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LOADING AND LEAKAGE OF KRYPTON IMMOBILIZED IN ZEOLITES AND GLASS

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INTRODUCTION

Krypton-85 is formed in nuclear power reactors and remains trapped until the fuel is reprocessed. Federal regulations limit the release of krypton-85 (^{85}Kr) to the environment, requiring recovery and storage of 85% of the ^{85}Kr produced in commercial light-water reactors after January 1, 1983.[1] One of the long-term storage options involves encapsulating ^{85}Kr in zeolites or glasses at high pressure and temperature.[2,3,4,5]

This paper presents experimental results for krypton encapsulation and leakage in sodalite, zeolite 5A, and Vycor "Thirsty" glass. The results show that all three materials are feasible for ^{85}Kr immobilization and long-term storage, although zeolite 5A and "Thirsty" Vycor are preferable due to lower leakage rates.

EXPERIMENTAL

The sodalite was specially prepared by W. R. Grace and has the formula $Na_6[(AlO_2)_6(SiO_2)_6]\cdot xH_2O$. The cubic unit cell diameter is 8.86 A and consists of adjoining beta cages separated by 2.2 A apertures. The beta cages can contain varying amounts of intercalated NaOH, which can be removed by leaching in water.

Zeolite 5A is available commercially, and was obtained from W. R. Grace. It has the formula $(0.8Ca+0.2Na)_{12}[(AlO_2)_{12}(SiO_2)_{12}]\cdot xH_2O$. The cubic unit cell has a 12.26 A diameter and is characterized by a 3 dimensional framework consisting of large (11.4 A) alpha cages and small (6.6 A) beta cages. The alpha cages are connected by 5 A apertures and beta cages are connected to alpha cages by 2.2 A apertures.

The "Thirsty" Vycor samples used are the porous form of Vycor glass made by Corning Glass, and were obtained from G. L. Tingey of Battelle Northwest Laboratory. "Thirsty" Vycor is a glass leached to give a 96% SiO_2-4% BO_2 glass. The average pore diameter is 40 A with a 28% void fraction.

Krypton was encapsulated by zeolite or glass samples at temperature and pressure conditions shown in Figure 1. Typical activation conditions under $\sim$0.2 Torr vacuum to remove water are shown as dashed lines in the left side of Figure 1.

The apparatus consists of a pressurizing system described previously,[3] and a 6 or 25ml Leco pressure capsule (State College, PA 16801) fitted with a cooling jacket and two independently controlled heaters to provide uniform temperature of $\pm$ 5°C along the capsule. Some of the thermocouples were calibrated at 650°C using a magnesium bath and showed less than 2°C error. Since the capsule seals were kept at 500°C, only the lower half of each capsule was used to encapsulate, while a steel plug filled the upper half to minimize convection. The capsule was unloaded and loaded in a dry glove box to minimize water sorption.

