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PREPARATION OF VITREOUS SOLIDS FROM ZEOLITES

by

P. R. Rushbrook

Materials and Process Chemistry
Chemical Development Operation
Hanford Laboratories

August 12, 1963

**HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON**

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PREPARATION OF VITREOUS SOLIDS FROM ZEOLITESI. INTRODUCTION

Synthetic alumino-silicate materials (zeolites) containing adsorbed Cs-137 and Sr-90 are currently proposed as packaging forms for these fission products when removed from radioactive waste solutions.

One property required of any final packaging form is high physical integrity whether the form is intended for shipment to other sites or for long term storage. The zeolite pellets may represent, without further treatment, adequate confinement of the radionuclides for either purpose. However, an added safety factor could be gained if the zeolites could be incorporated into a bulky solid mass not readily leachable with water. Other desirable properties of such solid forms are good thermal conductivity, high radiation stability, and easy recovery of the cesium or strontium by treatment with common reagents following storage or transport.

This report describes laboratory-scale exploratory studies seeking means of producing such solid bodies from cesium- or strontium-containing zeolites. The study is recognized to be incomplete; it was terminated when other studies indicated the zeolite pellets, without further treatment, represent a satisfactory package form.

II. SUMMARY

Fusion of cesium- or strontium-loaded zeolites, Linde 4-A^(R) and Linde 13-X^(R), with mixtures of boric oxide, lithium fluoride and silica produced glass-like solids over a wide range in composition. A promising mixture range contained 35 w/o zeolite, 0-5 w/o silica, 4-8 w/o lithium fluoride, and 55-60 w/o boric oxide. Fusion of such mixtures at 800 C, using zeolites fully loaded with

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cesium or strontium, produced transparent glass-like solids containing about 10 w/o cesium and 6 w/o strontium. The glassy solid occupied about the same volume as the original zeolite bed. The vitreous solids had a moderate leach rate in water but were readily slurried in common mineral acids. The radiation stability of these solids was not studied.

III. DISCUSSION

A. Starting Materials

The fission products Cs-137 and Sr-90 can be recovered from process waste streams by adsorption onto zeolites. These zeolites are synthetic aluminosilicate pellets supplied under various trade names by the Linde Corporation and others.

The representative zeolites chosen for this study were Linde 13-X and Linde 4-A. The composition of Linde 13-X is $0.83 \text{ Na}_2\text{O} \cdot 1.00 \text{ Al}_2\text{O}_3 \cdot 2.48 \text{ SiO}_2 \cdot X \text{ H}_2\text{O}$, and the composition of Linde 4-A is $0.96 \text{ Na}_2\text{O} \cdot 1.00 \text{ Al}_2\text{O}_3 \cdot 1.92 \text{ SiO}_2 \cdot X \text{ H}_2\text{O}$. The material, as received, contains from one to three moles of water per mole of zeolite. All preliminary studies were done using the sodium form of the zeolites. It was later shown that, within the limits of observation, cesium-loaded and strontium-loaded zeolites behave the same as the sodium-loaded form.

B. Desired Properties of Final Product

The final product should be suitable for either long term storage or shipment to other sites. It should, therefore, be an inert solid of high physical integrity. Since it will be radiolytically heated, it must be stable over long periods at 350 - 400 C. The final product should also remain solid, or at least non-volatile up to about 1000 C. The product should be virtually unleachable with water, but desirably, of such a nature that the fission product(s) can be recovered by reasonable chemical treatment.

It must not disintegrate during long exposure in a high-level beta-gamma-X-ray radiation field.

C. Preliminary Fusion Studies

There exists a class of compounds known as fluxing agents, comprised primarily of the alkali metal and alkaline earth compounds. Many of these compounds are also considered glass-formers. Since glasses are promising final product forms, both fluxing agents and glass formers were investigated.

The zeolite and the fluxing agent being tested were ground to a powder prior to the fusion attempt. The combined weight of zeolite and fluxing agent in each experiment was five grams. The powders were mixed in a Coors #1 porcelain crucible and heated to 900-1000 C for two hours. After cooling, the mixture was examined for a) evidence of melting or sintering, and b) physical integrity.

