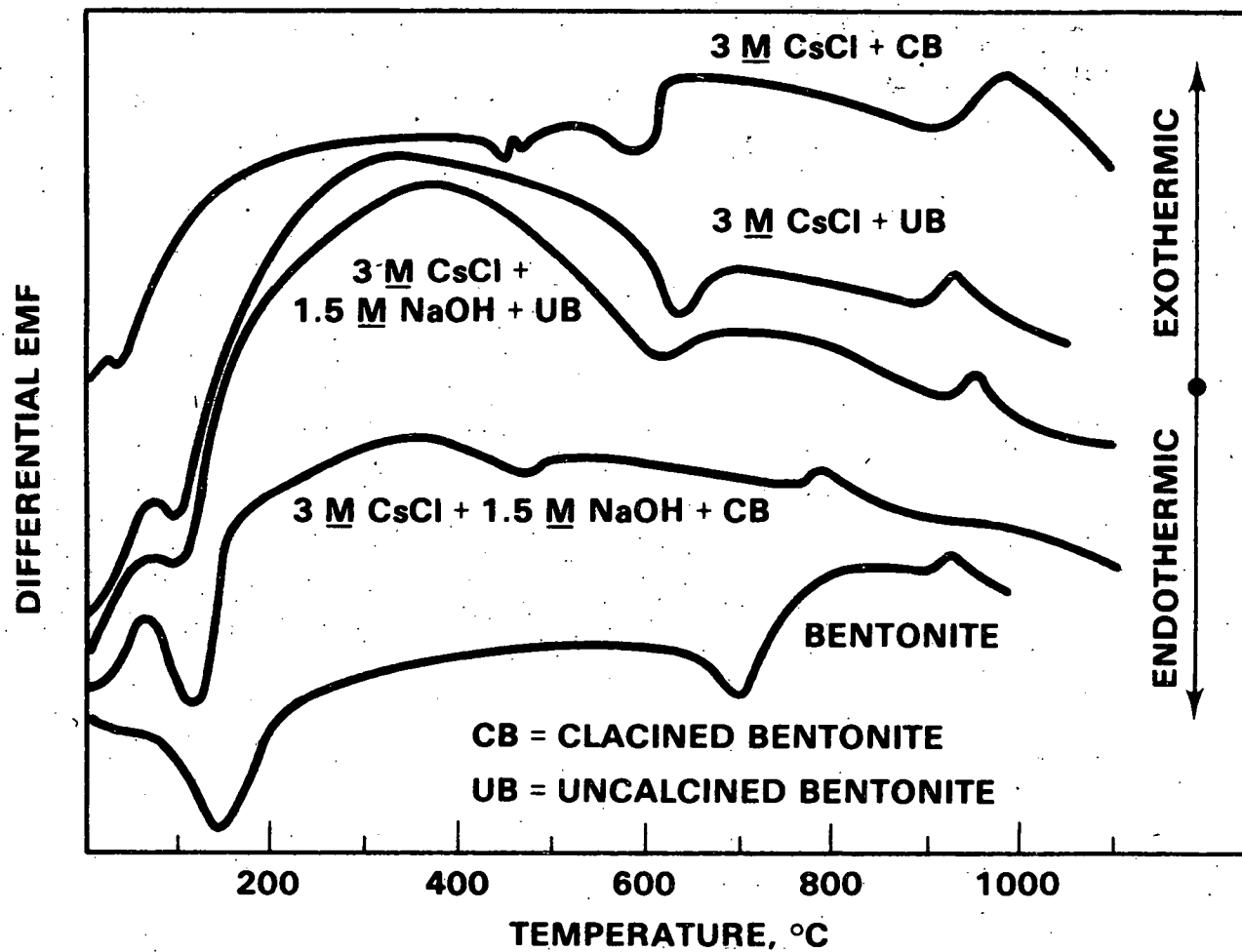


FIGURE 2
DTA CURVES FOR CsCl-BENTONITE REACTION

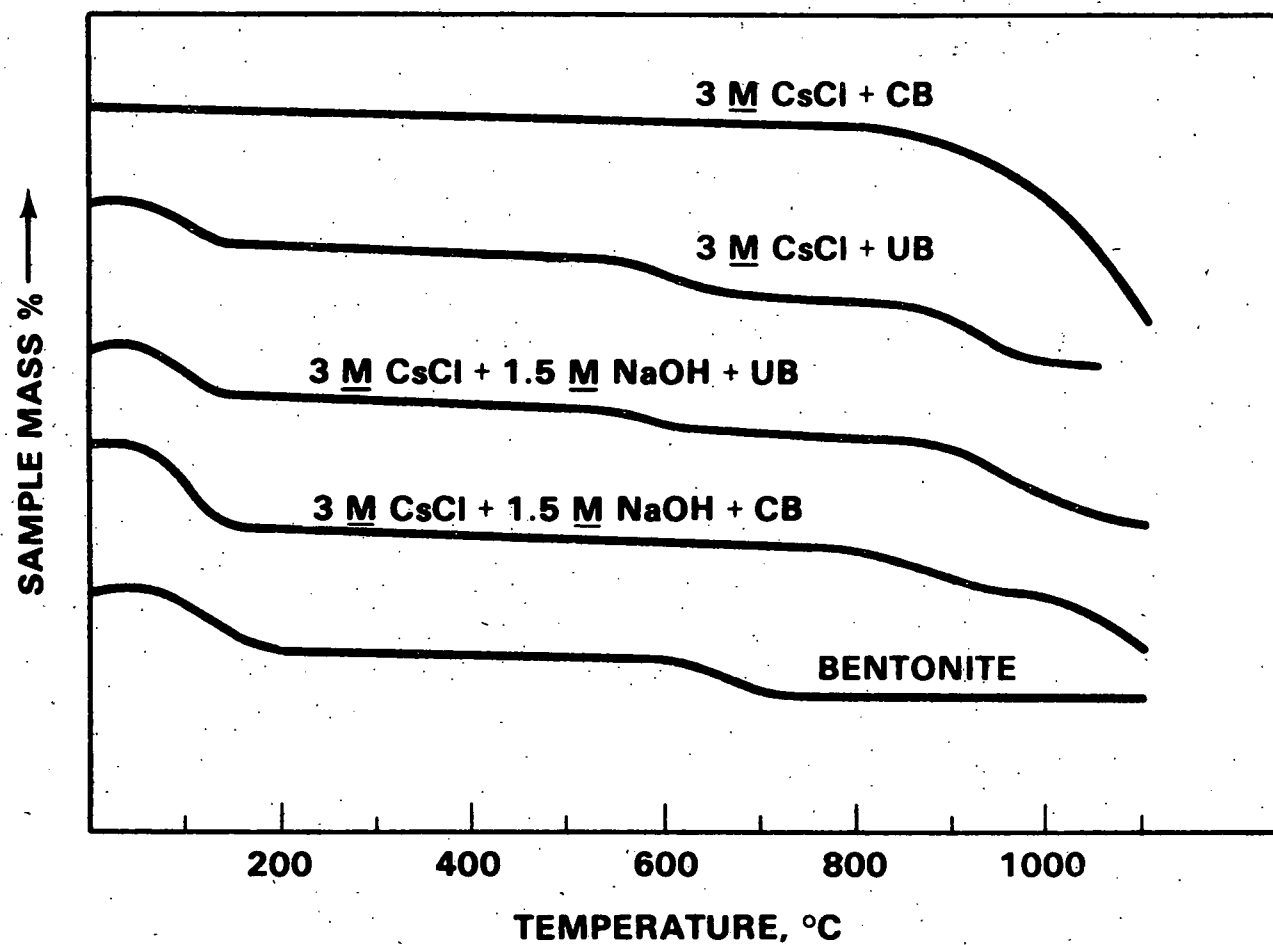


FIGURE 3
TGA CURVES FOR CsCl-BENTONITE REACTION

bentonite in the mixtures was possible, other exothermic reactions were also plausible. For instance, all bentonite samples contained an iron impurity which could have reacted with the chlorine to yield a volatile iron chloride. In some cases an iron-rich condensate was found on the rims of the crucibles. Loss of chlorine between 700° and 1000°C was also confirmed by X-ray fluorescence. By looking at the cesium contents of these samples (Table V), it is noted that no cesium was lost except in the reaction between 3M CsCl and calcined bentonite. No definite assignment was made to this exothermic peak.

If all of the Cs_2O which was found upon chemical analysis was assumed to be present as pollucite (where pollucite was found), a 79% yield of pollucite from 3M CsCl plus uncalcined bentonite was calculated. If, however, pure montmorillonite (the major constituent of bentonite) had been used instead of bentonite, a greater yield would have been obtained due to the absence of impurities.

