A Literature Search on the Effects of the Decay of ^{85}Kr to ^{85}Rb on Long-term Storage Options

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SUMMARY

One of the volatile radionuclides that requires removal from process off-gas streams during the reprocessing of used nuclear fuel (UNF) to meet regulations is Kr. Of the krypton isotopes that are present in UNF, ^{85}Kr is the only remaining radioactive isotope after the fuel has been out of the reactor for one year; all other isotopes (^{82}Kr, ^{83}Kr, ^{84}Kr, and ^{86}Kr) are stable. If UNF is reprocessed within about 50 y, Kr capture is needed to meet regulatory guidelines. The reference process for removing Kr from the off-gas streams within a reprocessing facility is cryogenic processing of the off-gas streams. However, other solid sorbent-based methods are being investigated for the removal of Kr. These processes can involve zeolites, Ag-loaded zeolites, or metal organic framework (MOF) materials. The reference immobilization process for storage of the Kr is pressurized canisters or canisters with co-deposited metal and Kr.

Once removed from the off-gas streams, Kr must be placed in storage until the ^{85}Kr has decayed to levels such that its release would meet regulatory guidelines. The current method of storage is high-pressure metal canisters. Historically, concerns have been expressed that the decay product of ^{85}Kr, ^{85}Rb, could cause corrosion and weakening in the canisters, ultimately leading to premature failure and release of ^{85}Kr. Vapor deposition in metal, immobilization in zeolites and immobilization in MOF materials have all been investigated as alternative storage media for Kr. Even these storage methods may still be susceptible to the chemical effects caused by decay of ^{85}Kr to ^{85}Rb. The intent of this document is to provide a review the available literature on topics relevant to the effects of Rb on the long-term storage of ^{85}Kr, examine the source terms in the context of this concern, and suggest a path forward to resolve any outstanding knowledge gaps.

We found that it is unlikely that ^{85}Kr storage in high-pressure containers will be compromised by corrosion from the decay product Rb, especially if the Kr recovery operations result in a gas composition with very low oxygen content. Similarly, the choice of immobilization through ion implantation is also unlikely to be significantly affected by ^{85}Kr decay.

Study of the immobilization and storage of ^{85}Kr on solid sorbents has been severely limited, and almost no literature was available on this topic or on related systems. The effects of ^{85}Kr decay in solid sorbents is likely both an interesting and challenging scientific topic, as both radiation damage and chemical transmutation must be considered when evaluating long-term stability. We conclude that based on limited data, zeolites are likely to experience less radiation damage than MOFs from the decay events and that the presence of Rb may be thermodynamically beneficial for long-term retention of Kr within the zeolite matrix. These effects are somewhat ameliorated by the very small amount of ^{85}Kr present. It is recommended that the benefits of solid sorbent immobilization for ^{85}Kr storage be analyzed and that careful consideration be given to answering the myriad of unknowns surrounding the effects of ^{85}Kr decay (both chemical and radiative) on the solids being considered.

Further experimental work to verify the viability of cylinder and ion implantation storage methods, and to better characterize the effects of ^{85}Kr decay on solid sorbents, will provide assurance that ^{85}Kr can be safely stored for the extended periods of time required by United States regulation. The work already underway at Oak Ridge National Laboratory to analyze legacy Kr waste forms will be highly beneficial to better understanding the effect of ^{85}Kr decay on storage methods that allow for contact between metals and Rb. Work has also been planned at Idaho National Laboratory that will investigate the resiliency of MOFs when exposed to radiation. These two current research efforts should be leveraged to answer outstanding questions regarding the impact of ^{85}Kr decay on storage methods, and future work should be planned based on the results of these studies.

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ACRONYMS

aJ	atto Joule (1×10^{-18} J)
Ci/tIHM	Curies per tonne (metric ton) initial heavy metal
g/tIHM	Grams per tonne initial heavy metal
GWd/tIHM	Gigawatt-days per tonne initial heavy metal
INL	Idaho National Laboratory
MeV	Million electron volts
MOF	Metal organic framework
ORNL	Oak Ridge National Laboratory
PNNL	Pacific Northwest National Laboratory
UNF	Used nuclear fuel
W/tIHM	Watts per tonne initial heavy metal

