UCRL-15560
S/C 6548801

UCRL--15560

DE84 002789

A STUDY OF SELECTED OFF-GASES PRODUCED
DURING THE IMMOBILIZATION OF NUCLEAR
WASTES IN THE SYNROC PROCESS

John H. Carpenter
James C. McMullen
Bruce A. Olmscheid
Paul Chezick

Department of Chemistry
St. Cloud State University
St. Cloud, Minnesota 56301

Final Report for the Year Ended
December 31, 1982

The logo for Lawrence Livermore Laboratory, featuring a stylized 'LL' monogram to the left of the text 'Lawrence Livermore Laboratory' which is arranged in three lines and slanted upwards to the right.

Lawrence
Livermore
Laboratory

MASTER

"A STUDY OF SELECTED OFF-GASES PRODUCED
DURING THE IMMOBILIZATION OF NUCLEAR
WASTES IN THE SYNROC PROCESS"*

Final Report for the Year Ended
December 31, 1982

John H. Carpenter
James C. McMullen
Bruce A. Olmscheid
Paul Chezick

Department of Chemistry
St. Cloud State University
St. Cloud, Minnesota 56301

*Work performed under University of California Lawrence
Livermore National Laboratory Subcontract 6548801

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

EDP

Abstract

The vaporization of cesium from the SYNROC mineral barium-cesium hollandite was studied over the temperature range 900°C to 1150°C using the transpiration method. With a dry argon-5% hydrogen carrier gas, the pressure of cesium over barium-cesium hollandite solid solution follows the relationship, $\log P_{\text{Cs}} (\text{atm}) = 2.743 - \frac{1.135 \times 10^4}{T(\text{K})}$. The heat of vaporization is 217 ± 15 kJ/mole. The presence of water vapor increased the volatility of cesium.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Introduction

The purpose of this work is to evaluate the type and quantity of off-gases that can be expected during the fabrication of the solid nuclear waste form known as SYNROC.^{1,2,3,4} In the SYNROC concept, waste elements are incorporated into synthetic minerals of the same or similar composition as naturally occurring minerals which are known to have retained these elements for periods of time up to many millions of years.

A preliminary study⁵ of the off-gases that might be produced in a typical sintering process showed that one of the most volatile of all the elements found in the waste is cesium. Calculated cesium volatilities are very high, particularly in the presence of water vapor.

In both SYNROC-C (the mixture of minerals proposed for commercial waste) and SYNROC-D (the mixture of minerals proposed for defense wastes), cesium is incorporated into barium hollandite ($\text{BaAl}_2\text{Ti}_6\text{O}_{16}$). The hollandite forms at a lower temperature⁶ (900°C) than the proposed sintering temperature of about 1200°C so when sintering begins, the cesium is already incorporated into the hollandite. The focus of this study has been on the vaporization of cesium from barium-cesium hollandite solid solution. The results of these measurements also provide a basis for evaluating cesium vaporization losses from SYNROC under severe environmental conditions.

Preparation of barium-cesium hollandite samples

The composition of the barium-cesium hollandite samples used in the vaporization studies was $\text{Ba}_{0.9}\text{Cs}_{0.1}\text{Al}_2\text{Ti}_6\text{O}_{16} \cdot \text{TiO}_2$. This corresponds to a $\text{BaO} \cdot \text{CsO} / \text{Al}_2\text{O}_3 / \text{TiO}_2$ ratio of $1/1/6.5$ which

is similar to the composition of Ringwood's best material.⁴

Samples were prepared using a variation of a method used by Dosch⁷ at Sandia National Laboratory.