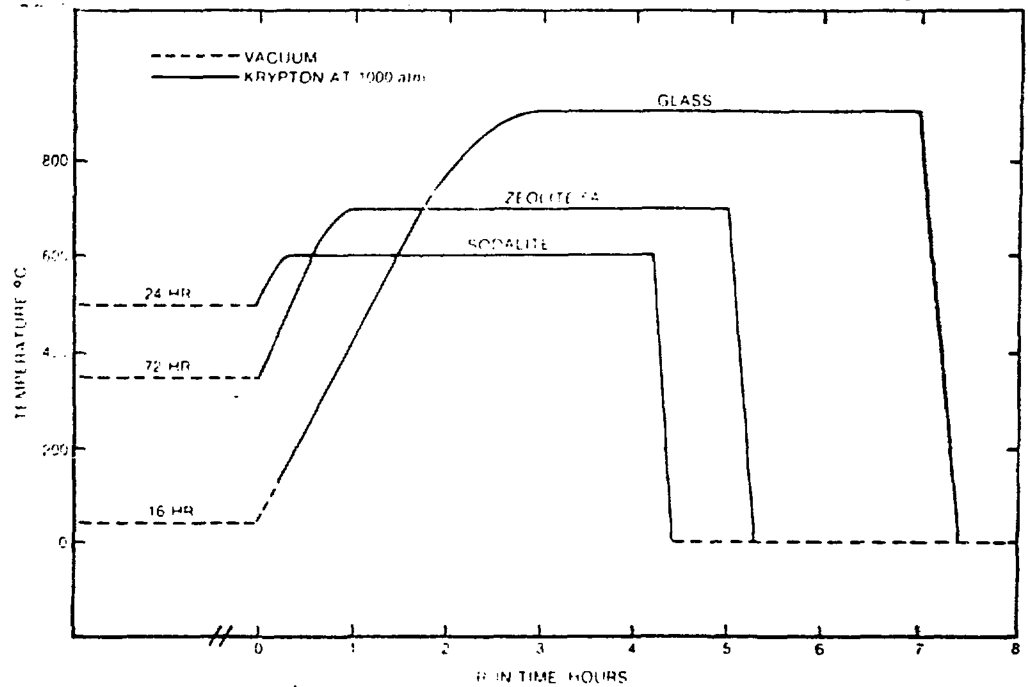


Figure 1: Pretreatment And Encapsulation Run Conditions.

Krypton loading was determined by rapidly heating the samples under vacuum and measuring the released gas composition using a CEC mass spectrometer.

Short-term krypton leakage measurements were made by thermogravimetric analysis (TGA) up to 900°C with a scan rate of 20°C/min. This method was accurate only for gas leakage above $\sim$5%.

Long-term (1-100 days) leakage measurements were made by heating samples in evacuated sealed quartz tubes and periodically analyzing the released krypton using mass spectrometry.

RESULTS AND DISCUSSION

A summary of krypton encapsulation and leakage is shown in Table 1 and Figure 2 for sodalite, zeolite 5A, and "Thirsty" Vycor.

Zeolite 5A showed the largest loading per unit weight. Due to the higher density of glass rods over pilled zeolite 5A, the volumetric loading of glass is comparable to zeolite 5A. The least amount of krypton was released below 800°C from Vycor and the most

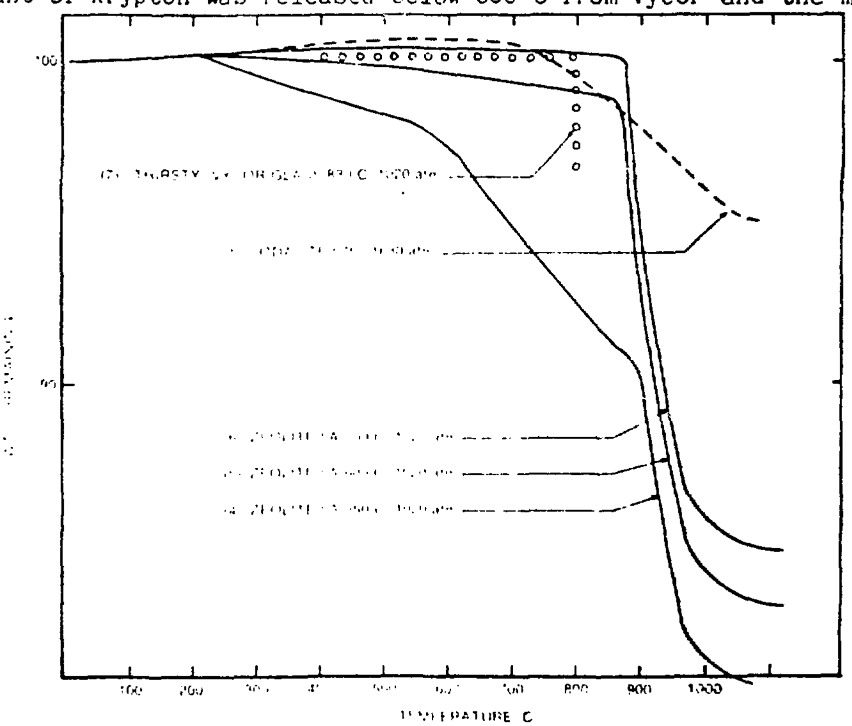


Figure 2: Thermogravimetric Curves Showing Weight Remaining of Krypton in Sodalite, Zeolite 5A, and "Thirsty" Vycor as a Function of Temperature.