A LITERATURE SEARCH ON THE EFFECTS OF THE DECAY OF ^{85}KR TO ^{85}RB ON LONG-TERM STORAGE OPTIONS

1. INTRODUCTION

One of the volatile radionuclides that requires removal from process off-gas streams during the reprocessing of used nuclear fuel (UNF) to meet regulations is krypton. Of the Kr isotopes that are present in UNF, ^{85}Kr is the only remaining radioactive isotope after the fuel has been out of the reactor for one year; all other isotopes (^{82}Kr, ^{83}Kr, ^{84}Kr, and ^{86}Kr) are stable (Jubin et al. 2011). If UNF is reprocessed within about 50 y, Kr capture is needed to meet regulatory guidelines (Jubin et al. 2012). The reference process for removing Kr from the off-gas streams within a reprocessing facility is cryogenic processing of the off-gas streams (Jubin et al. 2011; Soelberg et al. 2013). However, other solid sorbent-based methods are being investigated for the removal of Kr. These processes can involve zeolites (Christensen et al. 1982; Christensen et al. 1983; Knecht 1977; Miyake et al. 1984; Penzhorn et al. 1982a), Ag-loaded zeolites (Maeck and Pence 1970), or metal organic framework (MOF) materials (Soelberg et al. 2013; Banerjee et al. 2015; Liu et al. 2014; Liu et al. 2012; Thallapally et al. 2013a).

Once removed from the off-gas streams, Kr must be placed in storage until the ^{85}Kr has decayed to levels such that its release would meet regulatory guidelines. The current method of storage is high-pressure metal canisters. Historically, concerns have been expressed that the decay product of ^{85}Kr, ^{85}Rb, could cause corrosion and weakening in the canisters, ultimately leading to premature failure and release of ^{85}Kr. Vapor deposition in metal, immobilization in zeolites and immobilization in MOF materials have all been investigated as alternative storage media for Kr (Whitmell 1982; Whitmell 1985; Christensen et al. 1982; Christensen et al. 1983; Knecht 1977; Miyake et al. 1984; Penzhorn et al. 1982a; Maeck and Pence 1970; Soelberg et al. 2008; Mueller et al. 2006b). Even these storage methods may still be susceptible to the chemical effects caused by decay of ^{85}Kr to ^{85}Rb.

The intent of this document is to provide a review of the available literature on topics relevant to the effects of Rb on the long-term storage of ^{85}Kr, examine the source terms in the context of this concern, and suggest a path forward to resolve any outstanding knowledge gaps. The source terms and known chemistry of Rb are discussed first and then used to provide perspective on how potential storage methods may be impacted by Rb ingrowth.

1.1 Source Term

Calculations with the ORIGEN code (Croff 1983) were used to quantify the mass and activity of the noble gas fission products expected in the off-gas stream for a reference case to be used for this discussion. The fuel in this case had a burn-up of 60 GWd/tIHM and a 5 y cooling period – fuels currently in dry storage have been out of the reactor for more than 5 y. Calculations were performed with the SCALE code version 6.0 (ORNL 2009), and results for Kr and Xe are shown in Table 1. The amount of ^{85}Kr is rather small (0.3 mass% of the sum of the Kr and Xe inventory), but nevertheless cannot be freely released due to U.S. regulatory requirements.

Table 1: Noble Gas fission product estimates[1] for UNF having burnup of 60 GWd/tIHM and cooled 5 y

Isotopes	g/tIHM	Ci/tIHM	W/tIHM
Kr			
^{82}Kr	1.619		
^{83}Kr	64.77		
^{84}Kr	211.5		
^{85}Kr	29.53	11590	17.38
^{86}Kr	318.6		
Kr Total	626		
Xe			
^{128}Xe	8.605		
^{129}Xe	0.080		
^{130}Xe	17.09		
^{131}Xe	626.7		
^{132}Xe	2140		
^{134}Xe	2760		
^{136}Xe	4064		
Xe Total	**9616**		

[1] (Jubin et al., 2015)

1.2 The Decay of ^{85}Kr

Krypton-85 has a half-life ($t_{1/2}$) of 10.76 y and transmutes to stable ^{85}Rb by emission of a beta particle (ß), and an antineutrino ($\bar{\upsilon}$), both of equal energy (0.687 MeV). These emissions result in recoil of the daughter atom, Rb. Marks et al. (2013) provide the formulas for calculating the contributions to the recoil energy from the $ß^-$ and $\bar{\upsilon}$ (see Appendix A). The effect of this recoil is discussed in a later section.

With such a relatively short $t_{1/2}$, after 50 years of storage only 3.6% of the original stored amount of ^{85}Kr remains. Rubidium, a Group I alkali metal, is known to be corrosive, especially in the presence of an oxidant. Historically, the potential corrosion of ^{85}Kr storage containers by the decay product ^{85}Rb has been of concern (Pinchback et al. 1981). In addition, the energetic emissions resulting from $ß^-$ decay and any potential electrical or chemical changes (i.e., production of Rb^+, a charged particle, in place of neutral Kr) also have the potential to damage storage containers or materials.

