Development of a Polymer Catalyst for HANARO Detritiation

H. Chung† , H. S. Kang, S. W. Paek, J. H. Yoo, S. H. Shon*,
K. R. Kim, S. H. Lee, D. H. Ahn, H. S. Lee

† Korea Atomic Energy Research Institute
P.O.Box 105, Yusong, Taejon 305-600, Korea. Tel. 82-42-868-2377,
Fax. 82-42-868-2990. Email: hschung1@nanum.kaeri.re.kr

ABSTRACT

The use of heavy water as a reflector in HANARO results in the continuous exposure of deuterium oxide to neutron flux. Substantial quantities of tritium are generated by neutron activation of deuterium in the reflector. Airborne emissions and staff internal radiation doses could be caused by tritiated heavy water escaping from the system. A detritiation facility is thought to be effective in reducing the overall radiological impact. The detritiation process may consist of a catalytic exchange in the front-end and a cryogenic deuterium distillation section. In this paper, the catalyst manufacturing and its performance evaluation technology was presented. The waterproof polymer catalyst has a specific surface area larger than 400m^2/g. It showed a high reaction rate in the hydrogen isotope exchange reaction.

1. INTRODUCTION

Korean experience with large volumes of heavy water in nuclear reactor systems commenced in 1983 with the operation of the Wolsong Nuclear Power Plant in which 453.6 Megagrams of heavy water was used. The HANARO which came into operation in 1995 has 4,900 liters of heavy water in the reflector system. The use of heavy water as a reflector in HANARO results in the continuous exposure of deuterium oxide to neutron flux. Substantial quantities of tritium are generated by neutron activation of deuterium in the reflector. Airborne emissions and staff internal radiation doses could be caused by tritiated heavy water escaping from the system. Ameliorating the leaktightness of the system must be effective in reducing emissions and internal dose but is not a long-term solution. A detritiation facility is thought to

---

*Korea Electric Power Research Institute be effective in reducing the overall radiological impact. The detritiation process may consist of a catalytic exchange front-end and a cryogenic deuterium distillation section. In this paper, the catalyst manufacturing and its performance evaluation technology is presented.

2. TRITIUM BUILDUP IN HANARO

2.1. Reflector system

The reflector system consists of the reflector cooling system, reflector cover gas system, and D_2O leakage monitoring and collection system. The reflector cooling system is designed to remove 2.5 MWt heat from the reflector system and to maintain the quality of heavy water (conductivity below 0.5 mS/m, minimum isotope purity above 99.85 wt.%). During normal operation, the heavy water of 45 l/sec is continuously pumped from the top of the reflector tank through the heat exchanger and returned to the bottom of the reflector tank to dissipate up to 2.5 MWt of heat through the heat exchanger. A by-pass flow of 0.15 l/sec goes through the ion exchange columns for clean-up purposes. The reflector cover gas system consists of an expansion tank, sampling connection, a pressure relief valve, and all necessary interconnecting piping, valves, and instrumentation. This system is designed to cover heavy water expansion due to the temperature increase from the minimum temperature to the maximum design temperature for the reflector system (7℃ to 120℃). The main component is the expansion tank which can accomodate the maximum volumetric increase of 350 liters of heavy water. The D_2O leakage monitoring and collection system consists of a collection tank, collection lines provided with sight glasses, and moisture elements. Leaking heavy water is collected to a collection tank by gravity and transferred to an expansion tank of the reflector cover gas system by compressed air.

2.2. Tritium buildup

The reflector tank (2 m diameter and 1.2 m height) containing heavy water surrounds the hexagonal reactor core and accommodates various experimental holes. The total inventory of heavy water in the reflector system is about 4900 liters, and the volume of heavy water in the reflector tank is about 3000 liters. The buildup of tritium in the heavy water reactors caused by the (n, γ) reaction on deuterium is well known. This tritium nucleus disintegrates by emission of β rays to form ^3He, the half life amounting to 12.26 years. The rate of tritium buildup is usually assumed to follow simple exponential kinetics, determined by the effective neutron flux and the rate constant for decay of tritium to ^{3}He. The concentration then approaches an equilibrium value set by equality of the production and decay rates. The rate of tritium buildup depends on the neutron flux in the reflector region. The average neutron flux in the reflector region of HANARO is about 8.51×10^{13} n/㎠ · sec. The increase of tritium activity is not linear with time, but eventually achieves the equilibrium value. The specific activity of tritium after t years of the reactor operation is estimated by

$$A = A_m[1-\exp(-\lambda t)]$$

where, A_m is a saturation concentration in reflector (33.9 Ci/kg D_2O), λ is a decay constant of tritium (0.056/yr). The tritium concentration in HANARO increased up to 0.49 Ci/kg D_2O recently. The specific activity of tritium after t years of reactor operation is shown in Fig 1. It is estimated that the tritium concentration would become about 28 Ci/kg D_2O in the full power operation of 30 years.

