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TECHNICAL FEASIBILITY OF KRYPTON-85 STORAGE IN SODALITE

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INTRODUCTION

Federal regulations limit the release to the environment of krypton-85 produced by nuclear fission in commercial electric power generation systems.¹ These regulations apply to nuclear fuels irradiated after January 1, 1983.¹ To meet the EPA regulation, the ⁸⁵Kr produced must be collected and stored for sufficient time to allow radioactive decay to reach a level that will allow release consistent with the regulations.^{2,3} This paper presents experimental results and analyses to demonstrate the technical feasibility of encapsulation in zeolites to immobilize krypton-85 for safe, long-term storage.⁴

BACKGROUND

Previous work by Barrer and Vaughan shows that krypton can be encapsulated by sodalite to provide a product which might be suitable for long-term storage of krypton-85.^{5,6} Such a product is illustrated in Figure 1, where a structural model of sodalite cages (each ~6.6 Å free diameter with 2.3 Å cage opening) is shown with a trapped krypton atom (~3.5 Å). If each cage were occupied, a theoretical saturated loading, V_s , of 53 cm³ STP of krypton per gram sodalite can be calculated.⁵ This would give a storage volume equivalent to that in a pressurized cylinder of krypton gas at 46 atmospheres. Vaughan obtained equilibrium encapsulation loadings in the range 20-35 cm³ STP/g⁶ (equivalent to storage volumes for pressurized cylinders at 16 to 28 atm). Gas release rates measured at about 400 to 560°C could be used to predict low leakage rates at storage temperatures of about 150°C.^{5,6,7}

Figure 1. Model of sodalite cages. Upper cage contains a krypton atom. Relative cage opening shown on right side of upper cage.

THEORY

A Langmuir adsorption model (equations (1) and (2)) can be used to describe equilibrium loadings of krypton on sodalite,⁶

$$V_{eq} = \frac{V_s \cdot k(T) \cdot f(p, T)}{1 + k(T) \cdot f(p, T)} \quad 1$$

$$k(T) = \exp\left[\frac{H}{RT} + \frac{S}{R}\right] \quad 2$$

with V_{eq} and V_s the equilibrium and saturated loadings, respectively, f the fugacity, R the universal gas constant, T the absolute temperature, p the pressure, k the equilibrium constant, H the enthalpy, and S the entropy. The equilibrium loading increases with pressure but decreases with temperature of encapsulation.

The rate of encapsulation or leakage is described by Fick's law. Fick's law can be solved to describe the total krypton uptake during encapsulation as a function of time in equation (3) or to describe the rate of krypton leakage from sodalite in equation (4),

$$V = V_{eq} \left[1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{D n^2 \pi^2 t}{R_0^2}\right) \right] \quad 3$$

$$\frac{d \left(\frac{Q_1}{Q_{\infty}} \right)^2}{d t} = \frac{36 D}{\pi R_0^2} = \alpha D \quad \text{For } \frac{Q_1}{Q_{\infty}} < 0.3 \quad 4$$

with V the average concentration of krypton in sodalite, V_{eq} the

equilibrium loading, t the time, D the diffusivity, R_0 the average sodalite particle radius, Q_t the volume of gas released at time t and Q_∞ the volume released at infinite time.^{9,10,11}

The diffusivity is a strong function of temperature and is described by equation (5),

$$D = D_0 \exp\left(\frac{-E}{RT}\right) \quad 5$$

with E the activation energy and D_0 a constant.¹¹ Other factors which may affect the krypton diffusion include the concentration of different-sized cations in sodalite, the adsorbed water content, crystal defects, and the concentration of other gases, such as xenon.^{4,9,11,12}

EXPERIMENTAL PROCEDURE

Encapsulation⁴

Figure 2 shows a schematic of the encapsulation system. Samples were introduced into a 0.25-L pressure vessel and activated by heating overnight under vacuum at the run temperature. After activation, the vessel was pressurized to a run pressure for a given time. The vessel was then cooled at the run pressure, vented, and the samples removed to a dry glove box. The vented gas was returned to the storage cylinder for reuse. Gas sorption was measured using mass spectrometry.

Leakage Measurement⁴

Figure 3A shows the schematic for high-temperature leak-tests (300-500°C) which were made by placing a weighed sample of sodalite loaded with krypton in a quartz tube and evacuating it. The tube was heated at constant temperature and the gas evolution measured by a pressure gauge and a gas chromatograph.

Long-term storage tests shown in Figure 3B (50-300°C) were made by placing a sample in a quartz tube, which was evacuated and sealed. The tubes were kept in ovens at constant temperature, and then removed after predetermined storage times. The gas volume and composition released into the tube were measured by mass spectrometry.