During the first 10.76 y of storage, half of the ^{85}Kr will decay to ^{85}Rb. This will produce 14.77 g of ^{85}Rb per tIHM within the associated volume of stored Kr or Kr/Xe waste. Waste volumes for various Kr waste forms were estimated by Jubin et al. (2015). Thus, as the ^{85}Kr decays, the likelihood of significant corrosion increases. Storage of Kr in low-pressure (assumed 0.1 MPa) cylinders is attractive from the standpoint of reducing the risk of large gas releases in the event of corrosion-assisted rupture of a cylinder, but can result in substantially higher waste volume. The use of higher pressures (≥5 MPa) reduces the stored waste volume with a concomitant increase in the probability of leakage or cylinder rupture caused by Rb corrosion. Table 2 summarizes the resulting waste volumes and the concentration of ^{85}Rb that would be present in the waste form following one half-life of ^{85}Kr. These calculations assume the complete separation of Kr from the stable Xe fission products that have the potential of increasing the Kr waste volume by a factor of ~10.

Table 2: Waste volumes for noble gas fission products (Jubin et al. 2015)

Component	**Form**	**Volume (m^3/tIHM)**		**Concentration of Rb in waste form assuming uniform distribution (mols Rb/L)**	
		60 GWd/tIHM cooled 5 y			
		Fuel-born Only	**Fuel-born + Tramp[1]**	**Fuel-born Only**	**Fuel-born + Tramp[1]**
Kr	Low-pressure Cylinder (0.1 MPa)	0.165 (3.77 Type 1A cylinders)[2]	0.169 (3.86 Type 1A cylinders)[2]	0.022	0.022
Kr	High-pressure Cylinder (>5 MPa)	0.00330 at 5 MPa (230 W/cylinder)	0.00338 at 5 MPa (225 W/cylinder)	1.116	1.089

[1] “Tramp” contaminants are those carried by the process chemicals, in-leakage, or other sources of chemicals of like chemical nature to the one being immobilized.

[2] Type 1A cylinders are standard steel cylinders with an internal volume of 43.8 L.

The results summarized in Table 2 are the waste volumes for cylinders; the waste volume for immobilization of ^{85}Kr in a solid sorbent could vary widely based on the density of the sorbent, the loading of the sorbent, and any other production processes (such as compaction by hot pressing).

2. CHEMICAL PROPERTIES OF Rb

Rubidium is a Group I metal with a melting point of 39°C and a boiling point of 688°C. It is most common as a solid at room temperature, with a density of 1.53×10^3 kg/m^3. Liquid metal Rb has a density of 1.46×10^3 kg/m^3 at the melting point. Rubidium has two naturally occurring isotopes: stable ^{85}Rb (with a natural abundance of 72.2%) and radioactive ^{87}Rb, (with a natural abundance of 27.8% and a $t_{1/2}$ of 4.92×10^{10} y). Like other alkali metals, Rb is strongly reactive with water and can ignite in air. For this reason, it is recommended that it be stored and handled in an inert atmosphere. Pure Rb metal may not cause substantial corrosion to materials it contacts when handled in this way, but in the presence of oxygen it will form highly corrosive rubidium oxides. Thus, when evaluating any potential storage mechanism the presence of oxygen should be considered.

There are multiple processes that can be used to separate and purify Kr, and these methods can result in different oxygen concentrations in the product stream. The most common industrial separation is cryogenic distillation. This process inherently results in very low oxygen contamination because O_2 must be removed prior to distillation to avoid the formation of ozone (Gombert 2007). Fluorocarbon adsorption has been used less extensively but has the capability to capture and purify multiple noble gases based on their solubility in CCl_2F_2 (commonly known as R-12). The product stream from fluorocarbon adsorption has higher levels of contaminants than that from cryogenic distillation, and the oxygen content is estimated to be 1.4% (Little et al., 1983). The third process that can be used for Kr separation is adsorption on solid sorbents, such as zeolites or MOFs. While Liu et al. (2012; 2014) show that all air components pass through MOFs used to separate Kr and Xe from air, data regarding the oxygen content of both zeolites and MOFs when used to remove Kr were not found in publically available literature. However, it should be noted that zeolites in particular have a high affinity for water.