2.3. Tritium Removal

A number of hydrogen isotope separation processes have been developed for the production of heavy water[1]. In general, these can be applied to tritium separation. These processes include diffusion and membrane process, laser exitation, adsorption, water distillation, hydrogen distillation, electrolysis, and chemical exchange of

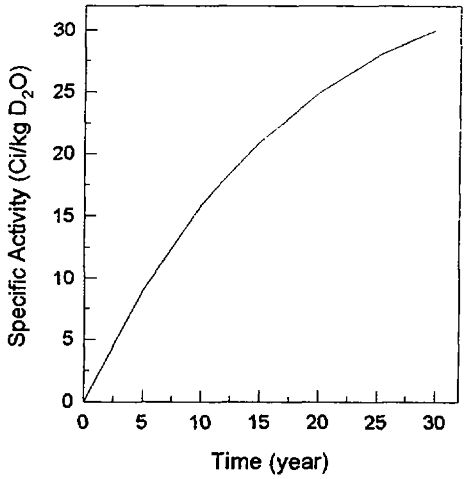

Fig.1. Tritium Accumulation

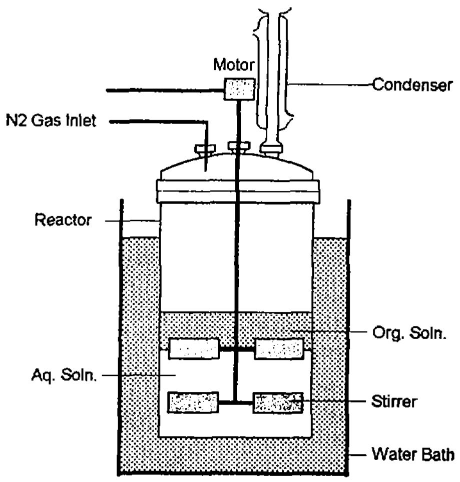

Fig.2. Polymerization Reactor

hydrogen isotopes between hydrogen and water. The power consumption of the processes is extremely high. The first three processes are suitable for small scale, whereas the last four processes are acceptable comparably with respect to commercial use. The combination of pertinent processes is also available to enhance the process effeciency, for instance, combined electrolysis-catalytic exchange(CECE) process. The other combinations are also likely. The combined LPCE(liquid phase catalytic exchange)-CD(cryogenic distillation) has been of interest recently, since LPCE reduces the energy consumed for the catalytic exchange process by employing an appropriate catalyst that is prosperously active even at room temperature.

The LPCE process employs hydrophobic catalyst to expel the water from the catalyst surface[2]. If the hydrophilic catalyst is used, then the water condensates in the pore. This hinders gas and liquid from transferring into the pore on which surface a large extent of catalytic activity is available. One of the methods enabling the catalyst to be hydrophobic is coating the supporting material with teflon for the repulsion of water. For practical purpose, the hydrophilic layer is combined with a hydrophobic catalyst layer to enhance the mass transfer between gas and liquid phase[3]. Another method is allowing the catalytic support to be made of polymer which is inherently hydrophobic as in this study. The polymer support should be characterized by high specific surface area, thermal and mechanical stabilities, suitablity for metal loading, etc. One of the likely candidates of polymer materials suitable for practical use is the styrene-divinyl benzene copolymer. This can be synthesized readily by suspension copolymerization[4]. The influencing parameters on the polymer properties are solvents, ratio amount of monomer to solvent, and crosslinkage that is defined as the ratio of divinyl benzene to total weight of monomer.

