3.13
8-20-81
JMK

①

B6582

DOE/ET/41900-9
(ESG-DOE-13354)

DR-2963

CERAMIC PHASES
FOR
IMMOBILIZATION OF ^{129}I

MASTER

DOE Research and Development Report

*Prepared for the United States
Department of Energy
Savannah River Operations Office
under Contract Number DE-AC09-79ET41900*

Rockwell International

Energy Systems Group
8900 De Soto Avenue
Canoga Park, California 91304

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.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or 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.

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

NTIS price codes

Printed copy: \$6.00

Microfiche copy: A01

CERAMIC PHASES
FOR
IMMOBILIZATION OF ^{129}I

By
E. R. Vance
D. K. Agrawal
B. E. Scheetz
J. G. Pepin
S. D. Atkinson
W. B. White

The Materials Research Laboratory
The Pennsylvania State University
University Park, Pennsylvania

DISCLAIMER

This book 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.

Rockwell International

Energy Systems Group
8900 De Soto Avenue
Canoga Park, California 91304

CONTRACT: DE-AC09-79ET41900
ISSUED: JULY 31, 1981

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

34

DISTRIBUTION

This report has been distributed according to the category "Nuclear Waste Management," as given in the Standard Distribution for Unclassified Scientific and Technical Reports, DOE/TIC-4500.

ACKNOWLEDGEMENTS

We thank the Smithsonian Institution for supplying us with crystals of mendipite and phosgenite and K.K.S. Pillay for performing the γ irradiation.

ABSTRACT

Materials for ultimate disposal of ^{129}I have been studied. At present, iodide-sodalite, though not ideal, appears to be the best material for ^{129}I immobilization from the aspects of ease of preparation, thermal stability, cost of materials, and leach resistance. Good consolidation of the material was achieved by sintering in air at 1000-1200°C, but the iodine content was significantly below stoichiometric expectations. Hot aqueous media preferentially removed iodine, apparently by OH^- substitution in near-neutral solutions, and $\text{I}^- \leftrightarrow \text{Cl}^-$ exchange occurred in brine. Alternation of the sodalite also took place. Soxhlet leach rates were $\sim 5 \times 10^{-4} \text{ g/cm}^2\text{-day}$ by total weight loss but physical weathering contributed significantly to this value. Moderate doses of radiation had no observable deleterious structural effects.

Iodoboracites seemingly cannot be prepared by ceramic or nonhydrothermal wet chemical techniques. Fe-iodoboracite has inferior thermal stability to iodide-sodalite and was completely altered to hematite after treatment at 200°C in deionized water.

Silver zeolites retained some iodine in the form of crystalline $\alpha\text{-AgI}$ at temperatures up to 1300°C even though heating above $\sim 700^\circ\text{C}$ altered the aluminosilicate framework. However, some of the iodine appeared to be present as soluble iodine, even in heated materials. Treatment at 200°C in deionized water or 2M NaCl significantly decreased the crystallinity of the aluminosilicate framework and the $\alpha\text{-AgI}$ reflections in the X-ray patterns were enhanced. Mild γ irradiations ($\sim 50 \text{ MR}$) affected the X-ray diffraction patterns of some of the zeolites.

Various lead oxyhalides had very poor thermal stability.

CONTENTS

	Page
Abstract	3
I. Introduction	7
II. Experiments	10
III. Sodalite	11
A. Material Preparation and Characterization: Thermal Stability	11
B. Powder Diffraction Patterns: Details	13
C. Interaction with Aqueous Media	20
D. Radiation/Transmutation Effects	24
IV. Boracite	26
A. Preparation Attempts	26
B. Thermal and Hydrothermal Alteration	26
V. Silver Zeolites	28
VI. Lead Oxyhalides	39
VII. Conclusions	40
References	41

TABLES

1. Solubilities and Thermal Stabilities of Some Simple Iodine-Bearing Materials	8
2. Powder Patterns of Sodalites, $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{X}_2$	19
3. Soxhlet Testing on I^- -Sodalite	21
4. Hydrothermal Leach Solution Analysis for I^- -Sodalite	23
5. Properties of Commercial Zeolites	28
6. I_2 -Loaded Zeolites: Action of Heat on Powder X-Ray Diffraction Patterns	33
7. Summary of Structural Effects of Hydrothermal Treatment and of Mild γ Irradiation on Ag-Zeolites	38

FIGURES

	<u>Page</u>
1. Weight Loss at 1000°C as a Function of Time for I ⁻ -Sodalite Pellet Fired Initially at 1000°C.....	14
2. Cumulative Weight Loss for I ⁻ -Sodalite Pellet, Initially Fired at 500°C, Then Fired at Increasing Temperatures for 2-hr Periods.....	15
3. Cumulative Weight Loss for NaAlSiO ₄ Pellet, Fired Initially at 500°C, Then at Increasing Temperatures for 2-hr Periods.....	16
4. X-Ray Powder Diffraction Pattern of I ⁻ -Sodalite Fired at 1000°C.....	18
5. Chemical Analysis of I ₂ -Loaded Silver Zeolites as a Function of Heating Temperature (1-hr duration).....	30
6. Effect of Iodine Loading on X-Ray Pattern of Silver Zeolite Ag-400.....	31
7. Action of Heat on X-Ray Patterns of Silver Zeolite Ag-400 Loaded with I ₂	32
8. Effect of Hydrothermal Treatment on X-Ray Pattern of Silver Zeolite Ag-600.....	34
9. Effect of Hydrothermal Treatment on X-Ray Pattern of Silver Zeolite Ag-900.....	35
10. Effect of γ Irradiation on X-Ray Diffraction (XRD) of I ₂ -Loaded Silver Zeolite.....	37

I. INTRODUCTION

Iodine-129 is a fairly abundant product of the nuclear fuel cycle and is somewhat toxic to man by virtue of its affinity for the thyroid gland. When spent fuel is dissolved for reprocessing, a very large fraction of the ^{129}I is liberated as a gas and can be collected by chemical scrubbers, charcoal, or zeolites.⁽¹⁾ In view of the long half-life of ^{129}I (1.6×10^7 yr), immobilization for periods as long as 10^6 yr might seem to be necessary for ultimate disposal. However, the long half-life means, of course, that the specific radioactivity is very modest. It has been pointed out^(2,3) that if all the iodine normally in the human body were ^{129}I , the radiation dose would still be below the allowable body burden.

Nevertheless, a large concentrated mass of ^{129}I would present a hazard. A very recent discussion has put forward strong arguments for seabed disposal of ^{129}I .⁽⁴⁾ However, such an option involves international law; in the present work, we have confined ourselves to the immobilization of ^{129}I in an underground repository.

Geological activity in an assumed underground repository during the $\geq 10^6$ -yr period would not be too unlikely, so ideally the ^{129}I -bearing material would not decompose on moderate heating ($\sim 600^\circ\text{C}$). Also, transportation of the made-up ^{129}I -immobilizing solid to a repository (or to an appropriate seabed location) would require the solid to have a reasonable degree of fire resistance; a temperature of $\sim 800^\circ\text{C}$ would be applicable here.

