ENCAPSULATION OF KRYPTON-85 IN ZEOLITE MOLECULAR SIEVE WITH A HOT ISOSTATIC PRESS

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ABSTRACT

This paper describes pilot and full-scale experiments which demonstrated the feasibility of immobilizing Kr-85 in a zeolite 5A/glass mixture and compacting it before disposal. The full volume of a one-liter hot isostatic press (HIP) was used to trap argon in zeolite 5A. For radioactive krypton the HIP was modified to isolate the Kr-85 in the work zone. Details of the HIP modifications, experimental procedure, and sample analysis are reported.

INTRODUCTION

EPA regulations now require that no more than about 15% of the krypton-85 produced from fuel placed in a commercial nuclear reactor after January 1, 1983 escape to the environment during the fuel cycle[1]. This would require a method of immobilizing most of the krypton released in reprocessing until it had decayed to low levels.

Early work at the Idaho Chemical Processing Plant (ICPP)[2,3] and at Kernforschungszentrum Karlsruhe (KFK)[4,5] showed that krypton may be trapped in a number of different molecular sieve materials by forcing it in at high temperature and pressure. Diffusion out of the pores is very slow at ambient temperatures; however the krypton may be sealed in by holding the high temperature until the zeolite structure breaks down into an amorphous phase, and the large interatomic spaces coalesce to microbubbles, in which the krypton and any other gases remain trapped.

In the particular procedure employed at ICPP zeolite 5A (hereafter referred to as zeolite)[6,7], which has been dried at 400°C for several days to reduce the water content to about 1%, is loaded into the HIP at ambient temperature, and the HIP is heated to 700°C for two hours. However zeolite with 3% water may be sintered at 520°C [4,5].

After cooling, the untrapped krypton is withdrawn. Typically 50 STPcc gas/g zeolite remains entrapped. Leakage measurements extrapolated to long times, show that less than 0.03% of the trapped krypton-85 inventory would leak out at a storage temperature of 300°C, the rest having decayed in the meantime[2,3].

This paper describes a demonstration of this process on a larger scale and with krypton-85.

EQUIPMENT

An "Isohipper" was obtained with one liter working volume, from Autoclave Engineers, Erie, PA. As in the typical HIP construction the outer, pressure-bearing wall was water cooled and insulated from the work zone and furnace as shown in Fig. 1.

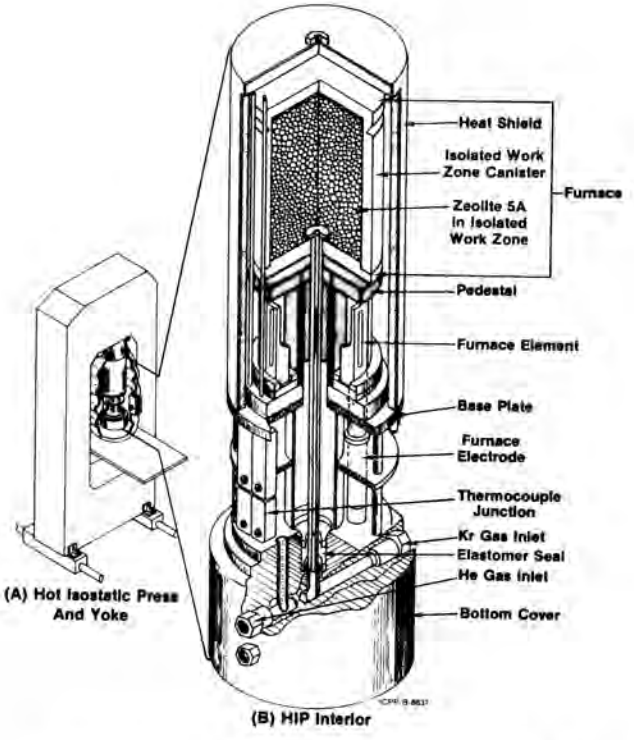
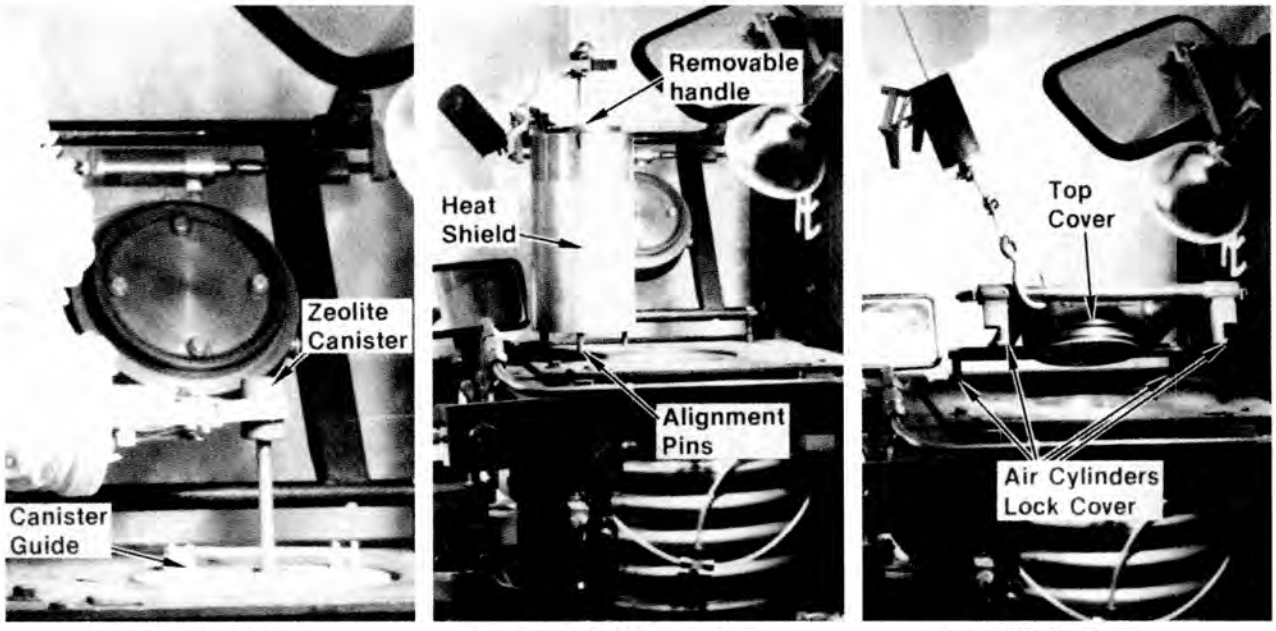


