Storage Possibilities for Radioactive Krypton (^{85}Kr)

A. THIJS and E. F. VANSANT
Department of Chemistry, University of Antwerp (U.I.A.), Universiteitsplein 1, 2610 Wilrijk, Belgium

Abstract. A review of the different storage possibilities for radioactive krypton (^{85}Kr) is given. Various strategies can be applied to store ^{85}Kr safely over many decades: storage in pressure containers and encapsulation in various solid matrices.

Krypton-85 is a radioactive gas which is produced in nuclear reactors and liberated mainly during the processing of spent fuel elements. Until now, this gas has been discharged to the atmosphere after dilution, but for the large reprocessing plants of the future, retention of the gas is envisaged.

Krypton-85 has a half-life of 10.7 years and its decay scheme possesses two beta lines and one gamma line.
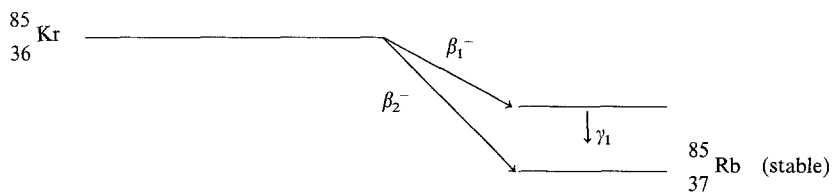
Radiation	Intensity	Mean Energy (MeV)
β_1^-	0.0043	0.0475
β_2^-	0.9957	0.2512
γ_1	0.0043	0.514

The two possible ways in which the human body can be affected by krypton-85 are external irradiation and inhalation. When inhaled, the ^{85}Kr basically irradiates the respiratory tract. Practically all the inhaled krypton is immediately exhaled. The impact of discharges of ^{85}Kr is therefore reduced in essence to the external irradiation due to the negatively charged beta particles and the gamma photon emitted when the ^{85}Kr decays.

The negative beta particles lead to the irradiation of the skin, while the gamma photon irradiates all the tissues of the organism. The aim of this paper is to cover all the procedures which can lead to the safe storage of ^{85}Kr over many decades.

Different methods to store radioactive ^{85}Kr have been studied in several laboratories.

1. Storage in Pressure Containers

The most immediate solution is to store ^{85}Kr in pressure containers using the techniques known for ordinary compressed gases.

The nature of ^{85}Kr poses special problems, such as: storage time ($\pm$ 100 years), safety precautions (irradiation), resistance against corrosion (chemical aggressivity of rubidium) and temperature rise due to ^{85}Kr decay.

Various strategies can be applied to the storage of ^{85}Kr in cylinders:

1.1. STORAGE IN LOW PRESSURE CYLINDERS

The storage of ^{85}Kr at ambient temperature and pressure in steel cylinders has been studied in the United States [1]. The low-pressure storage has the advantage of not causing unacceptable gas releases. The disadvantage is the great volume of storage vessels due to the low pressure in the containers.

1.2. STORAGE IN PRESSURE CYLINDERS

In contrast with low-pressure storage, this technique has the advantage that smaller volumes are necessary. High pressure storage has the risk of serious leakage and for long-term storage of ^{85}Kr the formation of Rb raises a corrosion problem. High purity gas is needed to prevent formation of corrosive and oxidizing agents by radiolysis.

1.3. STORAGE IN ADSORBENT-PACKED CONTAINERS

The gas can be stored in pressure containers packed with a suitable adsorbent such as activated carbon, zeolites, etc.

For the same quantity of Kr stored and for the same number of cylinders employed, lower pressures and hence more safety are possible.

A variety of adsorbent packing media have been examined such as zeolites [2,3], types of glass, crystalline and amorphous metals [4] and activated carbon [5]. The behaviour of the adsorbent at high pressures and temperatures and the thermal conductivity of the adsorbent bed is crucial for the storing of Kr in cylinders after its adsorption on a suitable sorbent.

In contrast to storage in pressure cylinders, this technique has the advantage that the filling of the cylinders is easier and safer.