Some iodine-loaded Ag-zeolites appear to have thermal stability up to $\sim 1000^\circ\text{C}$,^(1,5) but these materials are very expensive, though reportedly leach-resistant. Some studies of these materials have been performed in the present work (Section V). Pb-zeolites may be a possibility, but thermal stability is a problem.^(1,6,7) Barium iodate incorporated in cement⁽³⁾ has little thermal stability, but when onsite disposal is performed, the transportation problem essentially does not exist. Silver, palladium, platinum, and base-metal iodides

are more or less insoluble but, again, are expensive and have limited thermal stabilities (Table 1). The "insoluble" materials are generally the most expensive by virtue of the particular cations involved.

TABLE 1
SOLUBILITIES AND THERMAL STABILITIES OF SOME
SIMPLE IODINE-BEARING MATERIALS(7)

Material	Solubility in Cold Water (g/100 ml H ₂ O)	Melting Point or Decomposition (d) Temperature (°C)
AgI	$\sim 10^{-7}$	558
Ba(IO ₃) ₂ ·2H ₂ O	"insoluble"; "very slowly soluble" after dehydration	d 200 (-H ₂ O)
CuI	8×10^{-3}	605
β-HgI ₂	"very slowly soluble"	259
Hg ₂ (IO ₃) ₂	"insoluble"	d 250
PbI ₂	6×10^{-2}	402
Pb(IO ₃) ₂	3×10^{-3}	d 300
PdI ₂	"insoluble"	d 350
PtI ₂	"insoluble"	d 270
SbSI	"insoluble"	392

d = decomposes

In the present work, CuI was found to decompose (to CuO) in air at $\sim 180^{\circ}\text{C}$; thus, reducing conditions would be necessary to assure its survival at more elevated temperatures (see also Reference 4). Exposure to deionized water (water-to-solid ratio of 10:1 by weight in a welded gold capsule) at $200^{\circ}\text{C}/300$ bars/7 days caused some recrystallization with about 4% of the I passing into solution. In a parallel experiment with precipitated α-AgI, no dissolution or alteration of the solid was observed. Though stable in air up to the melting point, α-AgI may be adversely affected by photolysis from the repository radiation, as well as the (fairly trivial) β-radiation from the decay of ¹²⁹I.

Strachan and Babad⁽⁹⁾ have found that I^- -sodalite and IO_3^- -sodalite (see Section III; see also Reference 10) are thermally stable up to $\sim 1000^\circ\text{C}$, are easily prepared, and have fair leach resistance. The sodalite structure has also been studied in the nuclear waste management context for ^{85}Kr fixation,⁽¹¹⁾ as well as for immobilization of nonradioactive Na and Mo.⁽¹²⁾ Another candidate mineral for ^{129}I immobilization suggested by the GEIS report⁽¹⁰⁾ is boracite. Ferrous iodoboracite has also been reported to be thermally stable up to 700°C .⁽¹³⁾ Although this temperature is lower than those mentioned above for I^- -sodalite and Ag-zeolite, it is in the right range. Lead oxyhalides were also mentioned in the GEIS report⁽¹⁰⁾ as worthy of study.

At the outset, the main object of the present work was to synthesize iodoboracites by ceramic or wet-chemical techniques, since the information on iodide sodalite⁽⁹⁾ and the zeolites^(1,5-7) appeared to be fairly comprehensive. However, iodoboracite preparation was not successful, so it was decided to try to extend the previous work on sodalite and zeolites and to carry on a parallel investigation on the lead oxyhalides.

II. EXPERIMENTS

The principal experimental technique used in the present work was powder X-ray diffraction, which was carried out with a standard diffractometer using graphite-monochromated $\text{CuK}\alpha$ radiation. Some "powder" patterns were also obtained photographically from single crystals, using the Gandolfi three-dimensional random-rotation technique.

Hydrothermal experiments were mainly carried out in a pressure vessel with samples sealed in Au tubes. However, powders almost sealed in Pt tubes were also treated in ~ 500 ml of deionized water (the idea being to keep the solids more or less in place but to allow free access of water) in a 1-liter autoclave using a temperature of 200°C and a pressure of ~ 10 bars. Room-temperature experiments were carried out with ~ 100 mg of powdered solid in ~ 50 ml of leach solution and milling with plastic balls in polypropylene bottles for several days. The solids were then separated out by filtration and washing. No solution analyses were performed in these latter experiments.

Neutron irradiations were carried out using a flux of $\sim 5 \times 10^{12}$ $\text{n/cm}^2\text{-sec}$ (fast) + $\sim 1 \times 10^{13}$ $\text{n/cm}^2\text{-sec}$ (thermal) and the associated γ flux was $\sim 10^8$ R/hr.

III. SODALITE

A. MATERIAL PREPARATION AND CHARACTERIZATION: THERMAL STABILITY

Sodalite has the formula $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{X}_2$ ($\text{X} = \text{Cl}^-$, Br^- , I^- , OH^- , $1/2 \text{SO}_4^{2-}$, etc.), which can be written $6\text{NaAlSiO}_4 \cdot 2\text{NaX}$, showing its close compositional relation to nepheline. In nature, it is found associated with nepheline in silica-poor igneous rocks. In the sodalite structure,⁽¹⁴⁻¹⁶⁾ the anions occupy a BCC lattice and are each tetrahedrally coordinated to four Na^+ ions which are, in turn, incorporated in an aluminosilicate framework made up of AlO_4 and SiO_4 tetrahedra. The anions reside in cages which may, alternatively, contain molecular species such as H_2O , CO_2 , or noble gases.

Following Strachan and Babad,⁽⁹⁾ I^- -sodalite was prepared by mixing NaAlO_2 and NaI solutions with Ludox, an SiO_2 sol in NH_3 , in stoichiometric preparations. The mixture was stirred well for about 15 minutes until the gelled mass became uniform. The gel was then dried overnight at $\sim 100^\circ\text{C}$, ground in an agate mortar, and pressed into 1/4-inch-diameter pellets for heat treatment.