TABLE 1

SUMMARY OF ENCAPSULATION AND HIGH TEMPERATURE LEAKAGE DATA

RUN #	MATERIAL	PRETREATMENT CONDITIONS		ENCAPSULATION CONDITIONS		Kr LOADING	TGA DATA
		Temperature (°C)	Time (hr)	Pressure (atm)	Temperature (°C)	(STPcc/g)	%Kr Lost Prior to 800°C
1	Sodalite	575	16	1630	575	20	20
2	Leached Sodalite[a]	575	17	1020	600	27	60
3	K⁺-Exch Sodalite	450	15	1020	600	20	100
4	Zeolite 5A	100	16	1020	550	62	26
		250	1				
5	Zeolite 5A	100	16	1020	600	53	6.5
		250	1				
6	Zeolite 5A	350	72	1020	700	50	<0.2
7	"Thirsty" Vycor Glass	200	9	1090	890	19	<0.2
		500	1				

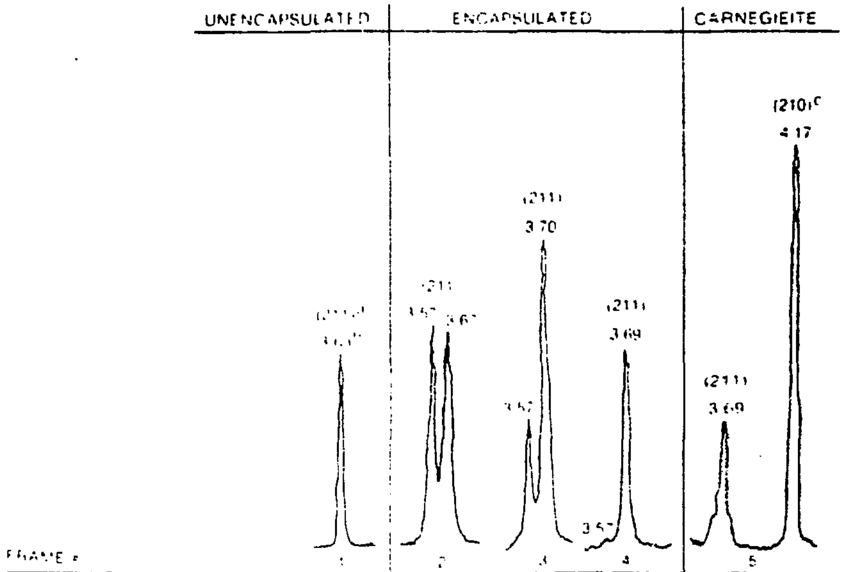
a Mole ratio of excess NaOH to sodalite = 0.28 compared with sodalite which is 0.5.
b All samples were evacuated at 160 µm Hg except for zeolite 5A Run #6, which was evacuated at 10µm Hg.

from sodalite. Thus, based on loading and short-term leakage, zeolite 5A and Vycor appear to be the most promising storage materials. Detailed behaviour is described in the following.

While krypton loadings in sodalite were larger in samples with about half the intercalated NaOH removed, higher leakage rates were also measured (Run 2). When a larger ion like potassium was exchanged for the sodium ions, the leakage was not reduced, possibly due to the concurrent leaching of the NaOH (Run 3).

X-ray analysis of sodalite has shown that structural changes occurring during pretreatment and encapsulation affect krypton loading. Figure 3 shows the correlation of peak splitting in the 211 reflection (2-4) and partial decomposition to carnegieite (5) during krypton loading.

As compared with unencapsulated material, Frame 2 shows a large peak splitting, a unit cell contraction and low krypton loading. Frames 3 and 4 show much less peak splitting, a unit cell expansion and greater krypton loadings. X-ray analysis of leached sodalite (removal of intercalated NaOH) has shown no peak splitting and a 2% increase in unit cell size with a krypton loading of about 30 cm^3/g. Frame #5 shows the presence of a large amount (~60%) of a decomposition product tentatively identified as a carnegieite phase,[6] which does not trap krypton. Tests have indicated that carnegieite forms during pretreatment or encapsulation near 600°C and 1600 atm. Carnegieite will not form at 550°C and 1000 atm.



	1	2	3	4	5
UNIT CELL SIZE Å	[illegible]	[illegible]	8.97	9.04	—
KR LOADING STP (Kr) g	—	2.6	14	19	4.5
ENCAPSULATION PRESSURE atm	—	1020	1020	1020	1630
ENCAPSULATION TEMPERATURE C	—	[illegible]	600	600	600

a hkl value
b d-spacing Å
c reflection due to carnegieite

Figure 3: X-ray Powder Diffraction Patterns of Sodalite Showing The Correlation Between Peak Splitting and Partial Decomposition With Krypton Loading.