Fig. 1. Hot Isostatic Press (HIP) Assembly for Two-gas Operation.

The HIP was used as received for a number of experiments to encapsulate argon in up to one liter of zeolite in various forms. Larger amounts of zeolite (16 liters at a time) were loaded with agron in a HIP by IMT Co., Boston, MA. Then the HIP was modified to confine krypton to the working volume by a thin-walled inner canister containing the zeolite-glass powder mixture, and connected to the krypton source. Excess pressure outside the canister held it in place. By not filling the entire HIP volume with krypton, a lower radioactive inventory was maintained and also the HIP walls were protected from the rubidium decay product. Two thermocouple junctions at different locations between the inner canister and the heat shield measured sample temperature.

The HIP was modified for remote disassembly and reassembly, so that the inner canister could be mounted and removed with manipulators, see Fig. 2. For assembly, the inner canister was inserted, gas inlet tube first, through a guide into the base. Then the guide was removed, the heat shield placed, the lid clamped shut, and the yoke moved around the assembly.

Because of the small quantity of krypton-85 available, it was decided to distill the gas from our source into a heavy-walled intermediate vessel, the "cryopump" in Figs. 3 and 4, then heat the cryopump to vaporize and drive about half the krypton into the sample canister.



(a) **Can Loaded** (b) **Heat-Shield Loaded** (c) **HIP Sealed**

Fig. 2. Stages in remote assembly of sample can and HIP for two-gas operation following (c) the yoke is moved over the lid.