Phase-pure I^- -sodalite was difficult to prepare, though preparations containing a fair amount of I^- -sodalite were made readily. The pellets were fired at different temperatures for different times to try to determine optimum conditions. The pellets were treated in the range 400 - 1350°C , and the rate of heating was kept reasonably low to minimize the problem of I_2 loss before the I^- reacted to form sodalite. X-ray diffraction showed that I^- -sodalite started to form on annealing at 500°C ; nepheline and NaI were also observed at this stage. Increasing the firing temperature increased the yield and crystallinity of the I^- -sodalite. On annealing at 1000°C , I^- -sodalite was the major phase, with traces of nepheline and some glassy material being present; excess diffuse scattering near $d = 3\text{\AA}$ was taken as evidence for the presence of a glassy phase. Higher temperatures appeared to promote glassy-phase formation; but even after heating at 1350°C , at which temperature partial melting had clearly occurred, a certain amount of I^- -sodalite was still present. For this type of preparation, the optimum conditions from the X-ray diffraction standpoint appeared

to be a few hours at 1000°C. No significant changes in the X-ray patterns were discernible on varying the firing time at 1000°C from 0.5 to 140 hours. Increasing the I⁻ content of the starting material from the stoichiometric value to 1.2, 1.5, and 2.0 times this value had little effect on the X-ray patterns for material fired at 1000°C; presumably the excess I⁻ was lost by volatilization. No significant differences relative to preparations fired at 1000°C in air were observed in X-ray diffraction of stoichiometric mixtures fired in welded Pt tubes at 1000°C or when the dried gels were left in air for several weeks before firing at 1000°C.

Scanning electron microscopy was performed on I⁻-sodalite pellets fired for a few hours in air at 1000°C. No grain structure or even significant amounts of porosity were observed at magnifications up to 1500X. These results were in keeping with qualitative observations on the impact resistance and generally good consolidation of material sintered at $\geq 1000^{\circ}\text{C}$. Very probably the desirable consolidation was achieved by a liquid-phase sintering mechanism; the presence of a glassy phase was deduced from the X-ray measurements (see above). Significant fractions (mm-sized pieces) of several preparations were partly transparent; however, this material was crystalline I⁻-sodalite, not amorphous material. The dependence of the relative abundance of the near-transparent material on the heating rate and firing temperature was looked at cursorily, using a firing time of 2 hours. The firing temperatures were 900°, 1050°, and 1200°C. The heating schedules of pelletized powders formed from the dried solution mixtures ranged from rapid insertion into the furnace set at the firing temperature to heating at $\sim 100^{\circ}\text{C/hr}$ to the firing temperature from 300°C or 600°C. The heating rate had no observable effect; roughly, the higher the firing temperature, the greater the amount of near-transparent material. The X-ray patterns were essentially identical.

The theoretical density of I⁻-sodalite is 2.62 g/cm³. For various air-sintered materials, the measured density lay in the range of 1.6-2.0 g/cm³ even though little porosity was observed (see above). Chemical analyses of various sintered preparations showed the iodine to be present only at about 8-13 wt %, compared with a theoretical value of 22%. This problem was also noted by

Strachan and Babad.⁽⁹⁾ Thus, iodine was clearly lost by volatilization (as expected from qualitative X-ray observations of the presence of nepheline and amorphous material — see above) from these preparations.

Further studies of the thermal stability of I^- -sodalite were undertaken by gravimetric work. The cumulative weight loss as a function of time on heating in air at 1000°C is shown in Figure 1, and the cumulative weight loss after heating for 2-hour periods at successively higher temperatures is shown in Figure 2. The approximate linearity of the weight loss versus temperature plot means that the weight loss increment of the preparation for each of the 2-hour heating periods was approximately temperature independent. This behavior presumably reflects the opposing factors of increasing consolidation of the material and of increasing tendency for volatile losses at increasing temperature. To decide on the major volatilized species, a 1/4-inch pellet weighing ~ 0.3 gm, fired at 1000°C in air, was sealed inside an evacuated fused SiO_2 tube large enough to have one end (containing the sample) in the hot zone and the other at ambient conditions. After 24 hours at 1000°C , the pellet had lost 12% of its weight, and I_2 crystals were observed in the cold part of the tube. This I_2 constituted 15% of the initial iodine content (assuming $\sim 60\%$ of the "theoretical" iodine content), or 1.9% of the initial weight of the pellet. The alkali loss degraded the part of the tube subjected to the heating, but X-ray diffraction of the reaction products revealed only low cristobalite, quartz, and possibly tridymite, a few lines being unidentified but none indicating the presence of crystalline sodium silicates or sodium iodide.

As a comparison, but for indicative purposes only, a gravimetric experiment as a function of temperature was performed with a pellet of synthetic nepheline fired initially at 500°C ; the weight loss, presumably mostly alkali, was comparable to that for the I^- -sodalite (Figures 2 and 3).

B. POWDER DIFFRACTION PATTERNS: DETAILS

As found by Strachan and Babad,⁽⁹⁾ two "extra" reflections corresponding to formally allowed ($h+k+l = 2n$) (220) and (332) reflection were observed in all

9364-34

Figure 1. Weight Loss at 1000°C as a Function of Time
for I⁻-Sodalite Pellet Fired Initially at 1000°C

9364-35

Figure 2. Cumulative Weight Loss for I⁻-Sodalite Pellet
Initially Fired at 500°C, Then Fired at Increasing
Temperatures for 2-hr Periods

9364-36

Figure 3. Cumulative Weight Loss for $\text{NaAlSi}_3\text{O}_8$ Pellet,
Fired Initially at 500°C , Then at Increasing
Temperatures for 2-hr Periods

preparations containing crystalline I^- -sodalite (Figure 4); Tomisaka and Eugster⁽¹⁶⁾ observed no (332) reflection for I^- -sodalite and their Table 5 does not show whether the (220) reflection is present or not. Strachan and Babad⁽⁹⁾ observed other low-angle lines, attributing them to a polymorph. However, these lines lay at d values which are obviously not equal (by up to 0.6° in 2θ) within reasonable experimental error to values predicted by unconstrained integral (hkl) reflections of the sodalite structure, and it seems much more likely that these extra lines derive from second-phase material. The lines at 4.084, 2.499, and 1.665 Å could well be due to the presence of high cristobalite.

Neither does it seem feasible that there is a real difference between I^- -sodalite and the structure they attributed to IO_3^- -sodalite. Since the lattice parameter of sodalite is quite observably dependent on the content of the "cages,"⁽¹⁶⁾ and since the ionic "radii" of IO_3^- and I^- are quite different (1.22 and 2.10 Å, respectively⁽¹⁷⁾), " IO_3^- -sodalite" would be expected to have a different lattice parameter from that of I^- -sodalite. Because of the different X-ray scattering powers of I^- and IO_3^- , at least some of the ($h+k+l = 2n$) reflections would undergo fairly drastic changes in their relative intensities. Also, because IO_3^- has C_{3v} symmetry rather than T symmetry (the symmetry of the empty cage site), some symmetry elements of the space group would be lost. However, if the C_3 axes were aligned in $\langle 111 \rangle$ directions of the cubic cell, a simple doubling of the unit cell could restore the lost symmetry elements. New reflections ($h+k+l = 2n$ in the doubled cell) would appear.

To examine this proposition, we tried to prepare IO_3^- -sodalite by ceramic techniques using $NaIO_3$ instead of NaI , sintering at $850^\circ C$ and $1000^\circ C$. The sodalites' diffraction patterns were indistinguishable from those of I^- -sodalite. A similar result occurred when preparation was attempted by forming in a welded Pt tube for 1 week at $850^\circ C$.