3. STORAGE OPTIONS FOR ^{85}Kr

Options for ^{85}Kr storage include storage as a compressed gas in gas cylinders, vapor co-deposition within a metal on the inside of a canister, or immobilization in a solid sorbent. If a solid sorbent is selected, the Kr-containing sorbent, once loaded, can then be disposed of through various methods such as direct disposal, hot press compaction, or other processing methods. In this section, we discuss the potential impacts of ^{85}Kr transmutation to ^{85}Rb on cylinder storage, vapor deposition, and immobilization on two common sorbents.

3.1 Cylinder Storage

Assuming that ^{85}Kr will be stored in high-pressure cylinders (canisters) to minimize waste volume, the resulting small amount of ^{85}Rb (generated initially at a rate of about 0.02 mole/y) is likely to exist within the metallic cylinder as an alloy with the metal walls and uniformly distributed on the canister walls. Corrosion by liquid metallic Rb has been studied for a variety of metals (Pontillon et al. 2010; Borgstedt et al. 1984; Penzhorn 1977; Whitmell 1982; Asai 1967; Asai and Kawashima 1966; Borgstedt and Guminski 1996c, f, h, i, k, a, g, b, e, d, j; Pinchback and Knecht 1978). Pinchback and Knecht (1978) evaluated stainless steel alloys and other alloys for use as canisters to hold pressurized Kr, specifically looking at the potential that Rb corrosion could compromise the canister integrity. They subjected coupons of various metal alloys (Inconel, 316 stainless steel, 304 stainless steel, and others) to liquid Rb at elevated temperature for over 200 days. They found that multiple alloys (notably including 316 stainless steel) were not corroded. One exception was 304 stainless steel that was corroded by the liquid Rb. While these test results are promising, it is unclear how realistic they are as they were conducted in the absence of oxygen. Borgstedt et al. (1984) conducted corrosion testing on several different metal alloys with non-purified Rb (containing Rb oxides and hydroxides). These tests were conducted at 150°C and 2000°C for up to 1250 d. Borgstedt and coworkers concluded that any corrosion was very limited and did not impact the integrity of the metals. Based on the results of these studies, it is likely that the presence of Rb in high-pressure ^{85}Kr storage cylinders will not negatively impact the long-term integrity of the canisters.

3.2 Ion Implantation

Co-deposition of Kr with metal vapor (also known as ion implantation) has been considered by multiple researchers (Whitmell 1985, 1982). This type of process would result in a metal matrix containing about 6 mass% Kr (Gombert 2007) and, since the concentration of ^{85}Kr is about 4 mass%, the resulting metal matrix would contain about 0.3 mass% Rb (Table 1) after all the ^{85}Kr decayed. At these concentrations a separate liquid phase would not be expected. The Rb^+ would become part of the metal matrix as an interstitial particle either as an ion or metal after gaining an electron from the metal through conduction, probably the conduction band. From a study of transmutation effects on crystalline materials potentially used for nuclear waste, it was determined that, even in these non-conducting materials, electrons were available from neighboring atoms or from the unoccupied conduction band and, at relatively high concentrations of the decaying atom, some defects were likely because of the changes in atomic volume (Jiang et al. 2012; Jiang et al. 2014; Van Ginhoven et al. 2010, 2011). At the low concentrations expected for the decay of ^{85}Kr to ^{85}Rb, the electrons might be extracted from the conduction band while little effect is expected on the overall crystal structure of the vapor deposited metal.

3.3 Immobilization in Solid Sorbents

One option to decrease the cost of Kr storage is to pack the canisters with the sorbent used to remove Kr from the off-gas. It is also possible to put more Kr in a canister if a sorbent is present. For example, Mueller et al. (2006) showed that more Xe could be placed in cylinders packed with a MOF. In this section, we discuss the storage options for Kr. Since an option is to pack the canisters with the sorbent used to remove the Kr, we start with a discussion of the effects that the decay of ^{85}Kr might have on the sorbents. Although we discuss the effects on these sorbent materials, we assume that if they degrade significantly the Rb would come into contact with, and possibly compromise, the canister.

3.3.1 Effects ^{85}Kr Decay on the Structure and Chemistry of Solid Sorbents

When ^{85}Kr decays to ^{85}Rb, there are two primary processes that may affect the solid sorbent structure and its long-term viability as a Kr waste form. The first process is that of the decay itself – the potential damage to the solid that can result from either β^- emission or from the recoil of the Rb. The second is that of the charge distribution that must result from the production of Rb^+ from a neutral Kr atom and the release of a charged β^- particle.