Corrosion problems, in particular the effects of Rb, are reduced by storage in adsorbent-packed containers. Assuming an adsorbent bed of 520 g on which are adsorbed 110 g of Kr enriched with 5% ^{85}Kr, the quantity of Rb is of the order of 10.6 mg per g adsorbent (following the decay of ^{85}Kr). This amount of Rb is very small when compared with the quantity of Kr and with the ability of the adsorbent to sorb this gas.

Possible interference by the Rb with the actual adsorption of Kr is reduced when we consider that the increase in Rb over time is matched by a drop in the mean temperature which favours adsorption.

2. Encapsulation in Solid Matrices

Increased safety can be achieved by immobilizing the gas in a solid matrix from which the gas can be released by a simple physical process such as thermal treatment or treatment with water.

Different methods for encapsulating gases in a solid phase are ion implantation/sputtering, low temperature metal vapor deposition and encapsulation in zeolites.

2.1. ENCAPSULATION IN METALS BY ION EXCHANGE

The krypton ions are incorporated into a metal matrix and covered with a layer of metal of the same nature as the matrix.

(i) *Pacific Northwest Laboratory Process (USA)*

In this process a thermionic plasma is used in which the electrons emitted by a heated filament and accelerated in an electric field collide with the krypton atoms. The krypton ions formed are then accelerated towards a negative electrode and the impact of these ions on the target electrode wrenches free atoms of metal. Simultaneously the krypton ions are directed towards a second negative electrode on which they become implanted. The metal atoms dislodged from the target then cover the receiving electrode (Figure 1).
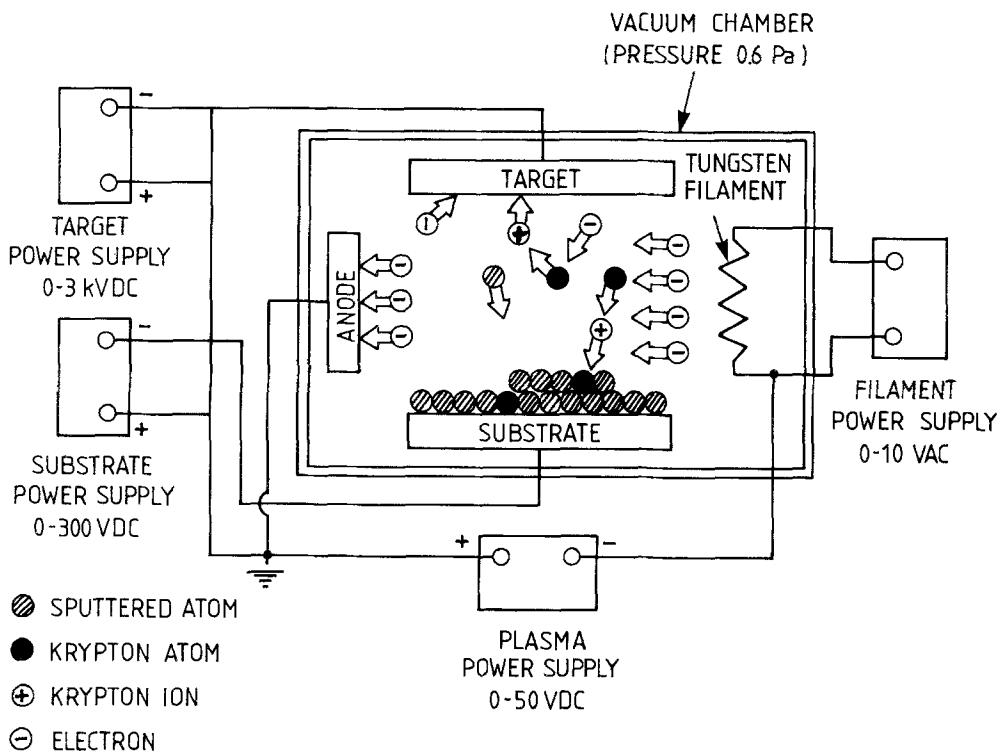

Fig. 1. Diagram of Pacific Northwest Laboratory Process.