3. SYNTHESIS OF A POLYMER CATALYST

Macroporous styrene-divinylbenzene(DVB) copolymer was synthesized. The proper pore size distribution was obtained by using a mixture of two or more diluents. In principal, good solvents produce small pores, while poor solvents result in large pores[5]. Inhibitor in the styrene and DVB monomer was removed by an aqueous solution of 10% NaOH. Then the monomers were washed three times with demineralized water. Solvents such as toluene, 2-pentanol, dimethyltetrahydrofuran, and isobutyl phathalate with an initiator were used in the suspension polymerization. Styrene, divinylbenzene, benzoyl peroxide and various diluents were poured into the flask in which an aqueous solution of 0.1% gelatin, 0.5% sodium dodecyl sulfate, and 1.0% NaCl was contained. The polymerization apparatus is shown in Fig. 2. The polymerization reaction was performed at 80℃ for about 15 h in a thermostated water bath. Then the beads were washed with ethyl alcohol and acetone alternatively. The rest of solvents inside of pores were removed with N_2 gas at 230℃ for about 15 h. The polymer samples were characterized by the BET and BJH technique[6]. The polymer beads were impregnated with Pt alcoholic solution in a rotavapor. Then H_2 reduction was performed at 230℃ for about 19 h. Synthetic condition and characteristics of the catalysts K1 and K2 are shown on Table 1 and 2, respectively. The pore size distributions of the catalysts are shown in Fig. 3. Increasing the crosslinkage provides the styrene backbone with the dense link of divinyl benzene, yielding more small pores. This explains the increase of surface area with the crosslinkage.

Table 1. Synthetic conditions of the catalyst supports

sample	cross-linkage(%)	ratio of monomer to solvent	ratio of good solv. to poor solv.
K1	55	1/2	1/2.5
K2	33	1/2	1/1.25

Table 2. Characteristics of K1 and K2

Catalyst / Properties	K1	K2
BET surface area(m^2/g)	403	335
micropore area(m^2/g)	161	69
mesopore area(m^2/g)	242	266
principal pore radius(Å)	17.1	19.0, 163.8
apparent density(g/㎖)	0.17	0.27
Pt loading(wt.%)	0.80	0.80

4. HYDROGEN ISOTOPE EXCHANGE REACTION

4.1. Theoretical

The isotopic exchange reaction between hydrogen and liquid water,

$$HD(g) + H_2O(l) \rightleftarrows H_2(g) + HDO(l)$$

can be considered in terms of two transfer steps.

$$HD(g) + H_2O(v) \rightleftarrows H_2(g) + HDO(v)$$

$$HDO(v) + H_2O(l) \rightleftarrows H_2O(v) + HDO(l)$$

The first step corresponds to the deuterium exchange reaction between hydrogen and water vapor over the metal active sites. The second step corresponds to the transfer of deuterium from deuterated water vapor to liquid water at the gas-liquid interface. It is important to know the catalytic activity of the catalyst in the vapor phase reaction in developing efficient catalysts for the hydrogen isotope exchange reaction. The catalytic activity was characterized by a transfer coefficient kr, as the moles of HD transferred per second per gram of catalyst. As the total deuterium content of the volume element is conserved,

$$F_{H2} \cdot dn + F_{H2O} \cdot dN = 0 \tag{4-1}$$

where F_{H2O} is the molar flowrate of water vapor and dN is the corresponding change in the mole fraction of HDO. The ratio of the partial pressure of water to hydrogen stream is π, hence $F_{H2O} = \pi \cdot F_{H2}$. Eq. (4-1) can be integrated to give

$$N = No - (n - no)/\pi \tag{4-2}$$

where no, No and n, N are the mole fractions of HD and HDO in the hydrogen and water vapor streams which enter and leave the differential element in the catalyst bed. So,

$$F_{H2} \cdot dn/dW = kr\,(N - \alpha_R \cdot n) \tag{4-3}$$

where kr is the transfer coefficient denoting the rate of isotope transfer per gram of catalyst, α_R is the equilibrium constant of the exchange reaction. Substitution of Eq. (4-2) into Eq. (4-3) and integrating over the catalyst mass leads to

$$\ln \frac{(No + \frac{no}{\pi}) - no(\alpha_R + \frac{1}{\pi})}{(No + \frac{no}{\pi}) - n(\alpha_R + \frac{1}{\pi})} = (\alpha_R + \frac{1}{\pi})\frac{kr}{F_{H2}} W \tag{4-4}$$

Eq. (4-4) can be simplified by using

$$(1 - ne)\,Ne = \alpha_R\,(1 - Ne)\,ne \tag{4-5}$$

Integration of Eq. (4-1) yields

$$ne = no - \pi\,(Ne - No) \tag{4-6}$$

As $ne \ll 1$ and $Ne \ll 1$, $Ne = \alpha_R \cdot ne$.