Although the apertures interconnecting the zeolite 5A cages are larger than the krypton atomic diameter, krypton is trapped in zeolite 5A by a pore closure at high temperature and pressure, as shown by the loss of crystallinity in the powder x-ray pattern shown in Figure 4. The higher short-term leakage in Figure 2 for Run 4 compared to Runs 5 and 6 is explained by a retention of crystallinity as shown in Figure 4. The higher sintering temperature used in Run 6 compared to Run 5 (Table 1) apparently has resulted in lower leakage as shown in Figure 2. The x-ray patterns for Runs 5 and 6 are identical. Preliminary studies show that above 600°C and approximately 20 gaseous cm^3 STP/g of sorbed water, loaded zeolite 5A can decompose to an anorthite form. However, in Run 6 a water content of 9 cm^3 STP/g yielded no decomposition product. Further work will be made to define decomposition conditions.

Similar krypton trapping by sintering "Thirsty" Vycor is observed. The sudden loss of weight near 800°C in the TGA in Figure 2 is due to explosive shattering of the glass powder, probably accompanied by the krypton release. At lower temperatures no krypton release is measured by weight loss.

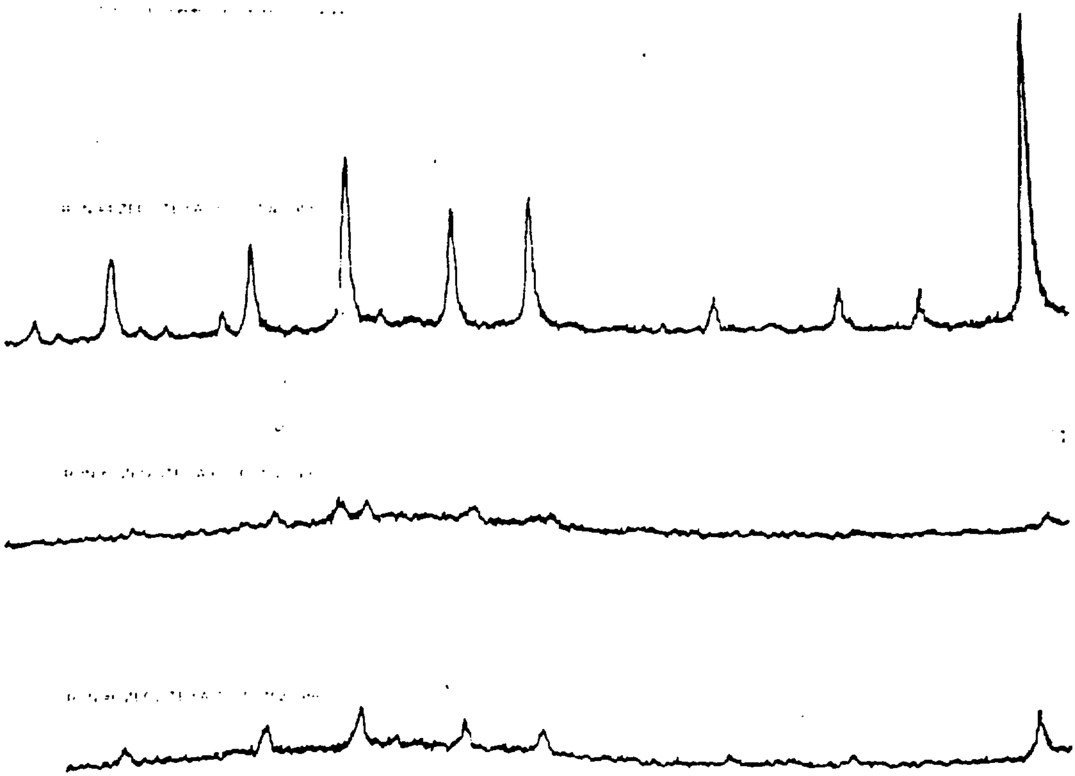


Figure 4: X-ray Powder Diffraction Patterns of Zeolite 5A, Run 4-6 (See Table I).