Titanium(IV) isopropoxide was added to a methanolic solution of CsOH. An aqueous solution of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Ba}(\text{NO}_3)_2$ was then added to the above solution and the resulting slurry was well mixed in a blender. After mixing, the result was usually a thin gel. This material was dried on a steam bath until all the methanol had evaporated, dried to a powder at 110°C in a drying oven, ground up, and then calcined in a box furnace for four hours at 650°C . The resulting powder was ground up, cold pressed into pellets, and fired in Ar-5% H_2 for 18 hours at 900°C . After regrinding and a second overnight firing at 900°C , the bluish-gray product gave x-ray diffraction pictures that showed the typical hollandite pattern with excess TiO_2 . X-ray diffraction pictures were carefully checked for the presence of other phases. A small amount of BaTiO_3 and Al_2O_3 was found. By comparing x-ray diffraction pictures of samples mixed with a known amount of these compounds, the samples were estimated to contain less than 5% BaTiO_3 and 5% Al_2O_3 . To assure that all the cesium had reacted, some samples were rinsed with distilled water before being used for vaporization measurements. No difference was found between rinsed and unrinsed material. Table 1 shows the results of analysis of samples for cesium and barium by x-ray fluorescence.

Vaporization Studies

No vaporization data for barium-cesium hollandite has been reported in the literature. We chose to use the transpiration method⁸ to obtain equilibrium vapor pressures of cesium. In this method, a carrier gas is flowed over a heated sample of the material to be studied. Any part of the sample that is vaporized through simple volatilization or reaction to form a volatile species is then equilibrated with the carrier gas, carried downstream, and deposited in a cooler portion of the apparatus. The deposited material is then analyzed for the desired element which in this study was cesium. If the carrier gas is saturated with the vaporized material, the vapor pressure of the gaseous species, P_g , may be determined from the following relationship:

$$P_g = P_t \left(\frac{n_g}{n_g + n_c} \right), \quad (1)$$

where P_t is total pressure, n_g is number of moles of gaseous species, and n_c is number of moles of carrier gas. The vaporization apparatus, which was constructed out of 99.8% alumina, is shown in Figure 1. Mullite tubing was tried but was found to react with the vaporized material. The apparatus was placed in the middle of constant temperature hot zone of a 50-cm long furnace. Of the two furnaces used, the shortest constant temperature zone was 7.0 cm with a maximum variation of 2°C at 1050°C. The carrier gas used was high purity dry (<3 ppm H₂O) Ar-5% H₂. A reducing gas was used since any sintering process would require an atmosphere to prevent the formation of a soluble

cesium molybdate. Four runs were made with wet Ar-5% H₂ carrier gas.

In these runs the carrier gas was saturated with water by running it through a gas dispersion tube immersed in a one-liter flask of room temperature distilled water, before introducing it into the furnace. The total gas flow was measured with a wet test meter.

Deposited material from the transpiration run was washed out of the collector tube with successive washings of 25 ml of distilled water. The washings were then analyzed for cesium by atomic absorption methods. The analytical method gave a precision and detection limit of 0.03 ppm Cs.

To assure that equilibrium was reached between the carrier gas and the heated sample so that the carrier gas was saturated with cesium, the apparent cesium pressure was measured at a variety of carrier gas flow rates. Figure 2 shows that with flow rates from 30 to 100 ml/min, cesium pressures at 1075°C remained constant--thus confirming gas saturation. The runs selected for Figure 1 were within 7°C of 1075°C and pressures were corrected to 1075°C. Most transpiration runs were made with flow rates of 35-50 ml/min at STP.

Results and Conclusions

The data for vaporization runs from 900°C to 1150°C are listed in Table II and the resulting pressures are plotted as a function of reciprocal absolute temperature in Figure 3.

The data best fit a straight line with the equation:

$$\log p_{\text{Cs}} (\text{atm}) = 2.743 - \frac{1.135 \times 10^4}{T(\text{K})} \quad (2)$$

Using the value for the slope and its associated standard deviation, and assuming that the gaseous species present is Cs(g), the heat of vaporization of Cs(g) over (Ba, Cs)-hollandite

solid solution is 217 ± 15 kJ/mole.