The following compounds were added to Linde 13-X and Linde 4-A at 2, 5, 10, and 25 weight per cent: sodium fluoride (NaF), potassium fluoride (KF), lithium fluoride (LiF), lead oxide (mixture), calcium fluoride (CaF₂), calcium iodide (CaI₂), lead fluoride (PbF₂), cupric fluoride (CuF₂), lead borate (Pb(BO₂)₂·H₂O), sodium peroxide (Na₂O₂), calcium carbonate (CaCO₃), zinc oxide (ZnO), lead metal (Pb), sodium hydroxide (NaOH), and boric oxide (B₂O₃). Only lithium fluoride and boric oxide showed evidence of fusing with the zeolites.

D. Formation of Glass-like Solids

1. Background

A glass is, normally, a mixture of the oxides of an alkali metal or alkaline earth, alumina, silica, and sometimes boric oxide. Indeed, according to one definition of a glass [Compt. rend. 240, 73-5(1955)], the zeolites themselves are capable of forming glass.

Fusions of mixtures with varying proportions of alumina, silica, and boric oxide indicated that glass-like solids will form over a considerable range in composition. Glass or glass-like is used to designate any transparent or translucent coherent solid formed as a result of heating and cooling the mixtures tested. To lower the melting point of the fusion mixture to 800 C or less, alumina and silica should be minimized and a low melting glass former, such as boric oxide, increased in proportion.

Experimental evidence and past experience suggested that lithium fluoride be included in the fusion mixture due to its excellent fluxing property.

2. Experimental Procedure and Observations

A series of fusions was made to study the interdependency for glass formation of those compounds which had exhibited the ability to form vitreous solids in the absence of zeolite.

In these experiments, cesium-loaded Linde 13-X in pellet form was mixed with powdered fluxing agents. The ingredients were weighed into a procelain crucible and heated for two hours at 800 C. Following the heating period, the crucibles were cooled to room temperature over a period of 15 hours and examined. (Henceforth this shall be called the standard method of fusion.) Table I shows the compositions tried and some observations on the character of the solids produced.

It is difficult to label the solids formed as good or poor at this point since the desired properties for the final product are so numerous. The prime objective is that the zeolite pellets will be bound together in a single mass. This occurred, at least to a limited degree, in almost all cases. If we go a step further and say that a "good" product would be one in which there was evidence of reaction, or at least dissolution of the zeolite, we can eliminate many of the compositions.

TABLE I

COMPOSITION OF VITREOUS SOLIDS
Weight Per Cent

<u>Solid Number</u>	<u>Linde 13-X</u>	<u>LiF</u>	<u>SiO₂</u>	<u>B₂O₃</u>
1	25	25	25	25
2	50	25	12.5	12.5
3	45	22	11	22
4	50	12.5	12.5	25
5	25	50	12.5	12.5
6	25	12.5	50	12.5
7	25	12.5	12.5	50
11	29	13	29	29
12	20	40	20	20
13	29	29	13	29
14	20	20	40	20
15	29	29	29	13
16	20	20	20	40
17	45	22	22	11
18	40	20	20	20
19	33	17	17	33
21	33	17	33	17
22	45	11	22	22
23	33	33	17	17
25	30	15	15	40
26	35	10	10	45
27	30	18	12	40
28	30	12	18	40
29	30	16	9	45
30	30	9	16	45
31	33	10	13	44
32	35	5	14	46
33	37	0	15	48
34	30	10	10	50
35	40	0	0	60
36	35	5	0	60
37	35	0	5	60
38	35	5	5	55
39	35	10	0	55
32b	36	2	14	48
32c	36	1	14	48

It was observed that the fusion temperature of the mixture increased as the proportion of silica increased. The samples with a significant proportion of silica did not form a true melt but only sintered. In some cases, the mass was held together by a flimsy matrix of fused boric oxide. It was also observed that the compositions which did not contain silica exhibited much less tendency to contract and crack their containers on cooling. For these reasons, silica (excluding that which is present in the zeolite itself) was eliminated from the fusion mixture.