In the case of radioactive decay the damage to ceramic materials, such as a zeolite, are unknown. The full radiation damage effects of the ß$^-$ on the solids have not been fully investigated (Marks et al. 2013). However, Marks et al. (2013) have worked out the energies associated with the recoiling decay daughter in $SrTiO_3$ as ^{90}Sr decays (β^- decay) through ^{90}Y to ^{90}Zr. The bond strengths (threshold displacement energies) in strontium titanate are sufficiently strong (typically 50 to 150 eV) to avoid radiation damage from the recoiling ^{90}Y and ^{90}Zr atoms. For the decay of ^{85}Kr, the average recoil energy for the ^{85}Rb daughter is 1.2 aJ[a] (7.3 eV) from the ß$^-$ and 0.5 aJ (3 eV) from the antineutrino (see Appendix A). We expect the bond strengths for zeolite materials to be similar to those in the titanate. This type of information regarding decay energetics allows us to conclude that the decay of ^{85}Kr (which is energetically of the same order of magnitude as ^{90}Sr decay) is unlikely to result in radiation damage in zeolites.

Secondly, the effects of the redistribution in charge must be considered. For $SrTiO_3$, the transmutation from Sr to Zr had some surprising structural stabilities that could not have been anticipated without the thorough examination of the possible phase transitions and the energetics associated with each. One comment at this point is that Marks et al. (2013) did not consider the kinetics of the phase transformations; it is unlikely that this information exists. The other transmutation that Marks et al. (2013) discussed was SrH_2 to ZrH_2 where much more information is available, both end members exist, and there is a clear phase transformation pathway (radioparagenesis) from SrH_2 ($PbCl_2$-type) to ZrH_2 (face-centered tetragonal). Thus, for the chemical transformation from Kr to Rb in both zeolites and MOFs, it is unclear what the overall effect is and how to calculate or experimentally determine it. Because Kr and the daughter Rb are isolated in cages within the structure, rather than being incorporated into the structure, the effects in these materials are probably much different than if the Kr were integral to the overall structure of the material. There is likely to be a structural effect of Kr transmuting to Rb based just on the size change [Kr (0.112 nm) and Rb (0.216 nm atomic; 0.161 nm ionic)] and how the charge change is compensated. A more thorough examination of the effect is outside the scope of this work, but should be considered for a future project.

Organic molecules, including MOFs, are more likely to be ionized from the recoiling Rb atom. The bond strength for a C-H bond is roughly 0.7 aJ (4.4 eV) with the C-C bond being slightly less. Ionization potentials are about twice that of the bond energies (Morrison and Boyd 1992). Also, the change in

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[a] aJ = atto Joule (1×10^{-18} J)

chemical state from a neutral atom to a charged ion may enhance the overall susceptibility to Kr transmutation.

3.3.2 Immobilization in MOFs

Several authors have suggested that Xe and Kr can be separated from each other on columns containing MOFs (Bae et al. 2013; Banerjee et al. 2015; Fernandez et al. 2012; Liu et al. 2014; Liu et al. 2012; Mueller et al. 2006b, a; Ryan et al. 2011; Ryan et al. 2013; Sikora et al. 2012; Soelberg et al. 2013; Thallapally et al. 2013a, b). At Pacific Northwest National Laboratory (PNNL), Xe and Kr in low concentrations have been separated from air (Fernandez et al. 2012; Liu et al. 2014; Liu et al. 2012; Soelberg et al. 2013; Strachan et al. 2010; Thallapally et al. 2013a, b). Packing a canister with a MOF can also allow the storage of more Kr for the same overall pressure (Mueller et al. 2006).

There are two types of Rb-bearing MOFs – one in which the Rb is used as a linker to produce the MOF structure and one in which the Rb is contained within the MOF cage, usually from ion exchange. Several MOF materials in which the Rb was part of the structure were located in the literature search (Gassensmith et al. 2011; Gassensmith et al. 2014; Kim et al. 2010; Morris et al. 2007; Xue et al. 2014; Yan et al. 2014; Zhang et al. 2013). Rubidium generated through decay of Kr would not be expected to become part of the MOF structure, but located in the cage originally occupied by the Kr, making ion exchange studies more relevant to the topic of this study. Most of the reported work is on the use of MOFs for CO_2 removal. In this case, the selectivity of the MOF for CO_2 decreases when Na^+ is replaced with Rb^+ (Zheng 2013). While this suggests that the build-up of decay Rb^+ might decrease the ability of the MOF to hold onto the Kr, Planchais and coworkers (2013) demonstrated that the larger cation blocks the passage from the MOF cage in the MOF MIL-141, thus suggesting that the presence of Rb with cationic and neutral radii both larger than that of Kr, may enhance the storage capabilities of the MOF selected for Kr storage.