Cylindrical electrodes were used because they can be covered with a protective layer of metal when the deposit is sufficient (Figure 3a). In this way the electrode itself constitutes the storage vessel and also acts as a second containment barrier. The krypton gas can be liberated again by heating the metal deposit. Increasing the temperature causes diffusion phenomena which favour losses of krypton. Phase change in the substrate generally causes krypton loss at the crystallization temperature of amorphous solids.

The loading capacity obtained in crystalline metals is of the order of 16–20 liter STP per kg of metal. On films of amorphous materials such as $[Gd_{0.11}Co_{0.73}Mo_{0.16}]$ and $[Fe,Y]$ loadings of 127 liter STP per kg of metal were obtained.

(ii) *AERE Harwell Process (UK)*

In this process ions are created in a krypton atmosphere at low pressure (10 Pa) by an electrical discharge between two concentric electrodes.

These ions are implanted on the outer electrode, which is at a negative potential. The polarity is then reversed so that the krypton ions, colliding violently with the inner electrode, dislodge metal atoms which cover the outer electrode. In this way the krypton is deposited on the inside of the outer electrode (Figure 2,3b).

The layers, deposited at ambient temperature, are stable up to about 600°C when using copper as the metal matrix. At 600°C the loss of krypton starts and continues up to about 700°C. When the layers are deposited at a higher temperature, the release of krypton starts
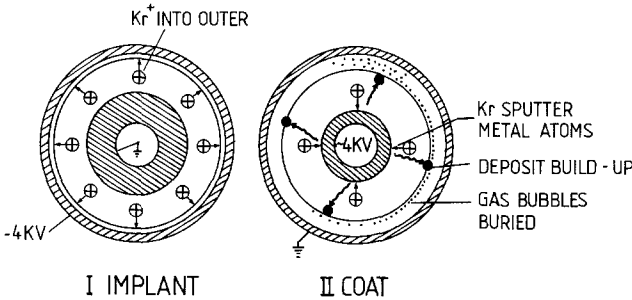
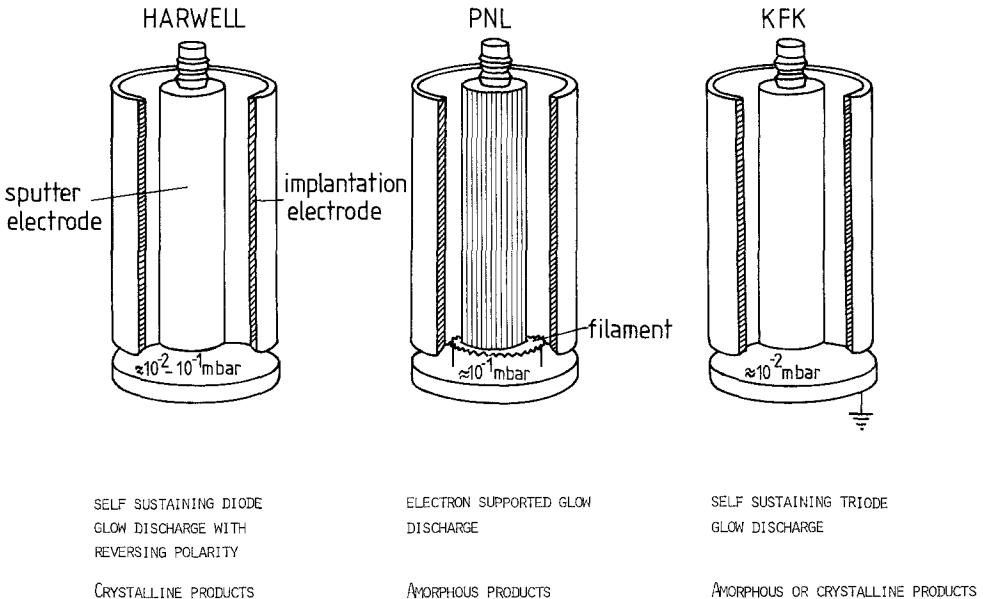

Fig. 2.   Diagram of the AERE Harwell process.

Fig. 3.   The different processes for implanting krypton in metal matrices.

at a higher temperature. Molybdenum and tantalum liberate the implanted krypton at temperatures of 950°C (Mo) and 1200°C (Ta).