Because of the small particle size of these products, leach rate data were not collected. Pollucite is one of the most insoluble, naturally occurring, cesium-bearing minerals. Leach rates of natural pollucite ore were measured and found to be on the order of 10^{-7} g Cs/cm²/day.

Cesium storage densities for monolithic pollucite are comparable to those of glass. Pollucite has a density of 2.9×10^3 kg/m³ and a cesium content of 42.6%. Therefore the theoretical cesium storage density is 1.24 kg of Cs per m³ pollucite. However, as-fired products (powders) tamped into capsules could be expected to have bulk densities which are roughly 50% of theoretical. Hence, this process would benefit greatly from hot press sintering or some other method of densification. If theoretical

densities could be approached, then a product with a cesium storage density close to that of glass but with far superior leach resistance would be possible.

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APPENDIX

TABLE A-I
CESIUM GLASS COMPOSITION (Mass Percent)

Glass No.	Cs ₂ O	SiO ₂	B ₂ O ₃	Na ₂ O	Li ₂ O	TiO ₂	Frit*, No.	Al ₂ O ₃	Comments
41	45.0	35.0	5.0	-	10.0	5.0	-	-	Clear, colorless, 950°C
44	40.0	42.4	10.0	7.6	-	-	-	-	Clear, colorless, 950°C
45	40.0	42.4	10.0	7.6	-	-	-	-	1200°C
46	39.9	37.0	15.4	7.7	-	-	-	-	1150°C
48	30	-	-	-	-	-	70 (73-1)	-	Clear, colorless → purple
50	40	-	-	-	-	-	60 (73-1)	-	Pink-purple, slight opal
51	45	-	-	-	-	-	55 (73-1)	-	Pink → colorless
52	50	-	-	-	-	-	50 (73-1)	-	Colorless
54	50	-	-	-	-	-	50 (73-1)	-	1200°C
55	40	-	-	-	-	-	60 (73-1)	-	1200°C
57	40	-	-	-	-	-	60 (1)	-	1200°C
58	40	-	-	-	-	-	60 (3)	-	1200°C
59	40	-	-	-	-	-	60 (4)	-	1200°C
60	40	-	-	-	-	-	60 (5)	-	1200°C
61	41.8	-	-	-	-	-	58.2 (6)	-	1200°C
66	46.4	36.1	5.2	-	7.1	4.7	-	0.5	Glass 1100°C
67	46.4	36.1	5.2	-	7.1	4.0	-	1.2	Glass 1150°C
68	46.4	36.1	5.2	-	7.1	2.8	-	2.4	Glass 1200°C
69	46.4	36.1	5.2	-	7.1	1.7	-	3.5	Glass 1350°C
71	46.4	36.1	2.6	-	7.1	-	-	7.8	Two-phase 1500°C
72	46.4	36.1	-	-	7.1	-	-	10.4	Two-phase 1500°C

*For frit composition see Table A-II.

TABLE A-II
FRIT COMPOSITION

<u>Component</u>	<u>73-1*</u>	<u>1</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
SiO ₂	37.0	49.1	46.7	52.2	44.4	46.5
B ₂ O ₃	15.1	24.2	19.0	13.5	18.1	12.0
Na ₂ O	5.5	9.1	6.9	7.0	6.5	12.4
K ₂ O	5.5	7.9	7.5	7.5	6.6	6.2
ZnO	28.9	-	10.0	10.0	14.9	14.0
CaO	2.0	1.9	2.4	2.4	2.4	2.2
MgO	2.0	1.9	2.5	2.4	2.4	2.2
SrO	2.0	3.9	2.2	2.4	2.4	2.3
BaO	2.0	1.9	2.4	2.5	2.4	2.2

*Battelle Pacific Northwest Laboratories, Richland, Washington.

TABLE A-III
LEACH RATES FOR CESIUM GLASSES

<u>Glass No.</u>	<u>Cesium Leach Rate (10^{-4} g. Cs/cm²/day)</u>		
	<u>24 hr</u>	<u>96 hr</u>	<u>120 hr</u>
Cs-41	0.18	0.30	0.05
Cs-44	0.67	-	0.64
Cs-45	1.25	-	1.31
Cs-46	0.21	-	2.10
Cs-48	2.22	-	9.16
Cs-50	3.00	1.93	3.16
Cs-51	16.4	1.32	0.049
Cs-52	9.60	4.03	7.47
Cs-54	6.29	-	-
Cs-55	10.1	-	2.01
Cs-57	1.51	-	0.69
Cs-58	21.7	4.33	-
Cs-59	3.80	5.79	-
Cs-60	3.58	2.85	-
Cs-61	5.82	-	0.85
Cs-66	0.58	0.62	-
Cs-67	0.67	0.30	-
Cs-68	0.53	0.56	-
Cs-69	0.26	0.12	-
Cs-71	13.7	1.30	-
Cs-72	32.9	0.86	-