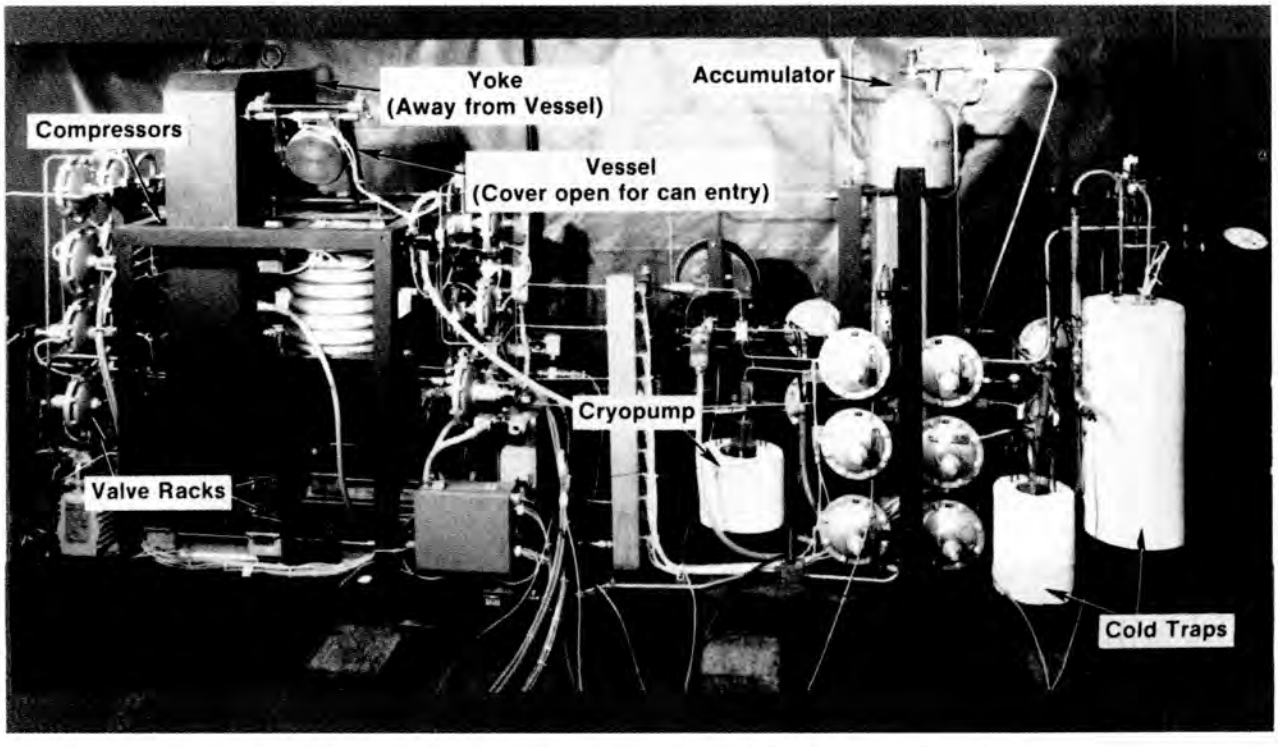


Fig. 3. Complete HIP and cryopumping apparatus inside the hot cell #1 cold trap on left. Source tank just beyond right edge. Remote controls outside of cell.