Certain MOFs currently under examination for ^{85}Kr capture (Ghose 2015) have been demonstrated to hold 5-6 atoms of Kr per cage. As only 5% of the total Kr captured will be ^{85}Kr, it is likely that the solids may be able to adsorb the associated radiation damage and possible charge redistribution without significant effect upon Kr retention and long-term storage. This is a hypothesis that requires further investigation because MOFs are likely to be more damaged than zeolites by the chemical and radiative events.

3.3.3 Immobilization in Zeolites

Several authors have investigated the affinity of Ag-zeolites for Xe (Daniel et al. 2013; Deliere et al. 2014; Fraissard et al. 1991). Given their affinity for Kr, zeolites might also be used to remove both Xe and Kr from off-gas streams. Other authors have also investigated zeolites as a matrix to encapsulate Xe or Kr (Bazan et al. 2011; Heo et al. 1999; Jameson et al. 1997; Sears et al. 2005; Seoung et al. 2014; Simon et al. 2015; Vansant et al. 1984; Penzhorn et al 1982a). Therefore, we discuss the possible effects of the transmutation of Kr to Rb in a brief review of the relevant literature associated with Rb-bearing zeolites.

Much of the publicly available literature discussing Rb-zeolites is focused on thermodynamic stability and ion exchange properties (Fraissard et al. 1991; Keane 1994; Kosanovic et al. 2008; Shepelev et al. 1991). These properties indicate that the Rb is thermodynamically more stable in a different location in the zeolite matrix than the smaller alkali ions. Small alkali ions tend to migrate to the zeolite cage while larger cations like Rb^+ tend to favor the "super cage" or sodalite cage and, in some formulations, the "hexagonal prism." Diffusion in Rb-zeolites suggests that the thermodynamic affinity for the larger alkali cations is greater than that for smaller cations (Barrer et al. 1980; Keane 1994; Neugebauer, Crawford and

Houston 2003). The larger alkali cation increases the energy barrier for the opening of the cage window (Heo et al. 1991), thus increasing the retention of adsorbed gases such as Kr. This effect might be beneficial for Kr storage, but will be balanced to some degree by the fact that Rb may not be in the most thermodynamically favorable location as it replaces Kr.

Penzhorn and coworkers (1982a) determined that Ar, Kr, and Xe can be isolated in zeolite A, mordenites, and chabazites even when they are hydrothermally vitrified between 340°C and 650°C. These gases remained fixed even in the presence of liquid Rb. They measured activation energies for the diffusion of Kr and found the diffusion coefficients to be very small. Depending on the formulation, zeolites can hold 2 to 4 Kr atoms per cage unit; Daniel and coworkers (2013) found 2 Xe per formula unit for Ag-loaded zeolite.

The results summarized here seem to indicate that as the Rb concentration increases in the zeolite, the materials become more stable thermodynamically and the lattices become more rigid, thereby isolating the remaining Kr in the zeolite cage. The latter might be of less importance than other radiation effects since roughly 5% of the total Kr is ^{85}Kr. Hence, it is unlikely that any zeolite cage will contain more than one ^{85}Kr, and blocking the cage opening with the Rb daughter results in a minor benefit.

As indicated above, the bond strengths in zeolites are significantly stronger than the recoil energies from the β^- and antineutrino emission from a ^{85}Kr decay. This coupled with the low concentration of ^{85}Kr suggests that the recoil effects are likely to be minor to negligible. Aluminosilicate materials are generally resistant to β^- irradiation. Thus, the effects of pure ß$^-$ irradiation from the decay should not cause significant structural damage. Since the damage to the zeolite structure is likely to be minimal, the release of Kr over time would not be expected to increase over the leakage rate from a zeolite containing no radioactive Kr.

As indicated in Section 3.2, there are effects on the sorbent material resulting from the transmutation of one atom into another (Jiang et al. 2012; Jiang et al. 2014; Van Ginhoven et al. 2010, 2011). The charge can be compensated though transfer of electrons from the Fermi band or from a multivalent atom with available oxidation states, e.g., Fe(II) and Fe(III). In a zeolite, the matrix is generally constructed from Al and Si—these elements do not have readily available alternate oxidation states. The small amount of ^{85}Kr present in a zeolitic waste form, however, is small, ~ 0.3 mass%. Most solids can tolerate this level of defects without deleterious effects.