RESULTS AND DISCUSSION

Equilibrium loadings of krypton on leached sodalite were measured in the ranges 400-500°C and 1220-1910 atm. The fitted parameters for equations (1) and (2) were very close to those obtained by fitting Vaughan's data at lower pressures.⁶ The parameters obtained by fitting Vaughan's and our combined data are: $V_S=45.2$ cm³/g; $H/R=2083.7$ K; and $S/R=-8.54$.⁴

When mixtures of krypton and xenon were used, the krypton equilibrium loadings decreased with xenon fraction (Henry's Law), as shown in Figure 4. Krypton loadings decreased by 25-30% as the gas mixture changed from 0 to 64% xenon. The xenon loadings were 1 to 5 cm³/g for oven-dried (OD) and spray-dried (SD) sodalites, respectively, indicating that xenon was generally excluded from the sodalite cages.

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Figure 4. Equilibrium krypton loading in sodalites as a function of gas composition at 500°C and 1220 atm.

Krypton loading in oven-dried sodalite powder (OD-2) is shown in Figure 5 as a function of time. Higher temperatures strongly increase the loading rate, e.g., 20 cm³/g is reached in 2 h at 575°C or in 10 h at 500°C. Leaching the OD-2 to remove excess NaOH (sample OD-2-L48H) also increased the loading rate. Not shown in Figure 5, the rate of loading in pillared sodalite was not different from the rate in powdered sodalite.

Diffusivities calculated from high temperature leakage rates are compared with Vaughan's results⁶ in Figure 6. Leached spray-dried sodalite leaks faster than unleached oven-dried sodalite. Not shown in Figure 6 are the effects of pilling, initial krypton loading on leakage and added xenon: pillared sodalite behaves the same as powdered sodalite, while a lower initial krypton loading increases the leakage rate.⁴ Diffusivities calculated from fitting equation (3) to the rate of krypton loading are identical to diffusivities calculated from krypton leakage from sodalite at low initial loadings.⁴ Added xenon lowers the rate of leakage of krypton from leached spray-dried sodalite by a factor of ~8, resulting in diffusivities lying about half-way between the OD-2 and SD-LG lines.

Figure 5. Krypton loading on oven-dried sodalite as a function of time at various temperatures and pressure.

The results of up to nine months of long-term leakage measurements are shown in Figure 7 for unleached sodalite. The lowest leakage was obtained with samples having a high krypton loading and a low water content. The sample containing $21 \text{ cm}^3/\text{g Kr}$ and $10 \text{ gaseous cm}^3/\text{g H}_2\text{O}$ was obtained by allowing the material with $21 \text{ cm}^3/\text{g Kr}$ and $5 \text{ cm}^3/\text{g H}_2\text{O}$ to contact air saturated with water vapor at 25°C for 14 h. Diffusivities calculated from the leakage measurements in Figure 7 are compared with high temperature values in Figure 6.

If the leakage rates shown in Figure 7 are extrapolated, the predicted leakage and its 95% confidence interval of total krypton at ten years varies from $0.05 \pm 0.3\%$ to $1.6 \pm 1.1\%$, with most of the values around $0.3 \pm 0.5\%$.⁴ The predicted loss of ^{85}Kr is approximately half of these values due to radioactive decay. After ten years, the exponential rate of radioactive decay of ^{85}Kr predominates over the square root rate of leakage, resulting in decreasing amounts of ^{85}Kr which can be found outside the sodalite crystals.⁷

Evacuated quartz tubes containing sodalite samples with encapsulated krypton were exposed to $\sim 2 \times 10^9$ rads of gamma radiation at $48\text{--}115^\circ\text{C}$, with a daily average of 60°C . There was no evidence of crystal damage or increased krypton leakage compared with laboratory control samples. However, a small amount of hydrogen but almost no oxygen was formed, in agreement with other results.¹³

Figure 6. Comparison of the temperature dependence of diffusion of krypton in OD-2 and SD-LG with Vaughan's results and with 264 and 150°C leakage measurements. High-temperature method used for open points; low temperature method for filled points. See equation (3) for α .

Figure 7. Rates of percent leakage at 150°C of krypton encapsulated in unleached sodalite at various Kr loadings and amounts of adsorbed water.

TECHNICAL FEASIBILITY EVALUATION

Based on these experimental results, the process that is technically feasible for a reference¹⁴ 2000 metric ton of heavy metal (MTHM) per year reprocessing plant producing ~ 17 MCi or ~ 190 m³ at STP would encapsulate krypton at approximately 20 cm³/g from krypton at temperatures greater than 575°C and pressures greater than 1660 atm with one batch a day in a 58-L high pressure vessel.⁴ Based on preliminary measurements at 500°C, the same process also would be feasible for a 70% krypton and 30% xenon mixture.⁴

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