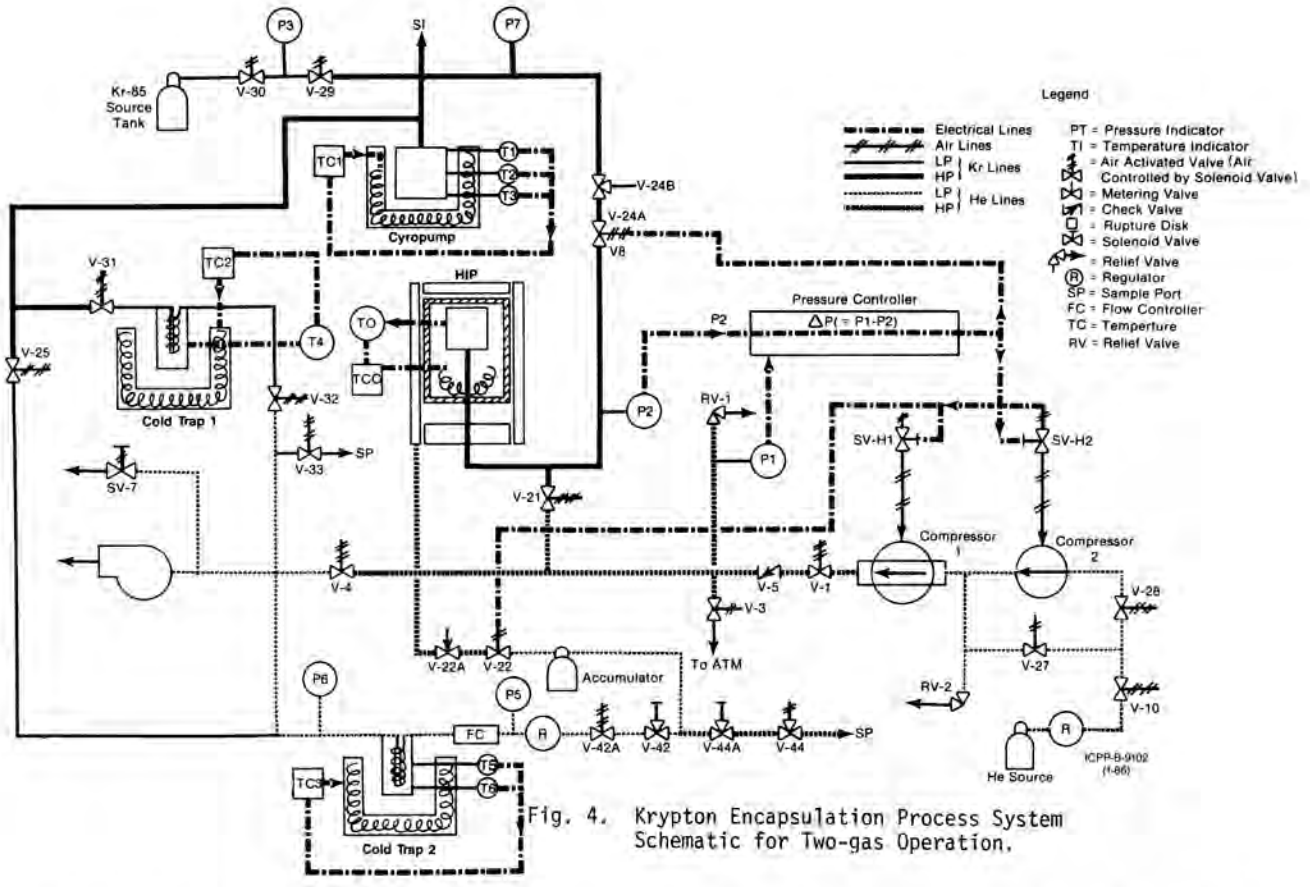


Fig. 4. Krypton Encapsulation Process System Schematic for Two-gas Operation.

The cryopump was a LECO 27cc vessel from Tempress Co., State College, PA. Thermal insulation was placed around the inlet to allow it to be warmed by the incoming gas, and thus to prevent plugging, especially by xenon.

A second, thin-walled vessel of 200cc "cold trap #1", filled with zeolite beads, withdrew the last trace of untrapped krypton from the sample at the end of the experiment. However it was also used as a first stage during cryopumping and for removing helium contamination from the krypton gas. The zeolite filling was used because of the much lower equilibrium vapor pressure of krypton absorbed on zeolite than of bulk krypton.

These vessels are visible in Fig. 3, along with a larger cold trap #2, designed to rapidly remove large amounts of helium. The piping manifold (Fig. 4) allowed the helium and krypton sections to be connected for vacuum testing (through V-21) and provided for isolation of appropriate parts of the cryopump, cold traps #1 and 2, the source tank, the inner canister, and the external gas volume during the rest of the experiment. A throttle valve, V-24, between the cryopump and the inner canister volume was used to regulate the flow of krypton to the sample at a slow enough rate that the external helium gas pressure could be kept higher than the krypton pressure by the helium pump. Another valve in series actuated automatically to release the krypton back to the source in case the excess external helium pressure dropped below the preset value, usually about 10 atm. This was to prevent unseating of the can by higher internal pressure and consequent mixing of the two gases. The heaters for the HIP, and for the cryopump and for trap #1 were supplied with a manually regulated current.

A saw was set up for remote sample cutting, with continuous washing and filtering of the wash water. The HIP, source tank, cryopump vessels, and saw were kept in a hot cell. All valves were operated remotely except on the high pressure source tank, which was left open during this set of experiments. The flexible liquid nitrogen feed line to the two cryopump vessels was moved by the manipulators.

MATERIALS

The gas supply was 17.7 STP liters of the krypton fraction from the offgas of fuel reprocessing at the ICPP, transferred to a 6.6 liter high pressure tank. The initial 2.92 atm. had decreased to 1.74 atm. by the end of the experiments. The gas was analyzed at 61.5% Kr, 18.7% Xe, 12.2% N_2, 2.9% O_2, 3.7% CO_2, 0.2% Ar, and 0.7% He by volume, and was estimated to initially contain 930 Ci of krypton-85.

Zeolite 5A has the formula $(Ca_{4.8}Na_{2.4})(AlO_2)_{12}$-$(SiO_2)_{12}(H_2O)_n$. The framework contains cages of two sizes, of which the krypton is initially absorbed in the larger "alpha" cages, 1.14 nm diameter. The zeolite was obtained as 2mm polycrystalline beads from W. R. Grace Co.