3.3.4 Ongoing Research Into the Effects of Kr Decay on Zeolites

In the late 1970s, an R&D effort to study ^{85}Kr encapsulation was performed at Idaho National Laboratory (INL). At INL, an off-gas treatment facility removed ^{85}Kr using cryogenic distillation and eventually encapsulated it within a zeolite matrix. Some of these samples were compacted through hot isostatic pressing. Upon completion of this study in the late 1970s, the samples were archived and stored. These aged samples consist of five small metal tubes containing a mixture of ^{85}Kr encapsulated in solid zeolite 5A material combined with a glass matrix. Considering when these materials were produced, the ^{85}Kr has undergone 3.7 half-lives, reducing the original ^{85}Kr inventory to 7.7% of its initial value. The samples were recently retrieved from archive storage and transferred from INL to ORNL. A test plan has been approved that will provide valuable information on long-term storage for ^{85}Kr. Various analytical techniques will be used to investigate sample characteristics. These techniques include, but are not limited to x-ray imaging, computerized tomography, scanning electron microscope/energy dispersive x-ray spectroscopy, transmission electron microscopy, x-ray diffraction, x-ray photoelectron spectroscopy, and x-ray absorption spectroscopy. Analysis of these aged samples is expected to provide information on issues, such as: (1) stability of the Kr loaded zeolite/glass matrix, (2) impact of the in-growth of Rb on the zeolite/glass matrix, (3) fraction of the Kr released from the waste matrix, (4) integrity of the capsule, i.e., any penetration/leakage, and (5) corrosion inside of the capsule at both the zeolite-glass/capsule interface and at locations away from the waste matrix. To date, analysis has been limited to non-destructive imaging, but preparations are being made for destructive analysis. A first step in the destructive analysis will be to examine the capsule and zeolite material with various microscopy techniques to determine if there has been any detectable corrosion or pitting from Rb decay product.

4. SUGGESTED FUTURE WORK

Multiple knowledge gaps have been identified throughout the course of this study. First, storage of gas in a canister has significant cost advantages over solid sorbent immobilization, and based on the results of this study it is likely to be a safe long-term storage mechanism. However, the work upon which this conclusion is based was not performed under an appropriate quality assurance program. It is recommended that the data from those studies either be qualified or elements of those studies repeated in work with an appropriate quality assurance program. The use of zeolites or MOFs to potentially place more ^{85}Kr-bearing gas in canisters, either at the same target pressure or significantly lower pressures, needs to be investigated and a cost-to-benefit analysis performed based on these results. This economic analysis is recommended for completion prior to embarking upon major experimental work related to immobilization in solid sorbents.

The effects of radiation and chemical transmutation in solid sorbents for this application are virtually unknown. To this end, the ongoing work at ORNL to examine the legacy ^{85}Kr storage samples should be continued and reported in publically available literature to begin addressing this knowledge gap. In addition, proposal of other studies as appropriate could be highly beneficial. Although unrelated to the needs of this program, two studies have been performed in which the effects of ^{85}Kr decay have been measured (Forman and Ghormley 1963; Micklitz 1968) and demonstrate that some property changes, such as electrical properties and phonon spectrum, can be measured in real time as ^{85}Kr decays. These studies need to be pursued irrespective of the decision to incorporate MOFs in pressurized canisters because they are viable candidates for the removal of Kr from process off-gas streams, and, hence, their resistance to radiation induced property changes is needed to project their useful lifetime as sorbents.

Finally, there appear to have been significant advances in theoretically constructing MOF materials. This is done with known MOF linkers and moieties that self-assemble. An extensive review article on this topic was written by Yang et al. (2013). In this article, they discuss the work of van Heest et al. (2012) in which they considered over 3,000 MOF materials for which experimental Xe and Kr sorption data existed and theoretical studies (Grand Canonical Monte Carlo) had been performed. In this study, they identified 13 out of 19 MOF materials that had higher preference for Kr over Xe. These studies and methodologies should be investigated for MOF selection, but also to determine the effects of replacing Kr with Rb. So, for example, the diffusion of Kr in a MOF containing Kr could be calculated, and then a percentage of the Kr atoms could be replaced with Rb to see how the calculated diffusion coefficient changed as the amount of Rb increased. It would appear that these types of studies would be critical to the understanding of the potential response of MOF materials with storage time.