Eq. (4-5) can be written as

$$(No + no/\pi) = ne\,(\alpha_R + 1/\pi) \tag{4-7}$$

Substitution of Eq. (4-7) into Eq. (4-4) results in the following expression.

$$kr = \left(\frac{1}{\alpha_R + \frac{1}{\pi}}\right)\frac{F_{H2}}{W} \ln\left(\frac{ne - no}{ne - n}\right) \tag{4-8}$$

4.2. Experimental

Hydrogen adsorption isotherms for the catalyst at 23℃ were determined in a conventional volumetric gas adsorption apparatus after the pre-adsorbed hydrogen were desorbed at 230℃ and 1×10^{-5} Torr for 2 hours. Then hydrogen adsorption isotherm was obtained in the pressure range of 30-250 Torr. After this experiment, the catalyst was loaded in a U-tube type reactor(Fig. 4). A gas mixture containing deuterium (D_2) and hydrogen (H_2) was allowed to pass through a bed of platinum on carbon. D_2 was converted into HD by the reaction $H_2 + D_2 \rightleftarrows 2HD$. Subsequently, the gas mixture was bubbled into the first saturator column containing distilled water which was kept at reactor temperature, followed by the second saturator column which was kept at a lower temperature than in the first column. The partial pressure of water vapor was thus adjusted to desired value by varying the temperature of the second saturator column. The humidified gas mixture was then allowed to flow downward through the catalyst bed. The deuterium content in the inlet and outlet gas stream was measured by gas chromatography using a stainless-steel column (3mm in diameter and 2m long) in which molecular sieve 5A (60/80 mesh) was contained .

4.3. Experimental results

Hydrogen adsorption isotherms for K1 and K2 catalysts at 23℃ are shown in Fig. 5. Extrapolation of this adsorption isotherm at zero pressure gives total hydrogen chemisorption value. Metal dispersion was calculated on the assumption that one hydrogen atom should adsorb on the surface of one metal atom. Platinum dispersions for the catalysts are 1.1 and 0.62, respectively.

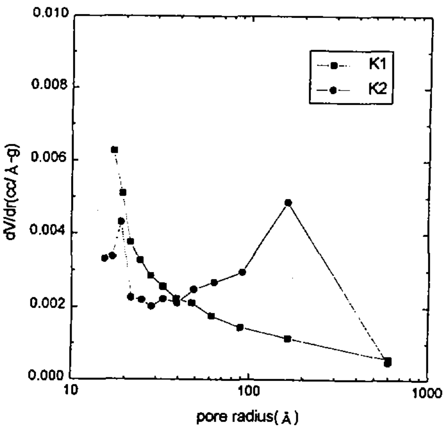

Fig.3. Pore Size Distribution

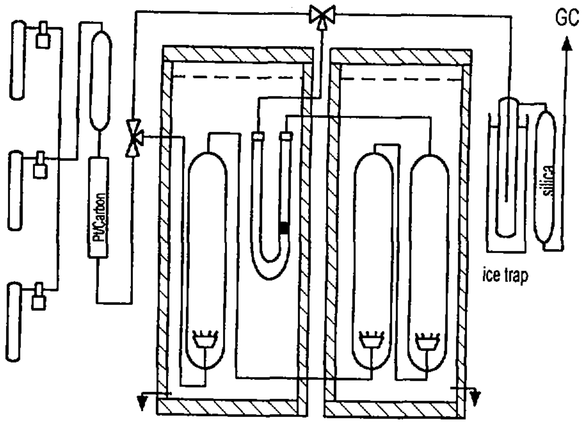

Fig.4. Adsorption Experiment

The transfer coefficients are shown in Fig. 6. The reaction temperature was 60℃, and the saturator temperature was 55℃ corresponding to the 80% of saturation humidity. Hydrogen flowrate was 14cc/s and the feed contained about 1 mole% D in hydrogen stream. The initial transfer coefficients for K1 and K2 are 24 and 5.0 moles HD/g · s, respectively. The transfer coefficients slightly decrease with reaction time. It is thus proved from this result that the catalytic activity of K1 is a little higher than that of K2. Further study on the effect of platinum cluster position in polymeric support on the catalytic activity and the cause of deactivation phenomena will be required for the development of more efficient catalyst.