Assuming that the atomic parameters of the sodium and oxygen ions in halide sodalites are the same as those of natural Cl^- -sodalite,^(14,15) the relative intensities of the halide sodalite diffraction lines were calculated. It is clear from Table 2 that (220) and (332) reflections are expected for I^- -sodalite.

CuK α RADIATION

N = NEPHELINE IMPURITY REFLECTIONS

DIFFUSE HUMP IN THE 20-40° RANGE OF 2θ IS INDICATIVE
OF THE PRESENCE OF X-RAY AMORPHOUS MATERIAL

9364-37

Figure 4. X-Ray Powder Diffraction Pattern of I⁻-Sodalite Fired at 1000°C

TABLE 2
POWDER PATTERNS OF SODALITES, $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{X}_2$

hkl	Cl ($a_0 = 8.870 \text{ \AA}$)				Br ($a_0 = 8.933 \text{ \AA}$)				I ($a_0 = 9.014 \text{ \AA}$)			
	d($\text{\AA}$)	I_{calc}	I_{obs}	I_{PDF}^*	d($\text{\AA}$)	I_{calc}	I_{obs}	I_{PDF}^*	d($\text{\AA}$)	I_{calc}	I_{obs}	I_{PDF}^*
110	6.272	32	24	75	6.317	2	3	6	6.374	3	<1	6
200	4.435	5	5	21	4.467	12	8	12	4.507	16	6	16
211	3.621	100	100	100	3.647	100	100	100	3.680	100	100	100
220	3.136	-	-	-	3.158	2	1	-	3.187	5	4	-
310	2.805	7	39	25	2.825	-	1	8	2.851	-	<1	2
222	2.561	16	22	56	2.579	6	14	18	2.602	3	4	12
321	2.371	18	17	55	2.387	26	20	40	2.409	30	16	35
400	2.218	-	1	6	2.233	2	3	6	2.253	2	4	10
411, 330	2.091	27	65	83	2.106	25	45	45	2.125	23	29	35
420	1.983	4	22	-	1.998	6	3	-	2.016	8	5	6
332	1.891	3	4	9	1.905	4	4	-	1.922	6	5	-
422	1.811	3	4	9	1.823	2	1	6	1.840	2	2	4
510, 431	1.740	3	6	8	1.752	-	1	6	1.768	3	1	4
521	1.619	2	11	-	1.631	4	3	-	1.646	5	7	8
440	1.568	8	16	5	1.579	7	6	4	1.594	6	7	6

The intensity of the (211) reflection was taken as 100 in each case. Observed intensities are considered accurate to ~25%; no special precautions were taken to avoid preferred orientation effects. Peak heights are given, but the peak widths did not vary by more than ~25%, so to this accuracy they will serve equally well as integrated intensities.

* I_{PDF} = intensities in Powder Diffraction File, taken from Reference 16, with exception of values for Cl^- -sodalite, which were taken directly from Reference 15; values for Cl^- -sodalite in Powder Diffraction File apply to natural material, not synthetic.

The Br^- - and Cl^- -sodalites were prepared by the same techniques as the I^- -sodalites. (We were unable to prepare F^- -sodalite; even in sealed Pt capsules, a mixture of nepheline and crystalline NaF resulted after gels were fired for 1 week at 850°C .) However, the predicted relative intensities overall were only in fair agreement with experimental values obtained in the present work and in that of Tomisaka and Eugster.⁽¹⁶⁾ Hand calculations of the structure factors for various I^- -sodalite reflections showed that the calculated intensities were not very sensitive to the precise choice of the atomic parameters of the Na and oxygen ions. In the present work, no elaborate precautions were taken to avoid preferred orientation effects, but many patterns of different preparations were registered.

C. INTERACTION WITH AQUEOUS MEDIA

Sodalite occurs naturally in silica-poor rocks such as nepheline syenites. Although these rocks formed at temperatures in the range of 600°C and probably in the presence of hydrothermal fluids, they are not stable in ambient groundwaters with a high activity of silica. Sodalite is known to be unstable in the presence of acidic solutions and rapidly converts to a gel.

Studies at $<100^\circ\text{C}$ — As previously mentioned, Strachan and Babad⁽⁹⁾ reported Soxhlet leach data on hot-pressed I^- -sodalite. When materials prepared at 1000°C and subsequently crushed to $\leq 20\text{-}\mu\text{m}$ powder were used, no significant changes in the X-ray patterns were observed in the solids after ball milling in deionized water of 0.02, 0.2, and 2M NaCl solutions at room temperature for several days. Nor was any effect observed when ground synthetic (see above) or natural Cl^- -sodalite (see below) was treated similarly with deionized water or NaI solutions.

Some Soxhlet data were also obtained using +60 -100 mesh powder (held in a 200-mesh container) produced by crushing material sintered at 1000°C . The solution analyses (Table 3) indicated that the material dissolved in an approximately congruent fashion. After 43 days, only 7% of the starting material was left in the container; the liquid from the last 32 days of the experiment was very turbid, indicating physical weathering of the material into very small particles (which

TABLE 3
SOXHLET TESTING ON I⁻-SODALITE

Test 1 +60 -100 Mesh Powder Material Formed by 1000°C Sintering Element (% of solid in solution)			
Leach Time (days)	Al	Na	I*
1	4	5	3
4	10	15	5
11	15	20	20
43	25	28	30

*Assumed 60% of theoretical content in starting material. Solutions changed only at times indicated in test. No weight-loss data recorded, except that only 7 wt % of sample remained after 43 days. The leach solution from the last 32 days was quite cloudy but no material settled out on standing.

Test 2 Same Material as in Test 1, but 42-60 Mesh Powder	
Leach Time (days)	Cumulative Weight Loss (%)
1	4.4
3	13.6
7	25.8
14	36.2

Derived Soxhlet leach rate $\approx 5 \times 10^{-4}$ g/cm²-day, making the most conservative estimate of surface, i.e., assuming the particles were spheres.

did not settle out on standing). However, when an aliquot of the liquid was evaporated to dryness, X-ray diffraction detected no crystalline material. The material left in the container showed sharp X-ray reflections from boehmite (AlOOH) and gibbsite [$\text{Al}(\text{OH})_3$]. The appearance of both these phases as alteration products is probably related to the fact that at 1 bar, the gibbsite/boehmite phase boundary is quite close to boiling-water temperatures.

A second experiment using +42 -60 powder was run, and this time just weight losses were recorded (Table 3). The derived leach rate was $\sim 5 \times 10^{-4} \text{ g/cm}^2\text{-day}$, quite a high value. These results were fairly similar to those of Strachan and Babad,⁽⁹⁾ for which the duration of the experiments was 14 days (Strachan, private communication).