TABLE A-IV
VISCOSITIES FOR SELECTED CESIUM GLASSES

<u>Sample</u>	<u>Composition</u> <u>Mass Percent</u>	<u>Temperature</u> <u>°C</u>	<u>Viscosity</u> <u>Poise</u>
Cs-30	45.0-Cs ₂ O	900	680
	35.0-SiO ₂	950	315
	10.0-Na ₂ O	1000	164
	5.0-B ₂ O ₃	1050	92.0
	5.0-TiO ₂	1100	54.0
Cs-41	45.0-Cs ₂ O	850	2200
	35.0-SiO ₂	900	180
	10.0-Li ₂ O	950	90.0
	5.0-B ₂ O ₃	1000	50.0
	5.0-TiO ₂		
Cs-51	45.0-Cs ₂ O	850	3880
	55.0 73-1 frit	900	530
	55.0 73-1 frit	950	190
	55.0 73-1 frit	1000	80.0
	55.0 73-1 frit	1050	38.0

TABLE A-V
GLASS CERAMIC FORMULATION (Mass Percent)

Sample	Cs ₂ O	SiO ₂	Al ₂ O ₃	Na ₂ O	CaO	B ₂ O ₃	Other Oxides	Comments
GC-1	13.0	52.9	4.1	17.9	4.7	-	-	1300°C, glass
GC-2	15.2	65.9	5.2	5.0	-	8.7	-	1500°C, glass
GC-3	15.3	77.2	4.8	-	-	2.7	-	1500°C, no melt
GC-4	23.7	51.1	7.5	14.0	3.6	-	-	1500°C, glass
GC-5	24.9	56.6	8.8	3.4	-	6.2	-	1400°C, glass
GC-6	25.3	57.1	7.9	-	-	9.7	-	1500°C, no melt
*GC-7	36.2	45.5	13.1	3.6	1.6	-	-	1500°C, no melt, pollucite
*GC-8	40.7	38.6	14.8	1.0	0.4	-	-	1500°C, pollucite
*GC-9	36.2	45.5	13.1	3.6	1.6	-	-	1500°C
*GC-10	40.7	38.6	14.8	1.0	0.4	-	-	1500°C, pollucite
*GC-11	36.2	45.5	13.1	3.6	1.6	-	-	1500°C
*GC-12	40.7	38.6	14.8	1.0	0.4	0.4	-	1500°C
†GC-13	27.1	52.6	9.8	7.2	3.2	-	-	1500°C
†GC-14	31.6	49.1	11.5	5.4	2.4	2.4	-	1500°C
†GC-15	27.1	55.2	10.7	1.7	-	5.2	-	1500°C
†GC-16	31.6	51.1	12.2	1.2	-	3.9	-	1500°C
†GC-17	25.0	45.9	9.1	-	-	10.0	10.0 ZrO ₂	Fused ceramic
†GC-18	25.0	40.9	9.1	-	-	15.0	10.0 ZrO ₂	Fused ceramic
†GC-19	25.0	45.0	9.1	-	-	10.0	10.0 BaO	Glass + crystal
†GC-20	25.0	40.9	9.1	-	-	10.0	15.0 BaO	1500°C, glass
†GC-21	25.0	55.9	9.1	-	-	-	10.0 P ₂ O ₅	Fused ceramic
†GC-22	25.0	50.9	9.1	-	-	-	15.0 P ₂ O ₅	Fused ceramic
†GC-23	25.7	46.1	9.3	10.5 (K ₂ O)	-	-	8.5 ZrO ₂	Fused ceramic
†GC-24	25.7	41.6	9.3	15.0 (K ₂ O)	-	-	8.4 ZrO ₂	Fused ceramic
GC-25	24.9	41.6	9.1	-	-	14.3	10.0 BaO	1500°C, glass + crystal

*7,8 made with kaolin; 9, 10 with bentonite, 11,12 with pyrophyllite.

†17-24 patterned after the Corning pollucite glass-ceramics.

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