5. CONCLUSION

The use of heavy water as a reflector in HANARO results in the continuous exposure of deuterium oxide to neutron flux. Substantial quantities of tritium are generated by neutron activation of deuterium in the reflector. A detritiation facility is thought to be effective in reducing the overall radiological impact. The detritiation process may consist of a catalytic exchange in the front-end and a cryogenic deuterium distillation section. In this study, the catalyst manufacturing and its performance evaluation technology was studied. The following are major conclusions.

- It is estimated that the tritium concentration would become about 28 Ci/kg D_2O in thirty years.
- The combined LPCE and CD process is considered to be appropriate in HANARO detritiation. The LPCE process is simple and safe.

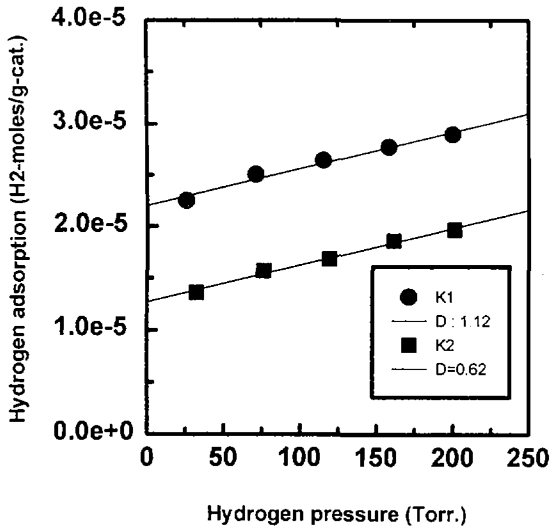

Fig.5. Hydrogen Adsorption Isotherms

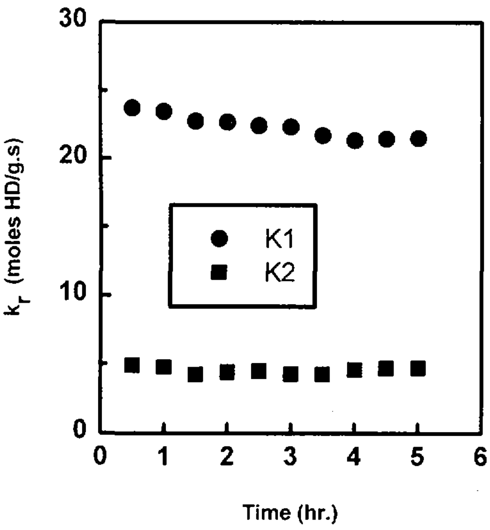

Fig.6. Transfer Coefficients

- The waterproof polymer catalyst for the LPCE process was prepared by the suspension copolymerization of styrene and divinyl benzene.
- The catalyst has a specific surface area larger than $400m^2/g$, and it showed a high reaction rate in the hydrogen isotope exchange reaction.
- Preliminary experimental results show the possibility of the application of the catalyst to HANARO detritiation.

REFERENCES

[1] H. K. Rae, et al., "Separation of Hydrogen Isotopes," ACS Symp. Ser., 1977.

[2] W. H. Stevens, "Process for Hydrogen Isotope Exchange and Concentration between Liquid Water and Hydrogen Gas and Catalyst Assembly Therefore," U.S. Patent No.3,888,974, June 10, 1975.

[3] J. P. Butler, J. den Hartog, and F. W. R. Molson, "Process for the Exchange of Hydrogen Isotopes Using a Catalyst Packed Bed Assembly," U. S. Patent 4,126667, Nov. 21, 1980.

[4] F. W. Billmeyer, Jr., Textbook of Polymer Science, 2nd ed., John Wiley & Sons Inc., 1971.

[5] W. L. Sederel and G. J. De Jong, J. Appl. Polym. Sci. **17**, 2835, 1973.

[6] E. P. Barrett, L. G. Joyner, and P. P. Halenda, J. Amer, Chem. Soc., **73**, 373, 1951.