Studies at 200°C — A polished natural single crystal of Cl^- -sodalite (analysis showed it to contain 0.05 wt % of SO_4^{2-} in addition to Cl^- ; the Cl^- was 91% of its theoretical value and the X-ray patterns showed a weak (210) reflection) showed gross surface etching when it was autoclaved in 500 ml of deionized water at 200°C for 24 hours. Hydrothermal experiments in welded Au tubes were performed on three samples of I^- -sodalite which consisted of powder plus consolidated material. One preparation was fired at 1265°C and contained a fair amount of glassy material and a trace of nepheline in addition to I^- -sodalite. Another, fired at 1000°C, had a similar constitution, and a third preparation, fired at 800°C, contained a fair amount of nepheline in addition to I^- -sodalite. Reaction conditions were 7 days at 200°C/300 bars in deionized water with a solid-to-liquid ratio of 1:10 by weight. The material prepared at 1000°C was also treated with 2M NaCl solution in a parallel experiment.

The results were quite variable. The material prepared at 1265°C showed an apparently unmodified I^- -sodalite phase plus analcime upon X-ray diffraction of the remaining solids. The material fired at 800°C consisted of unaltered I^- -sodalite, a second sodalite phase with a contracted lattice parameter for which the intensity distribution of the Bragg peaks was more reminiscent of Cl^- -sodalite than I^- -sodalite, and analcime. The second sodalite phase presumably reflects replacement of I^- by OH^- ; this would contract the lattice parameter,⁽¹⁶⁾

and the replacement of I^- by a relatively weak X-ray scatterer like OH^- would explain why the pattern resembled that of Cl^- -sodalite. The material fired at $1000^{\circ}C$ was virtually completely altered to analcime, with a small amount of hydroxyl-sodalite and an undetermined phase. However, for the I^- -sodalite in 2M NaCl, only a small amount of analcime was formed, the remainder being a sodalite phase in which the lattice parameters and Bragg intensity distribution were characteristic of virtually pure Cl^- -sodalite, though some I^- , OH^- , and residual H_2O could be present.

Analyses of the solutions are shown in Table 4. It is clear that a large fraction of the I^- was released, but the precise amount is not known because the I^- contents of the starting materials was not found by chemical analyses. It is safe to say, however, that probably more than half the iodide was lost to the solution in all runs apart from the one with the $800^{\circ}C$ -fired material, which was mostly consolidated rather than in powder form.

TABLE 4
HYDROTHERMAL LEACH SOLUTION ANALYSIS FOR I^- -SODALITE

Sample Firing Temperature	Leachant	Al	Si	I (ppm by wt in solution)
$1265^{\circ}C$	D.I. H_2O	50	<0.5	5100
$800^{\circ}C$	D.I. H_2O	5	140	760
$1000^{\circ}C$	D.I. H_2O	65	60	8000
$1000^{\circ}C$	2M NaCl	15	500	8800
100% dissolution value*		~15000	~37000	~10000

*Assuming 60% of "theoretical" loading for iodine. Sample-to-solution = 1:10 by weight. Treatment was 7 days at $200^{\circ}C$ /300 bars. Numbers in columns are ppm by wt.

Similar experiment performed with nepheline gave the percentages of Na, Al, and Si in solution as ~20, ~20, and ~10, respectively.

In these experiments, no nepheline survived. However, a powdered nepheline preparation formed by firing at 1200°C was treated similarly to the preparations described above, using deionized water only; only a small amount of alteration, to nepheline hydrate, was observed, though an appreciable amount of dissolution took place (see Table 4).

D. RADIATION/TRANSMUTATION EFFECTS

Although self-irradiation of ^{129}I fixers would be minimal because of the long half-life of ^{129}I , it seems reasonable that an I-fixer would be buried in a repository together with other HLW, so that it could well experience modest "external" doses of radiation. As shown by Gandolfi photography, a crystal of the natural Cl^- -sodalite (see above) retained its integrity and crystal structure after reactor-irradiation to a dose of $2 \times 10^{17} \text{ n/cm}^2$ (fast) + $\sim 10^9 \text{ R}$ of γ -rays. Two synthetic I^- -sodalite preparations, one fired at 1265°C and the other fired at 800°C (see above), were similarly irradiated. Apart from turning a deep blue color (not dissimilar to the color change resulting from purely ionizing radiation such as X-rays), no change in the crystal structure was revealed by powder diffractometry. No sign of free iodine was present. The blue color would derive from centers such as F centers.⁽¹⁸⁻²⁰⁾

When ^{129}I transmutes to ^{129}Xe , the xenon would very probably assume the noble gas configuration. The lattice would experience a charge compensation difficulty, but the Xe^0 would act like a positive charge on the anion site and would probably form an electron-type color center. However, the fact that the sodalite can tolerate some amount of F centers⁽¹⁸⁻²⁰⁾ suggests that sodalite can withstand some halide loss: in 10^6 years, only 4% of ^{129}I will transmute to ^{129}Xe .

Note that a similar kind of discussion will apply to the $^{85}\text{Kr} \rightarrow ^{85}\text{Rb}$ transmutation in ^{85}Kr -loaded sodalite.⁽¹¹⁾ In this case, the half-life is only 10.8 years, however, so this problem will be much more severe. In this case,

OH^- is acting as a charge compensator for Kr^0 , and the mitigation⁽²¹⁾ of the transmutation problem might proceed according to:

H^0 would doubtless form molecular H_2 and tend to cause pressure buildup in a confined (sealed) canister, but it would probably diffuse through the canister wall quickly enough to avoid such buildup. β^- -induced radiolysis of OH^- ions might act as a further source of atomic hydrogen; but because of the solid nature of the sodalite, there would be a high probability of recombination with the complementary radicals formed in the radiolysis.

IV. BORACITE

A. PREPARATION ATTEMPTS

Like sodalite, the structure of the mineral boracite, $\text{Mg}_3\text{B}_7\text{O}_{13}\text{Cl}$, is such that Cl^- ions reside in cages.⁽²²⁾ The general formula is $\text{R}_3\text{B}_7\text{O}_{13}\text{X}$, where R = divalent cation and X = halide ion; quite a wide variety of boracites have been grown. Indeed, much attention has been paid to their synthesis, as many boracites show interesting ferroelectric properties. However, for the iodides, there appears to be no published information on ceramic preparation or non-hydrothermal wet-chemical preparation. In the present work, no success was obtained with stoichiometric mixtures of Pb/CdI_2 , Pb/CdO , and B_2O_3 sealed inside silica tubes and heated in the $650\text{--}900^\circ\text{C}$ range. The product was X-ray amorphous unless cooled very slowly; metal borate crystals were produced in this event. Nor was any success obtained with mixtures as above and, additionally, with $\text{NiI}_2 \cdot 6\text{H}_2\text{O}$ substituted for $\text{PbI}_2/\text{CdI}_2$; here, sintering in air resulted in near-immediate iodine loss. Wet slurried stoichiometric mixtures of MgO , boric acid, and MgI_2 were made; no sign of Mg iodoboracite was observed by X-ray diffraction after the mixtures were dried.