The loading capacity, obtained in a copper matrix, is of the order of 20 liter STP per kg of metal.

With an iron matrix a deposit containing up to 25 liter STP per kg could be obtained. The release starts at about 520°C for iron. With aluminium less energy is required for a deposit of 25 liter Kr per kg. The release of krypton starts at about 300°C.

(iii) German Karlsruhe Process

This process tries to combine the two processes mentioned above by using the principle of a self-sustaining discharge in the krypton achieved by a system of 3 electrodes. Two of the electrodes are cylindrical and concentric. The inner electrode (diameter 4 cm) with a negative potential of 4 kV serves to produce the atoms of metal. The outer electrode with a negative voltage of about 1 kV receives the metal-krypton deposit. The function of the third, zero-potential electrode is to collect the electrons (Figure 3c).

For implantation of krypton in a crystalline metal, the inner electrode is made of a homogeneous metal. Copper and titanium are used to form krypton deposits. For implantation of krypton in an amorphous matrix, an electrode containing inclusions of a second metal are used. Iron–zirconium and copper–zirconium electrodes were tested.

The loading capacity is about 32 liter Kr STP per kg deposit. At 400°C, the krypton release rates are 100% for the Cu matrix, 0.1% for the Ti matrix and 0.01% for the amorphous matrix.

2.2. ENCAPSULATION IN ZEOLITES

The phenomenon of trapping gas molecules in molecular sieve zeolites is well known [6].

Zeolites are highly porous crystalline aluminosilicates having channel systems of well-defined geometry and characteristic critical apertures (2–10 Å in diameter). The void volume of such systems amounts to 20–50% of the total crystalline volume. The intracrystalline cavities to which access is gained through narrow openings may act as reservoirs in which gases can be trapped.

The process of trapping (or encapsulation) relates to cases in which the critical dimension of the gas molecule is slightly larger than the effective pore opening of the zeolite.

Earlier work in this field shows that various gases, in particular inert gases, can be forced into the pores of zeolites by applying elevated temperatures and pressures. Quenching to ambient temperature under pressure results in trapping of the gas inside the zeolitic cages. Release of the encapsulated molecules (decapsulation) can be achieved by heating the loaded zeolite or by treatment with water which can displace the sorbed molecules because of its stronger interaction.

It is also possible to modify the structure of the cavities (after trapping the molecules) so that the adsorbed gas molecules are blocked in the zeolite structure. The narrowing of the apertures can be obtained by replacing the cations of zeolites (usually Na or K) by other cations of greater size, or by chemisorption of additional atoms or atom groups on the zeolitic structure.

2.2.1. High-Temperature/High-Pressure Encapsulation of Gases in Zeolites

Gas molecules whose critical dimension (expressed as the kinetic diameter σ) is larger than the effective pore opening of the zeolite, are forced into the pores at high pressures and

elevated temperatures. When the temperature is lowered and the pressure thereafter released, the gas molecules may be imprisoned until the crystals are again heated.

This high-temperature, high-pressure encapsulation of gases in zeolites was first reported by Sesny and Shaffer [7], who succeeded in efficiently trapping large amounts of Ar, CH_4 and Kr in K-A type zeolites.

Barrer and Vaughan studied high-temperature, high-pressure sorptiön of He, Ne, Ar and Kr in tridymite and cristobalite [8], heulandite and stilbite [9] and basic sodalite and cancrinite [10]. They concluded that the method is applicable for small non-polar molecules in a variety of zeolites, both synthetic and natural, as well as some non-zeolitic mineral materials [11].

Later, Chan and Anderson [12] reported the encapsulation of Ar, N_2 and CO_2 in 3A (i.e. K, Na-A) zeolite.

Fraenkel [13, 14] studied hydrogen encapsulation in zeolites. Most efficient in hydrogen trapping were the Linde-A type zeolytes, especially those containing combinations of Cs^+ and Na^+ as exchangeable cations. Itabashi and Takaishi [15] studied the high-temperature/high-pressure encapsulation of Kr in (K, M^{II})-A zeolites with $M^{II} = Ca^{2+}, Co^{2+}, Mn^{2+}$ or Zn^{2+}.