LONG-TERM LEAKAGE

The krypton fractional leakage (Q_t/Q_∞) depends on storage time (t) and temperature (T) as shown in equation 1:

$$Q_t/Q_\infty = t^{\frac{1}{2}} \left(\frac{36D_0}{\pi R_o^2}\right)^{\frac{1}{2}} \exp\left(-E/2RT\right) \qquad (1)$$

This equation describes krypton leakage from sodalite but has not been tested for zeolite 5A and "Thirsty" Vycor. To measure temperature effects on leakage, results are plotted versus 1/T as log (percent leakage/$t^{\frac{1}{2}}$), which decreases with decreasing leakage.

Sodalite leakage follows the $t^{\frac{1}{2}}$ relation, except for an initial period of higher leakage, probably due to some small cracks in the sodalite crystals.[3] Long-term tests were made at 150, 210, and 288°C, with Kr and water loadings of 15-25 and 8-50 cm^3 STP/g respectively and up to 81 days storage times. The krypton leakage was found to decrease with krypton loading and increase with water loading, as shown in Figure 5. If these results are extrapolated to 10 years and initial krypton loading of 22 cm^3 STP/g, less than 1% leakage is obtained at 190°C and 10 cm^3 STP/g of H_2O.

Tests were made with both leached and 50% potassium-exchanged sodalite. Although higher krypton loadings were obtained for leached sodalite, leakage tests over 20 days at 150°C showed leached and potassium-exchanged sodalites leaked 2 and 10 times as fast as ordinary sodalite, respectively.

Krypton leakage from zeolite 5A and "Thirsty" Vycor were measured for 30 and 68 days at 260°C. While zeolite 5A had an apparent initial leakage of 0.09% (30 days) increasing to 0.1 in 68 days, "Thirsty" Vycor had a very low initial leakage (0.002%) rising to 0.004% in 68 days. Both are superior to sodalite, which releases 2-3% of its krypton under similar conditions. However the leakage is higher for zeolite 5A or "Thirsty" Vycor which haven't been completely sintered.

No effect due to particle size of glass ground and sieved to 1.5, 0.9, and 0.4 mm was observed in krypton leakage at 298° and 527°C for 84 days. The effect of water and krypton loadings on long-term krypton leakage has not yet been studied, and the theoretical leakage behaviour such as shown by equation (1) has not yet been ascertained.

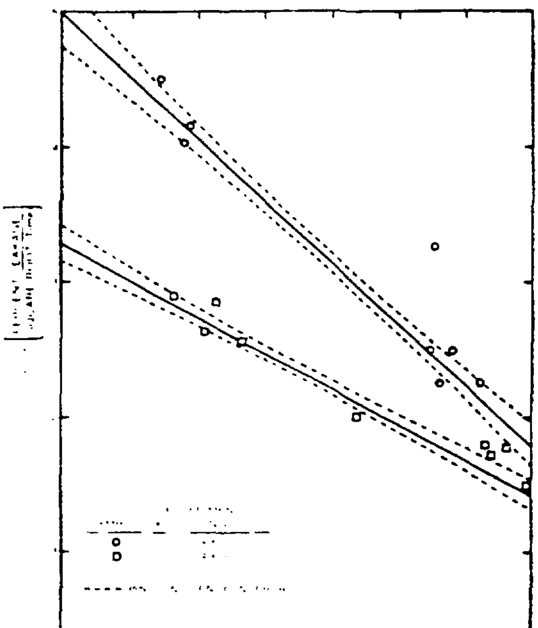


Figure 5: The Effect of Water and Krypton Loadings on Krypton Leakage from Sodalite at 210°C.

CONCLUSION

Based on experimental loading and leakage tests, zeolite 5A and "Thirsty" Vycor glass are preferred to sodalite as a medium for immobilizing krypton-85 for long-term storage, with respective loadings of 50 and 16 cm^3 STP/g. If the long-term leakage results measured at 260°C and 62 days are extrapolated to 10 years storage using equation (1), about 0.05 and 0.2% krypton leakage would be observed with "Thirsty" glass and zeolite 5A, respectively. For a total estimated krypton-85 production from a 2000 metric ton commercial fuel reprocessing plant of 190 m^3 at STP of 6% ^{85}Kr in Kr, total annual volumes of immobilized krypton would be 6.5 and 4.5 m^3 of "Thirsty" glass and zeolite 5A, respectively. Further tests are under way to evaluate krypton loading conditions and the effect of adsorbed water and temperature on long-term leakage.

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