B. THERMAL AND HYDROTHERMAL ALTERATION

Two small (~ 1 mm) crystals of $\text{Fe}_3\text{B}_7\text{O}_{13}\text{I}$, obtained by MRL from the North American Pacific Laboratory, were studied. As mentioned previously, the limit of thermal stability of the material is $\sim 700^\circ\text{C}$.⁽¹³⁾ When a small fragment of one crystal was heated to 900°C in air, the crystal turned black and X-ray diffraction showed lines due only to hematite. Two separate hydrothermal runs using ~ 0.1 mg of sample and ~ 300 mg of deionized water sealed inside Au tubes and run at $200^\circ\text{C}/300$ bars for 7 days were performed. In both cases, the material turned dark red in transmitted light, and X-ray diffraction showed this solid material to be hematite; analyses of the leach solution showed, within experimental error, that all the iodide had dissolved, with $\leq 0.5\%$ of the Fe going into solution. The leaching solution was not analyzed for boron.

Some comparative measurements were made on natural Mg-boracite crystals. No change in the X-ray diffraction pattern of a natural crystal was observed after heating in air for 1 hour at 900°C; but heating in air for 1 week at 1050°C caused complete decomposition into the borate, $\text{Mg}_3(\text{BO}_3)_2$. No weight loss was detected when a single crystal weighing ~60 mg was immersed in static deionized water for 2 weeks. Treatment of a polished natural crystal in the autoclave for 12 hours at 140°C produced considerable attack on the polished surface. At 300°C (30 hr, 100 bars), another crystal lost 15% of its weight and the surface turned opaque, acquiring a yellow-brown color similar to that produced by heating the natural crystals in air at 800-900°C.

V. SILVER ZEOLITES

As mentioned earlier, Ag- and Pb-zeolites of various kinds have been proposed^(1,5-7) as good candidates for disposal of ^{129}I . By increasing the Si/Al ratio of the zeolite, acid resistance can also be increased.

Normal commercial zeolites were studied in the present work (Table 5). They were loaded with I_2 by holding them in a static I_2 atmosphere at $\sim 130^\circ\text{C}$ (partial I_2 pressure of ~ 1 atm) for several hours. The weight gains were $\sim 15\%$, depending on the H_2O content, which in turn depended on the air humidity. These values agreed quite well with the suppliers' specifications, as expected, since I_2 loading is not very dependent on humidity.⁽⁵⁾

TABLE 5
PROPERTIES OF COMMERCIAL* ZEOLITES

Trade Name	Formula	Wt % Ag	Wt % I_2 Pickup at $\sim 130^\circ\text{C}$
Ag-400	$\text{Ag}_{84}\text{Na}_2\text{Al}_{86}\text{Si}_{106}\text{O}_{384} \cdot x\text{H}_2\text{O}$	37	20.0 ± 0.5
Ag-600	$\text{Ag}_{55}\text{NaAl}_{56}\text{Si}_{136}\text{O}_{384} \cdot x\text{H}_2\text{O}$	28	21.0 ± 0.5
Ag-900	$\text{Ag}_{7.6}\text{Na}_{0.4}\text{Al}_8\text{Si}_{40}\text{O}_{96} \cdot x\text{H}_2\text{O}$	20	16.0 ± 0.5

*Ionex Research Corporation, Post Office Box 602, Broomfield, Colorado 80020

Gravimetric studies were made on I_2 -loaded and unloaded samples after heating at various temperatures. Assuming no synergistic effects, the difference in fractional weight change for the loaded and unloaded material as a function of heat treatment would give the I_2 content of the loaded material as a function of heat treatment. For temperatures below $\sim 700^\circ\text{C}$, the zeolite structure was maintained and gravimetric measurements had to be made immediately after heat treatment; otherwise, significant errors due to H_2O absorption from the air resulted. (A preferable technique would be continuous weight recordings as a function of temperature in a dry atmosphere.) X-ray diffraction showed the structure of the zeolites to be modified when heated above $\sim 700^\circ\text{C}$, and no problem with H_2O absorption occurred for such material. The data were in good agreement with

chemical analysis, the results of which are shown in Figure 5. X-ray diffraction showed that at least some of the iodine in the loaded zeolite was present as crystalline α -AgI in both the heated and unheated material, as expected from previous studies of I_2 -loaded zeolites for which the source of the I was CH_3I , not elemental iodine.^(5,23) Some X-ray patterns are shown in Figures 6 and 7, and the results are given in Table 6.

It can be seen from this table that the basic results are: For the unheated material, at least some of the sorbed iodine produces crystalline α -AgI. However, moderate heating removed the X-ray evidence of the AgI. At $\sim 800^\circ C$, the zeolite framework collapsed, giving rise to amorphous material plus crystalline AgI; the AgI reflections were stronger than those observed in the unheated material even though the I_2 content was considerably less. Further heating produced some recrystallization and disproportionation of the aluminosilicate. The changes in the zeolite lattice in the I_2 -loaded materials closely paralleled those observed in the unloaded materials.

From the chemical formulation of the materials (Table 5), it is easily seen that if each Ag^+ ion were employed in forming α -AgI, approximately 20-40 wt % of I_2 would be absorbed. However, the actual values were considerably lower (see also Reference 23). In addition, most of the zeolites turned a brown color when they absorbed iodine. This brown material was readily leached out by cold water. Somewhat surprisingly, chemical analysis showed this brown material to be elemental iodine and not I_3^- ions, even though the brown color persisted after heating to high temperatures. A leached sample was chemically analyzed, and it is clear that this material constitutes a fairly negligible fraction of the I_2 loading.

After hydrothermal treatment in Teflon tubes at $200^\circ C/300$ bars/7 days with deionized water or 2M NaCl solution, using a solid-to-liquid ratio of 1:10 by weight, the zeolites lost crystallinity to some extent and the X-ray pattern was dominated by α -AgI reflections. The AgI reflections increased in intensity (Figures 8 and 9). Because of the presence of apparently soluble iodine sorbed onto the as-loaded materials, no solution analyses were performed. The NaCl had no observable influence on the results.