The degree of glass formation, as indicated by variations in transparency and reflective properties, decreased as the proportion of lithium fluoride was increased. All compositions with 25 w/o zeolite formed good solids with no visible particles of zeolite remaining. It was observed, however, that excess lithium fluoride separated and formed an upper solid phase at room temperature. Further testing on the effect of lithium fluoride showed that a minimum of 4 w/o was necessary to fuse the zeolite in two hours at 800 C in the presence of large amounts of boric oxide. It is possible that even smaller amounts of lithium fluoride could be used if coupled with longer fusion times.

The low melting characteristics of the fusion mixtures are due mainly to the presence of boric oxide. As the proportion of boric oxide was increased, the degree of glass formation also increased. All mixtures with a high weight per cent of boric oxide formed melts with very few impurities visible. These impurities were usually recognizable as undissolved silica.

During the fusion of the high boric oxide mixtures the material appeared to expand until it occupied a volume about three times the initial volume.

The expansion started at about 450 C and ended abruptly at about 650 C. The phenomenon resembled foaming. At the point of maximum expansion the bulk of the mixture was a liquid in the bottom of the container. The thin film of foam which formed was apparently supported by a gas, probably water vapor released from the solids. More thorough drying of the solids prior to fusion, agitation during fusion, or simply puncturing the layer of foam might avoid the apparent expansion.

The maximum weight per cent of zeolite which will produce a glass-like solid under the specified conditions appears to be about 35. It was impossible to produce a good glass of 50 w/o or more zeolite. Fusion of a 40-45 w/o zeolite mixture might be attained if the fusion time were increased beyond two hours, and would undoubtedly occur at higher temperature. A 35 w/o zeolite glass occupies about the same volume as the original zeolite bed. The density of the glass formed by composition 27 (fused in stainless steel) was 2.44; the density of the other satisfactory glasses would be expected to be similar.

It was mentioned that the solids formed from all compositions except No. 36 cracked or shattered on cooling. All of these fusions were made in porcelain crucibles. Attack on the crucibles was significant in all cases and may have contributed to the shattering of the crucibles. Compositions which produced the best solids (No.'s 27, 32, 34, and 36) were also fused in stainless steel cups by the standard method. All formed excellent solids. Composition 27 had small amounts of undissolved solids visible (probably SiO_2). There were small cracks (0.5 - 1.0 mm) at the edge of the sample but these were not sufficient to weaken the solid. The glass was dark green due to the leaching of iron or nickel from the stainless steel. In solid 32, about 10 per cent

of the zeolite remained undissolved. This glass was also dark green and there were numerous cracks (0.5 - 1.0 cm long) starting at the edge of the solid indicating severe strain. Solid 34 was more transparent and "glass-like" than any of the others and was a brighter green than solid 32. There were only traces ($\sim 2\%$) of undissolved zeolite visible. The solid had many cracks (2 to 5 cm long in a 5 cm diameter cup) that appeared to be following cleavage planes. Solid 36 had no trace of undissolved zeolite. Dissolution of iron or nickel was much less than in the other fusions in stainless steel cups. There were random cracks at the edges of the solid; however, they were only 0.1 to 0.2 mm long.

3. Leaching and Chemical Disintegration of Solids

Glass of composition No. 27 and fused in a stainless steel cup was leached with water at 60 C. The leaching rate was determined by weight loss from a piece of glass of known surface area. The data are summarized in Table II.

TABLE II

LEACHING RATE OF SOLID NO. 27 BY 60 C WATER

<u>Time (hr.)</u>	<u>Average Leaching Rate, mils/mo.</u>
0 - 1.0	162
1 - 2.0	261
2 - 3.0	309
3 - 5.5	324
5.5 - 10.1	307
10.1 - 12.1	267
12.1 - 36.1	255

The leaching rate was relatively low during the first hour due to a protective oxide coating on the surface of the solid. Once this surface film was removed, the leaching rate increased to an average equilibrium rate of 288 mils/mo. In a similar experiment at 95 C, the equilibrium leaching rate was 1950 mils/mo. Solid 27 was completely disintegrated to a slurry by treatment with four volumes of 6M HNO_3 , at 90 C. The slurry contained a large amount of easily suspended white solids.