The powdered glass frit was in wt%: SiO_2 58, B_2O_3 19, Na_2O 16, CuO 2, and Li_2O 5. We powdered some of the zeolite, and pressed 50cc pellets in the HIP, using rubber forms. For some pellets we mixed the zeolite with the glass frit or with finely powdered aluminum metal. This sinters during encapsulation to help immobilize the zeolite.

EXPERIMENTAL PROCEDURE

The zeolite was loaded into the open canisters with stem already attached, the lid was welded on, and the can was vacuum tested. After insertion of the can and reassembly of the HIP (see Fig. 2), both were tested for leak tightness with respect to each other and the outside.

The sequence of events during encapsulation is illustrated in Fig. 5. The HIP exterior was prefilled with about 50 atm. of helium, and helium pressurization was continued as soon as krypton was available from the cryopump. On completion of krypton transfer the inner sample canister was valved off and the HIP was heated during continued addition of helium to counterbalance the relatively greater pressure increase of the krypton with temperature. After 1-1/2 hours at 700°C, the sample was cooled to about 600°C, and the untrapped krypton was exhaustively removed by cryopumping, whereupon the external pressure compacted the inner canister and the sample. The helium was withdrawn, the HIP cooled to room temperature, and the inner sample canister removed remotely.

Altogether 5 samples of zeolite beads or beads and glass frit mixture were loaded with the gas mixture containing radioactive krypton.

The large amounts of zeolite to be loaded with argon were placed into an open can, which was placed manually into the HIP. Since these were single-gas runs, no pressure balancing was needed, and rapid heating to the sintering temperature was possible. After cooling, the cans were sealed, then compacted in the HIP.

RESULTS

Encapsulation conditions and gas loadings achieved are presented in Table I for all of the small samples loaded with radioactive krypton and a representative group of the larger samples loaded with argon. The two radioactive samples analyzed show good gas loadings, considering the low pressures employed. Two of the other three samples, which were not analyzed should contain even higher loadings considering the higher encapsulation pressures. The leakage rate of these five samples has not been determined.

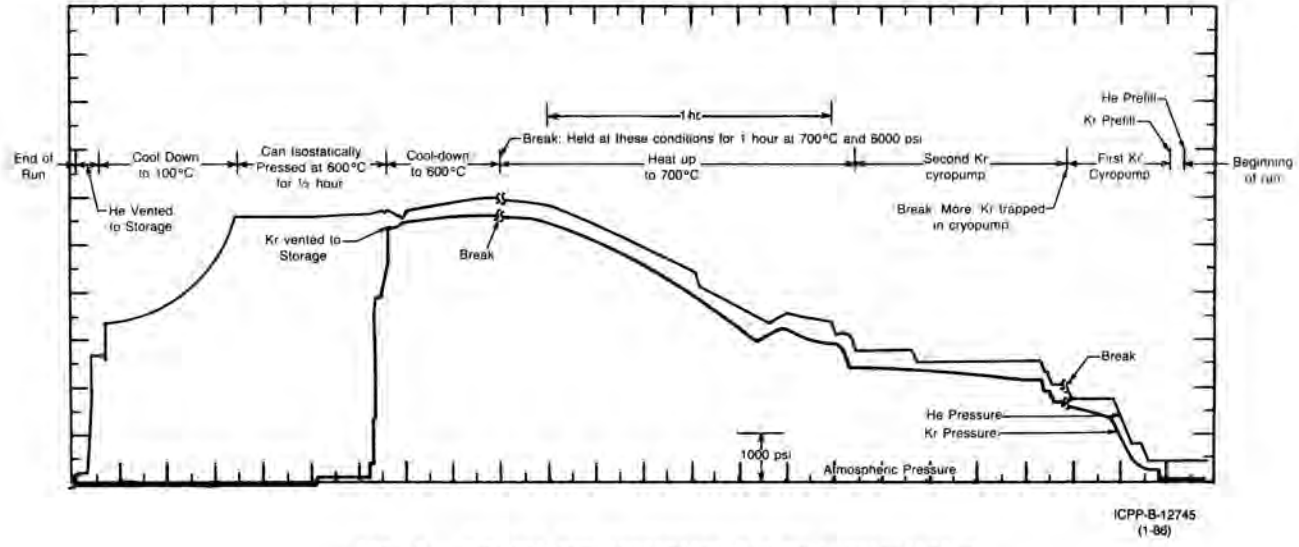


Fig. 5. Typical Run Conditions for Kr Encapsulation Into Zeolite, Progressing Right.