9364-38

Figure 5. Chemical Analysis of I₂-Loaded Silver Zeolites as a Function of Heating Temperature (1-hr duration)

9364-39

Figure 6. Effect of Iodine Loading on X-Ray Pattern of Silver Zeolite Ag-400

Figure 7. Action of Heat on X-Ray Patterns of Silver Zeolite Ag-400 Loaded with I_2

TABLE 6

I₂-LOADED ZEOLITES: ACTION OF HEAT ON POWDER X-RAY DIFFRACTION PATTERNS

	Ag-400	Ag-600	Ag-900	Sample A*
Unheated	Crystalline zeolite + AgI	Crystalline zeolite + AgI	Crystalline zeolite + AgI	Crystalline zeolite + AgI
200 ⁰ C	Crystalline zeolite + AgI	Crystalline zeolite + AgI	Crystalline zeolite	Crystalline zeolite
300-700 ⁰ C	Crystalline zeolite	Crystalline zeolite	Crystalline zeolite	Crystalline zeolite
800 ⁰ C	Some loss of crystallinity	Crystalline zeolite	Crystalline zeolite	Trace AgI + amorphous + weakened original reflections
900 ⁰ C	AgI + amorphous	Trace AgI + amorphous	Some loss of crystallinity	AgI + amorphous
1000 ⁰ C	AgI + new aluminosilicate reflections	AgI + amorphous	Trace cristobalite, new aluminosilicate reflections, AgI, amorphous	AgI + new aluminosilicate reflections
1100 ⁰ C	AgI + new aluminosilicate reflections	AgI + amorphous	Cristobalite, AgI amorphous	AgI + amorphous
1300 ⁰ C	AgI + weak aluminosilicate reflections	AgI + new aluminosilicate reflections	Cristobalite, AgI, amorphous	AgI + weak aluminosilicate reflections

*Sample A = commercial product; origin confidential

200°C/50 BAR/8 DAYS IN DEIONIZED WATER

9364-41

Figure 8. Effect of Hydrothermal Treatment on X-Ray Pattern of Silver Zeolite Ag-600

DOE/ET/41900-9
(ESG-DOE-13354)

200°C/50 BAR/8 DAYS IN DEIONIZED WATER

9364-42

Figure 9. Effect of Hydrothermal Treatment on X-Ray Pattern of Silver Zeolite Ag-900

The loaded Ag-zeolites were also irradiated to a gamma-ray dose of ~ 50 MR in the TRIGA reactor at PSU, with the reactor shut down. The γ flux is, of course, considerably lower than when the reactor is operational, but a neutron flux would have rendered the samples very radioactive because of the high neutron cross-section for the production of ^{110m}Ag ($t_{1/2} = 252$ days).

Evidently, no significant amounts of iodine were volatilized, as no iodine was observed to have condensed on the walls of the sealed silica tubes in which the samples were contained during the irradiation. However, X-ray diffraction showed that the α -AgI reflections increased in intensity relative to the zeolite host reflections for the Ag-400 and Ag-600 samples (Figure 10), while no such change was observed for the Ag-900 sample or Sample A. A possible reason for the differences from sample to sample is that the equilibrium H_2O content of Ag-400 and Ag-600 is greater than that for Ag-900 (that of Sample A is unknown) and radiolytic changes will tend to increase with H_2O content (see Reference 24, for example).

Summarizing these results, it can be seen that the incorporation of I_2 in Ag-loaded zeolites is a complicated process. In unheated material, only part of the I is apparently incorporated as crystalline α -AgI, the rest being incorporated in molecular units so that no sharp diffraction lines result from it. Heating to moderate temperatures (~ 300 - 900°C) removes the X-ray evidence of α -AgI. Only when the framework is modified by the heat treatment (~ 900 - 1300°C) does the α -AgI re-form. The atomistic features of the I_2 sorption will be discussed in more detail elsewhere.⁽²⁵⁾ Both hydrothermal treatment at 200°C and modest doses of γ irradiation were capable of enhancing the fraction of the iodine incorporated as α -AgI. This is summarized in Table 7.

It is clear that single-crystal X-ray work, possibly supported by Raman and infrared spectroscopy, would be needed to further clarify the atomic-scale behavior of iodine in these materials.

9364-43

Figure 10. Effect of γ Irradiation on X-Ray Diffraction (XRD) Pattern of I_2 -Loaded Silver Zeolite

TABLE 7
SUMMARY OF STRUCTURAL EFFECTS OF HYDROTHERMAL TREATMENT AND OF
MILD γ IRRADIATION ON Ag-ZEOLITES

	Hydrothermal (200°C)	~ 50 MR of γ Irradiation
Ag-400	Some modification and loss of crystallinity of zeolite, AgI reflections considerably enhanced	Some enhancement of AgI reflections
Ag-600	Considerable loss of crystallinity of zeolite, AgI reflections considerably enhanced	AgI reflections considerably enhanced
Ag-900	Some modification of zeolite, AgI reflections enhanced	No change
Sample A	Some modification and loss of crystallinity of zeolite, AgI reflections considerably enhanced	Virtually no change

VI. LEAD OXYHALIDES

In Reference 10, several Pb oxyhalides were mentioned as possible ^{129}I hosts. cursory studies of the thermal stabilities of these materials were made. As it turned out, all were unstable above $\sim 300^\circ\text{C}$, so detailed study of other properties did not appear to be warranted and no attempts at producing iodine-bearing analogues were made.

A natural crystal of mendipite of nominal formula $\text{Pb}_3\text{Cl}_2\text{O}_2$ (References 26-28) was found to partially decompose when heated to 400°C for a few days. The initial sample was not phase-pure, and neither the impurity phases in the starting material nor the alteration products were identified. A powdered natural crystal of phosgenite, $\text{Pb}_2(\text{CO}_3)\text{Cl}_2$ (References 28 and 29), showed slight thermal alteration after heating for 1 day at 300°C . Again, none of the alteration products was identified. Hydrothermal treatment at $200^\circ\text{C}/300$ bars using deionized water for 7 days produced $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ as an alteration product. However, phosgenite has been observed as a corrosion product of metallic Pb in seawater,⁽²⁹⁾ so it is clearly stable in conditions of high Pb and Cl^- activity.

Synthetic lead oxyhalides were produced by ball-milling PbO powder with NaCl and NaI solutions in polypropylene bottles for several days. X-ray diffraction showed that schwartzembergite, $\text{Pb}_3\text{Cl}_2(\text{IO}_4)\text{OH}$, was produced, albeit not phase-pure, but this material decomposed on heating at 300°C . Blixite,^(28,30) $\text{PbCl}(\text{O},\text{OH})_2$, and $\beta\text{-Pb}_7\text{O}_6\text{Cl}_2$ (structure undetermined but complete reaction of the PbO and the NaI occurred) were made, but these preparations were also unstable above 300°C . Several of these products showed considerable line broadening when heated and others showed line shifting when heated, probably due to OH^- loss, but with apparent preservation of the host phase. The decomposition products of the various synthetic preparations were not fully accounted for by X-ray diffraction, but Pb_3O_4 constituted a significant fraction of the decomposed materials.

VII. CONCLUSIONS

Given the low specific radioactivity of ^{129}I , it is difficult to see ^{129}I immobilization as a particularly pressing problem in the field of nuclear waste management taken as a whole. For human populations, the simple solution to the problem of ^{131}I in fallout from nuclear explosion, that is to say, ingestion of stable I via KI tablets, would also mitigate ^{129}I absorption.

Apart from the seabed disposal option, the best compromise between cost and the solution to the supposed ^{129}I toxicity problem lies, in our view, somewhere between immobilization in cement and in sodalite. The problem of stoichiometric I content of sodalite preparations could be considerably eased by vacuum hot-pressing⁽⁹⁾ or hot isostatic pressing, but this probably adds more processing complexity than an iodine recycle option in the production cycle. Of course, the hot-pressing would lead to better consolidation and thus reduce leaching.