Grand Canonical Monte Carlo techniques have also been successful in modeling zeolite materials as well. Recent work has combined the theoretical and the experimental to investigate the properties and mechanism in porous silica and zeolites (Gurdal and Keskin 2013; Simon et al. 2015; Sears et al. 2005; Builes et al. 2015; Chang et al. 2015; Zeng et al. 2015). These methods need to be investigated for the replacement of Kr with Rb in zeolites currently being considered for Kr separation and storage. It should be noted that some of the MOFs that are the subject of theoretical Xe and Kr loading studies have been checked experimentally at PNNL and found to have lower loadings than predicted. Most likely the lower experimental loadings are caused by the much lower partial pressures of Xe (400 ppmv) and Kr (40 ppmv) in air that are typical for a reprocessing facility and used in experimental studies at PNNL.

5. CONCLUSIONS

Reprocessing of UNF that has been out of the reactor for less than about 50 y requires the removal of ^{85}Kr from the process off-gas streams. This is needed despite the relatively small amount of that isotope in the combined Xe and Kr inventory (Table 1). The decay of ^{85}Kr to ^{85}Rb presents challenges to the materials that will potentially be used to remove and store the Kr recovered from the off-gas. To address some of these problems, a thorough literature survey was completed, and the results of that analysis are summarized in this document.

One storage option is high-pressure gas in canisters. We found that it is unlikely that ^{85}Kr storage in high-pressure containers will be compromised by corrosion from the decay product Rb, especially if the Kr recovery operations result in a gas composition with very low oxygen content. Similarly, the choice of immobilization through ion implantation is also unlikely to be significantly affected by ^{85}Kr decay. However, this conclusion is based on past studies that were not performed to the quality assurance rigor needed to qualify a waste form (method) or the processes for a UNF reprocessing facility. Therefore, either the past data must undergo a review and acceptance, or the main elements of those studies repeated in a study performed to the appropriate quality assurance level.

Study of the immobilization and storage of ^{85}Kr on solid sorbents has been severely limited, and almost no literature was available on this topic or on related systems. The effects of ^{85}Kr decay in solid sorbents is likely both an interesting and challenging scientific topic, as both radiation damage and chemical transmutation must be considered when evaluating long-term stability. We conclude, based on limited data, that zeolites are likely to experience less radiation damage than MOFs from the decay events and that the presence of Rb may be thermodynamically beneficial for long-term retention of Kr within the zeolite matrix. These effects are somewhat ameliorated by the very small amount of ^{85}Kr present. In most materials, this leads to small amounts of Rb in the solid as the Kr decays. It is recommended that the benefits of solid sorbent immobilization for ^{85}Kr storage be analyzed and that careful consideration be given to answering the myriad of unknowns surrounding the effects of ^{85}Kr decay (both chemical and radiative) on the solids being considered. Again, irrespective of the decision to incorporate MOFs or zeolites in storage canisters, the resistance of these materials to radiation induced property changes is important to their use as sorbents to remove Kr from the off-gas streams.

Further experimental work to verify the viability of cylinder and ion implantation storage methods, and to better characterize the effects of ^{85}Kr decay on solid sorbents, will provide assurance that ^{85}Kr can be safely stored for extended periods of time as is required by United States regulation. The work already underway at ORNL to analyze legacy Kr waste forms will be highly beneficial to better understanding the effect of ^{85}Kr decay on storage methods that allow for contact between metals and Rb. Work has also been planned at INL that will investigate the resiliency of MOFs when exposed to radiation. These two current research efforts should be leveraged to answer outstanding questions regarding the impact of ^{85}Kr decay on storage methods, and future work should be planned based on the results of these studies.

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APPENDIX A

Calculation of ^{85}Rb Recoil Energies

A-1. Calculation of Recoil Energy

The equation given in Mark et al. (2013) is

$$E^{max} = \frac{Q(Q + 2mc^2)}{2Mc^2}$$

Where Q is the energy of the ß$^-$ emitted (MeV), m is the mass of the electron (9.109×10^{-31} kg), M is the mass of the atom of interest (kg), c is the speed of light (3×10^8 m/s). For ^{85}Kr, Q is 0.687 MeV and M is 1.41×10^{-25} kg. The units on mc^2 are joules and the conversion between J and MeV is 6.24×10^{12} MeV/J. Substituting these values into the equation yields 7.3×10^{-6} MeV or 7.3 eV (1.2 aJ).

Equally energetic and contributing to the recoil is the neutrino (antineutrino) that is emitted during ß$^-$ decay. Mark et al. (2013) give the following equation for calculation of the recoil energy from the emitted neutrino.

$$E^{v} = \frac{Q^2}{2Mc^2}$$

Thus, for ^{85}Kr, the recoil energy for the neutrino is 3 eV (0.5 aJ).