The high-pressure/high-temperature technique for encapsulating ^{85}Kr in zeolites has been studied in the United States. Basic sodalite and substituted forms of A-zeolites (K, Rb, Cs) are usable for trapping Kr. Loading capacities of 40 to 50 liter Kr STP per kg zeolite were obtained. Chabazite and erionite seemed less interesting for trapping Kr. Under the same conditions of pressure and temperature no more than 1 liter Kr per kg zeolite could be incorporated. This small loading capacity is probably due to the insufficient opening up of their pores. Concerning the thermal stability, there was no loss of Kr observed below 150°C.

The zeolitic Kr encapsulates were tested for their radiation stability by exposing loaded zeolites to gamma radiation in doses comparable to those received throughout the storage period. No negative effect has been observed during the radiation stability tests.

The formation of rubidium has no unfavourable consequences. It might even help to close the pores and thereby contribute to cut down the losses of krypton.

2.2.2. Chemifixation of Noble Gases in Zeolites

Penzhorn et al. [16] studied the chemifixation of noble gases (Xe, Kr and Ar) in type A zeolites (3A, 4A and 5A) as well as in other zeolites such as mordenite (zeolon 900 Na) or chabazite (zeolon 500).

This immobilization of gases in zeolites which have larger pore openings than the van der Waals diameter of the gases, is obtained when the fixation temperature is raised to 500–650°C and the samples are activated until a certain amount of water is left in the zeolite framework. The degree of loading seemed to be critically dependent upon the initial water content.

The fixation occurs via pore closure by a water catalyzed bond opening and rearrangement of Al and Si ions. At high temperatures and pressures both Si and Al ions as well as cations can move in the crystal structure. During cation movement the bridge oxygens are subjected to strain and can be attacked by H^+ ions preceding the OH^- ions, whereby OH groups are formed which will occupy the corner of a tetrahedron (SiO_3OH). The Si and Al ions from the neighbouring incomplete tetrahedrons will tend to escape and change places in such a way that a new structure will be formed. Incomplete tetrahedrons can also attract an OH^- ion and form another SiO_3OH group. Interaction of neighbouring SiO_3OH groups will yield water and regenerate an oxygen bridge.

This chemifixation by hydrothermal treatment involves a permanent transformation of the

matrix as opposed to the high-temperature/high-pressure encapsulation, where the crystal framework remains unaltered and several sorption/desorption cycles are possible.

The vitrified zeolite containing trapped noble gas is quite resistant towards water, in contrast to observations made by Sesny and Shaffer with type A zeolites containing encapsulated gas, which release the conditioned gas when exposed to water.

Ca-substituted type 5A zeolites can encapsulate 20–30 liter Kr at STP per kg at 520°C and at a pressure of 300–500 atm. At 2000 atm, it is almost possible to attain a loading of 80 liter STP per kg. The krypton encapsulated in type 5A zeolites starts to be released at temperatures above 650°C. From 720°C modification of the crystalline structure occurs and practically all the encapsulated gas escapes. The release of krypton from type 5A zeolites is smaller by several orders of magnitude than that from type 3A zeolites.

The Kr encapsulates performed by the method of Penzhorn were found to be stable towards gamma radiation up to 300 MRad.

2.2.3. *Encapsulation of Gases in H-Zeolites by Chemisorption of Additional Atom Groups in the Zeolite*

Gases can also be encapsulated in zeolites by an adsorption process followed by a structural modification procedure resulting in a narrowing of the silicate pore system. This immobilization technique for trapping gases in H-zeolites was studied by Vansant et al. [17,18]. The advantage of this immobilization method is its ability to work at 'normal' temperatures (essentially room temperature) and pressures ($p < 101.325$ kPa).

It was investigated whether, by implantation of additional framework groups in the zeolitic channels, gas molecules with a kinetic diameter larger than the reduced pore size of the zeolites could be excluded. Such an implantation of additional atom groups was performed by chemisorption of reactants such as silane (SiH_4), diborane (B_2H_6), dichlorodimethylsilane ($H_2Si(CH_3)_2$), trichloromethylsilane (Cl_3SiCH_3), boron-nitrogen compounds, etc. on structural hydroxyl groups of an H-zeolite.