The runs in which water was present are plotted on Figure 3 as triangles. They average 3.5 times higher than runs at the same temperature with dry carrier gas. This effect would be expected since the gaseous species CsOH and $\text{Cs}_2(\text{OH})_2$ are more volatile than Cs(g) under the same conditions.⁵

References

- ¹A. E. Ringwood, *Safe Disposal of High-Level Nuclear Reactor Wastes: A New Strategy*, Australian National University Press, Canberra, 1978.
- ²A. E. Ringwood, S. E. Kesson, N. G. Ware, W. O. Hibberson, and A. Major, "The SYNROC Process: A Geochemical Approach to Nuclear Waste Immobilization," *Geochemical Journal*, 13 [4] 741-65 (1979).
- ³A. E. Ringwood, S. E. Kesson, N. G. Ware, W. O. Hibberson, and A. Major, "Immobilization of High-Level Nuclear Reactor Wastes in SYNROC," *Nature (London)*, 278 219-223 (1979).
- ⁴A. E. Ringwood, "Immobilization of Radioactive Wastes in SYNROC," *American Scientist*, 70 [2] 201-207 (1982).
- ⁵J. H. Carpenter, "A Study of Selected Off-Gases Produced During the Immobilization of Nuclear Wastes in the SYNROC Process, Final Report for the Year Ended December 31, 1981." Tech. Rept. No. UCRL-15457, Lawrence Livermore National Laboratory, Livermore, CA, December 31, 1981.
- ⁶C. Hoenig, R. Rozsa, F. Bazan, R. Otto, and J. Grens, "Preparation and Properties of SYNROC D Containing Simulated Savannah River Plant High-Level Defense Waste," Tech. Rept. No. UCRL-53195, Lawrence Livermore National Laboratory, Livermore, CA, July 23, 1981, p. 34.
- ⁷R. G. Dosch, Private Communication, 1981.
- ⁸U. Merten and W. E. Bell, "The Transpiration Method" in *The Characterization of High Temperature Vapors*, p. 91-114, J. L. Margrave, Ed., Wiley and Sons, New York, 1967.

Table I. Cesium and Barium Content of Vaporization Samples

	Theoretical	Unrinsed Sample	Rinsed Sample
Cesium	1.6%	1.3%	1.0%
Barium	15.2%	13.7%	12.4%

Table II. Transpiration Data for Cesium Vaporization from (Ba, Cs)-Hollandite Solid Solution

Run No.	Temperature (°C)	Time (min)	Flow Rate, STP (ml/min)	*ppm Cs	$P_{Cs} \times 10^6$ (atm)
11	1081	1589	36.7	32.8	2.28
12	1082	1560	44.6	37.6	2.21
13	1087	1423	37.7	35.6	2.71
14	1024	1463	48.7	9.10	0.522
15	1087	1513	37.9	29.1	2.07
16	1018	1396	51.0	7.84	0.448
17	1072	971	37.1	24.2	2.73
18	1072	1252	99.9	55.4	1.80
19**	1022	1639	50.1	57.8	2.84
20	1097	1000	64.6	39.6	2.48
21	1071	983	45.6	12.7	1.15
22**	1018	1462	48.3	52.4	4.56
23	1072	1015	59.7	29.2	1.96
24	1079	1084	31.0	17.7	2.16
25	954	2598	44.6	10.9	0.384
26	955	2620	37.5	7.9	0.323
27	1001	1492	45.9	14.8	0.883
28	1076	1036	90.6	56.4	2.46
29	1073	984	62.3	26.0	1.74
30	1049	1487	44.3	26.1	1.71
31	1072	1143	38.5	21.2	1.97
34	898	3976	51.1	6.1	0.122
35	1049	996	47.2	23.4	2.04
36	1153	981	36.8	78.4	8.89
37**	994	1012	47.9	26.6	2.24
38**	1070	987	53.7	55.3	4.25
39	1069	993	45.6	19.3	1.73
40	1071	989	37.2	23.4	2.58
41	1039	1480	48.4	31.3	1.79
42	1134	1166	37.3	48.9	4.60

*in 25.0 ml **wet Ar-5% H₂, Vapor pressure of water (mm Hg):

Run 19, 25.36; Run 22, 28.10; Run 37, 24.11; Run 38, 22.58

Figure 1. Transpiration Apparatus

A, Transpiration Tube; B, Diffusion Barrier; C, Sample;
D, Effusion Orifice; E, Collector Tube; F, Thermocouple

Figure 2. Variation of Cesium Pressure with
Carrier Gas Flow Rate at 1075°C

Figure 3. Temperature Dependence of Cesium Pressures
over (Ba, Cs)-Hollandite Solid Solution