Our other conclusions are as follows:

- 1) The X-ray diffraction patterns from halide sodalites have been clarified, and previous inconsistencies in available data have been brought to light. Fluoride and iodate sodalite apparently could not be prepared by dry-firing techniques.
- 2) I^- -boracites show little hope for production by ceramic techniques, though production by precipitation cannot be ruled out. However, from the limited studies performed here, their leach behavior would not be satisfactory.
- 3) Some progress on the mechanism of I_2 absorption by Ag zeolites has been made by the use of X-ray diffraction.
- 4) Lead oxyhalides exhibit little thermal stability.

REFERENCES

1. D. W. Holladay, "A Literature Survey: Methods for the Removal of Iodine Species from Off-Gases and Liquid Waste Streams of Nuclear Power and Nuclear Fuel Reprocessing Plants, with Emphasis on Solid Sorbents," ORNL/TM-6350, Oak Ridge National Laboratory, Oak Ridge, Tennessee (1979)
2. C. F. Smith and J. J. Cohen, "Perspectives and Reconciliation of Viewpoints on the Risk Assessment Issues," in Waste Management 1980: The State of Waste Disposal Technology, Mill Tailings and Risk Analysis Models, R. G. Post, ed., University of Arizona, p 151 (1980)
3. M. T. Morgan, J. G. Moore, H. E. Devaney, E. C. Rogers, C. Williams, and E. Newman, "The Disposal of Iodine¹²⁹," in Scientific Basis for Nuclear Waste Management, G. J. McCarthy, ed., Plenum, New York, p 453 (1979)
4. L. L. Burger, "Determining Criteria for the Disposal of Iodine-129," Battelle Northwest Pacific Laboratory, Report PNL-3496 (1980)
5. D. T. Pence and W. J. Maeck, "Silver-Zeolite: Iodine Absorption Studies," Idaho Nuclear Corporation Report IN-1363 (1970)
6. D. T. Pence, F. A. Duce, and W. J. Maeck, "Metal Zeolites: Iodine Absorption Studies," Idaho Nuclear Corporation Report IN-1455 (1971)
7. L. P. Murphy, B. A. Staples, and T. R. Thomas, "The Development of Ag⁰Z for Bulk ¹²⁹I Removal from Nuclear Fuel Reprocessing Plants and PbX for ¹²⁹I Storage," Allied Chemical Company Report ICP-1135 (1977)
8. Handbook of Physics and Chemistry (1978-1979) 50th Edition, R. C. Weast, ed., CRC Press, Inc.
9. D. M. Strachan and H. Babad, "Iodate and Iodide Sodalites for the Long-Term Storage of ¹²⁹I," Ceramics in Nuclear Waste Management CONF-790420, DOE Publication, p 349 (1979)
10. Draft Environmental Impact Statement: Management of Commercially Generated Radioactive Waste, Volume 2, Appendix P, U.S. Department of Energy Report DOE/EIS-0046-D
11. R. W. Benedict, A. B. Christensen, J. A. Del Debbio, J. H. Keller, and D. A. Knecht, "Technical Feasibility of Krypton-85 Storage in Sodalite," in Scientific Basis for Nuclear Waste Management, C. J. Northrup, ed., Plenum, New York, p 85 (1980)
12. G. J. McCarthy, R. G. Johnston, and D. E. Pfoertsch, "Thermal Stability of Supercalcine: II. The Scheelite, Sodalite and Pollucite Solid-Solution Phases," Bul. Amer. Ceram. Soc. 57, 358 (Abstract) (1978)

13. P. K. Gallagher, "Thermal Stability of Some Boracites," *Thermochimica Acta* 29, 165 (1979)
14. L. Pauling, "The Structure of Sodalite and Helvite," *Ž. Krist.* 74, 213 (1930)
15. J. Lons and H. Schulz, "Strukturverfeinerung von Sodalith, $\text{Na}_8\text{Si}_6\text{Al}_6\text{O}_{24}\text{Cl}_2$," *Acta Cryst.* 23, 434 (1967)
16. T. Tomisaka and H. P. Eugster, "Synthesis of the Sodalite Group and Sub-solidus Equilibria in the Sodalite-Nosean System," *Mineral. Journal.* 5, 249 (1968)
17. H. D. B. Jenkins and K. P. Thakur, "Reappraisal of Thermochemical Radii for Complex Ions," *J. Chem. Educ.* 56, 576 (1979)
18. R. M. Barrer and J. F. Cole, "Interaction of Sodium Vapor with Synthetic Sodalite: Sorption and Formation of Color Centers," *J. Phys. Chem. Solids* 29, 1755 (1968)
19. D. J. Schiffer, C. Z. von Doorn, and P. T. Bolwijn, "Preparation of Cathodochromic Sodalites," *J. Amer. Ceram. Soc.* 55, 256 (1972)
20. L. T. Todd and M. K. Babrinarayan, "Enhancement of Coloration Sensitivity of Sodalite by Vacuum Annealing," *Bul. Amer. Ceramic Soc.* 58, 1193 (1979)
21. E. R. Vance, R. Roy, J. G. Pepin, and D. K. Agrawal, "Chemical Mitigation of the Transmutation Problem in Crystalline Nuclear Waste Radiophases," *J. Mater. Sci.*, in press (1980)
22. T. Ito, N. Morimoto, and R. Sadanaga, "The Crystal Structure of Boracite," *Acta Cryst.* 4, 310 (1951)
23. C. Donner and T. Tamberg, "Zur Abscheidung von Methyljodid and Silberzeolithin," *Z. Naturforsch.* 27, 1323 (1972)
24. L. A. Bursill, E. A. Lodge, and J. M. Thomas, "Zeolite Structures as Revealed by High-Resolution Electron Microscopy," *Nature* 286, 111 (1980)
25. E. R. Vance and D. K. Agrawal, "X-Ray Study of I_2 Sorption on Some Silver Zeolites," submitted for publication (1981)
26. O. Gabrielson, "The Crystal Structure of Mendipite, $\text{Pb}_3\text{O}_2\text{Cl}_2$," *Arkiv. Min. Geol.* 2, 299 (1961)
27. I. A. Bannister, "The Crystal-Structure and Optical Properties of Matlockite (PbFCl)," *Mineral. Mag.* 23, 587 (1934)

28. E. Welin, "Notes on the Mineralogy of Sweden: VI. X-Ray Powder Data for Minerals from Langban and the Related Mineral Deposits of Central Sweden," Ark. Min. Geol. 4, 499 (1968)
29. H. G. Midgley, "A Further Occurrence of Phosgenite, $Pb_2(CO_3)Cl_2$," Mineral. Mag. 31, 883 (1958)
30. O. Gabrielson, A. Parwel, and F. E. Wickman, "Blixite, A New Lead-Oxyhalide Mineral from Langban," Arkiv. Min. Geol. 2, 411 (1961)