Similarly, the encapsulation of gases in a zeolite could be realized by modifying the zeolite. Depending on the difference between the diameters of the zeolite windows and the gas molecules and on the nature of the modifying reactant, three essentially different encapsulation procedures were developed: the CAO-, ACO- and HP-procedures.

– The CAO (chemisorption – adsorption – oxidation) procedure can be applied in cases where there are large differences between the gas molecules and the zeolitic pores. First, the pore size is reduced by chemisorption of a suitable reactant. The gas to be occluded is then adsorbed on the modified zeolite, whereafter the loaded zeolite is oxidized resulting in a closure of the channel windows.

– The ACO (adsorption – chemisorption – oxidation) method can be applied for small differences in diameters of gas molecules and pore sizes. The gas to be encapsulated is first adsorbed in the unmodified H-zeolite. The modifier is then chemisorbed on the zeolite while the equilibration pressure of the occluded gas is maintained. During the chemisorption the gas is already encapsulated. Finally, a further stabilization of the gas-substrate system is realized by oxidation of the chemisorbed groups.

– The HP (hydration–polymerization) procedure can be applied when the modifier molecules are too large to reach the internal hydroxyl groups in the zeolite. The gas is first adsorbed on the H-zeolite, whereafter the loaded zeolite is partially hydrated. Finally, a modifier such as $Cl_2Si(CH_3)_2$ or Cl_3SiCH_3 reacts with the hydration water, forming polymers on the

external surface. This polymerization coats the zeolite and encloses the adsorbed gas molecules.

Using this encapsulation method, krypton could be immobilized in H-mordenites under 'normal' conditions of pressure and temperature. For Kr trapping, a loading capacity of 50 liter STP per kg H-mordenite was obtained. Thermal stability up to $500\,^{\circ}C$ has been achieved. Krypton encapsulates were tested for their stability against water, acids, mechanical grinding and γ-irradiation. No significant influence of such treatments on the stability was observed.

Acknowledgement

References

1. C. L. Bendixsen and J. A. Buckam: Allied Chemical Corporation, Idaho Falls (1974).
2. R. A. Brown *et al.*: 14th *ERDA Air Cleaning Conference* (1976).
3. R. M. Barrer and D. E. N. Vaughan: *Surface Science* **14**, 77–92, (1969).
4. R. E. Blanco and W. E. Clark: *ORNL*, 4473 (1970).
5. P. N. Henrion *et al.*: EUR 64/19, Report.
6. G. A. Cook: *Argon, Helium and the Rare Gases*, Interscience, N.Y. (1961), p. 228.
7. W. J. Sesny and L. H. Shaffer: U.S. Patent No 3316691 (1967).
8. R. M. Barrer and D. E. W. Vaughan: *Trans. Faraday Soc.* **63**, 2275 (1967).
9. R. M. Barrer and D. E. W. Vaughan: *Surface Sci.* **14**, 77 (1969).
10. R. M. Barrer and D. E. W. Vaughan: *J. Phys. Chem. Solids* **32**, 731 (1971).
11. R. M. Barrer and D. E. W. Vaughan: *Trans. Faraday Soc.* **67**, 2129 (1971).
12. Y.-C. Chan and R. B. Anderson: *J. Catal.* **50**, 319 (1977).
13. D. Fraenkel and J. Shabtai: *J. Am. Chem. Soc.* **99**, 7074 (1977).
14. D. Fraenkel, R. Lazar, and J. Shabtai: *Alternative Energy Sources* (Hemisphere, Washington, D.C., 1978), vol. 8 pp. 3771–3802.
15. K. Itabashi and T. Takaishi: 5th *Int. Conf. on Zeolites*, June 2–6, Naples, Italy (1980).
16. R.-D. Penzhorn and P. Schuster: European Patent No. 0029875.
17. E. F. Vansant, P. De Bièvre, and G. Peeters: U.S. Patent No. 4414005 (1983).
18. A. Thijs, G. Peeters, E. F. Vansant, I. Verhaert, and P. De Bièvre: *J. Chem. Soc., Faraday Trans.*, 1 **79**, 2835 (1983).