TABLE I

Representative Krypton Encapsulation Experiments With The HIP

Material		Conditions, at 700°c			Gas Load, ncc/g		
Form	Amount	Major gas	Pressure atm	Time min.	Major	Total[a]	Water
Zeolite Pellet	50cc	Ar	1000	180	46	46	1.3
Pellet, 80/20 Zeolite/Powder Aluminum	50cc	Ar	1000	120	36	36	0.6
Pellet, 70/30 Zeolite/Glass	50cc	Ar	1000	120	37	37	0.9
Zeolite Beads	1000cc	Ar	1000	210	50	50	1.6
Zeolite Pellet	50cc	Ar	1000	210	43	43	1.3
75/25 Zeolite/Glass	16L	Ar	1000		36	36	
Zeolite Beads	8g	Kr[b]	450	60	18	32	1.5
Zeolite Beads	12g	Kr[b]	560	60	18.7	38	1.2
70/30 Zeolite Beads/Glass	15.7g	Kr[b]	680	60	[c]		
70/30 Zeolite Beads/Glass	15.7g	Kr[b]	1000	60	[c]		
Zeolite Beads	12g	Kr[b]	375	45	[c]		

[a]Includes all gases except water.
[b]Mixture of stable and radioactive krypton.
[c]No gas analysis or x-ray spectrum taken. Remaining runs above had amorphous spectra.

Good gas loadings were obtained with the one and 16-liter samples of zeolite 5A beads, and with the large pre-pressed pellets as shown in the table.

A number of problems required equipment modification or special procedures during the experiments. Initially the valves and vacuum pump were controlled by interlocks to allow one operation at a time, i.e., distillation from source to cryopump, transfer from cryopump to canister, HIP heating under pressure, etc. The purpose was to prevent accidental opening of the wrong valve, resulting in contamination or loss of the krypton. But several events required unforeseen configurations: (1) the need to use trap #1 to aid cryopumping, (2) the need for trap #1 and the vacuum pump simultaneously to purify the krypton from a massive helium contamination (trap #2 was inoperable due to a stuck flow regulator). Most of the interlocks were therefore eliminated to acquire the needed flexibility. Automatic controls on maximum and minimum pressure differential between the krypton and the helium within the HIP, and on the maximum allowed total pressure were retained.

The mixing of helium and krypton was caused by a power failure under pressure, which resulted in unseating of the sample canister. The responsible combination of fail-open (V-22 and V-23) and fail-close (V-29 and V-30) valves was therefore reprogrammed. The krypton was successfully purified and recovered by drawing it through V-24, trap #1, and V-32.

Maintaining the slight excess helium pressure around the inner canister while heating the HIP proved difficult, because of a low pump capacity, and a tendency for an abrupt increase in krypton pressure during the middle of the heating period.

Successful cryopumping required (1) getting rid of the last trace of non-condensable gas, the 0.7% He initially present, and (2) minimizing lead volumes between cryopump, canister and associated gauges. It also seemed advisable not to cool the vessel walls too far ahead of the condensate level inside, so as to avoid xenon plugging of the inlet.

A number of unexpected radioactive contamination problems were encountered. Krypton dissolved in the silicone vacuum grease around the canister inlet seal, and also in the vacuum pump oil. The former disappeared in a few days. The fine zeolite particles in the wash water from the sample cutting easily became airborne once the water dried.

SUMMARY

A small commercial HIP was modified for remote operation and for separate gases in the sample zone and the heater/insulation zone. It was used to encapsulate into beads of zeolite 5A a krypton fraction of the offgas from fuel reprocessing, containing 62% krypton, including 3.5% krypton-85. Total gas loadings of at least 38 STP cc/g were obtained at an encapsulation pressure of 560 atm. In non-radioactive large scale tests using the unmodified HIP, argon loadings as high as 50 STP cc/g were obtained with a one-liter batch of zeolite 5A beads, and somewhat smaller loadings with pre-pressed 500cc pellets of powdered zeolite, in some cases mixed with powdered glass frit or powdered aluminum metal. Also, 16-liter batches of zeolite-encapsulated argon were prepared for us at a commercial facility.

Automatic operation was gradually replaced by manual operation to obtain needed flexibility. Successful cryopumping was achieved by eliminating all unnecessary lead volumes, and by removing all but traces of non-condensable gas (helium).

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