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Reconfigured metallic membrane technology for maintaining hydrogen concentration below 4% in fuel debris canisters.

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RECONFIGURED METALLIC MEMBRANE TECHNOLOGY FOR MAINTANING HYDROGEN CONCENTRATION BELOW 4% IN FUEL DEBRIS CANISTERS

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ABSTRACT

The use of hydrogen in the energy sector has been in the headlines in recent times due to its promising future as a replacement for fossils and its sustainable production from a wide variety of feedstocks including traditional hydrocarbons derived from fossil fuel and biomass, residual hydrocarbons or wastes, and even other molecules out of the carbon cycle, such as ammonia or water. There are, however, other applications where the presence of hydrogen is not desired. One of such processes is in the storage waste streams from nuclear reactors where pressure build-up due to hydrogen gas generation by decomposition of water during transportation and storage of fuel debris canisters can result in catastrophic explosion and damage of facilities. In this research a reconfigured metallic hydrogen permeable membrane is tested to act as a valve on the canister lid to maintain hydrogen concentration below 4% in fuel debris canisters.

Keywords: fuel debris, canister, waste, storage, hydrogen, metallic, membrane, nuclear power.

INTRODUCTION

As part of decommissioning of Fukushima Daiichi Nuclear Power Plant (1F), Tokyo Electric Power Company (TEPCO) investigates how to retrieve and store fuel debris then how to transfer and store fuel debris canisters. According to the decommissioning of Three Mile Island Station 2 in the United States, following cases are reported that high-energy α rays, included in nuclear waste or fuel debris, cause hydrogen gas generation by decomposition of water during transportation and storage of fuel debris canisters. Hence, establishing a reliable method to maintain the hydrogen gas concentration below the lower explosive limit is essential to complete decommissioning 1F safely. In association with hydrogen energy technologies, hydrogen adsorption and hydrogen permeable membrane are well investigated all over the world.

Current fuel debris canister design is presented in Figure 1. The material, storage conditions of fuel debris, etc. are as described below although these are subject to change according to further investigations.

- Fuel debris canister
  - Material: SUS304 or SUS316L
  - Size: inside diameter: 220 mm; inside height: 1500 mm
  - Structure: See figure below
  - permeable membrane module is assumed to embed to canister's lid
- Fuel debris
  - Composition: UO2 (including fission products [FP]), zirconia alloy, stainless steel, low-alloy steel, Ni-based alloy, concrete, B4C, seawater, etc.
  - Particle sizes: 1-4 mm
  - Storage condition: pallet-shaped dry solid form** supposedly in an inactive gasatmosphere.
- Environments inside fuel debris canisters
  - High-dose radiations; α ray, β ray, γ ray, etc.
  - Generation of corrosive substances, radioactive gas/dust under the influence of high-dose radiations
    - - e.g., chlorides, sulphides, Cs137, etc.
  - Internal temperature: Room temperature to 150°C
  - Gas fluidity: 2.0 mm/s (at 1000 W/m^3)
  - Potentially adding of neutron adsorbent, iodine, etc.
  - Keeping dry condition
- Storage environments for fuel debris canisters
  - Planning to be stored in a normal warehouse environment.
- Possible approaches might include, but not limited to:
  - Hydrogen separation membrane and membrane module

- Hydrogen adsorption catalyst and metal
- A novel module that can adsorb/decompose hydrogen then adsorb generated water, etc

One type of hydrogen permeable membrane known to be hydrogen-selective is palladium metallic membrane. Currently, the main efforts are being directed and focused on reducing the cost of these type of membranes and to increase the mechanical strength, longevity, and manufacturing reproducibility. Two of the most studied strategies to reduce the cost of the membranes are: (a) optimizing the amount of palladium necessary to achieve a fully dense and conformal layer and (b) increasing the useful lifespan since these membranes are susceptible to suffer deactivation due to poisoning and cracking because of thermo-mechanical stress. Taking into account the typical equation widely used to describe the hydrogen permeation flux (JH2) through a Pd-based membrane (so-called Richardson equation as shown in Equation (1)) as function of hydrogen permeability (k), metal thickness (t) and hydrogen pressure driving force ($P^n_{high} - P^n_{Low}$), where P_{high} is the hydrogen partial pressure inside the canister and P_{Low} is the hydrogen partial pressure outside of the canister lid, it is obvious that decreasing of the metal thickness triggers an increase of the permeation capability of the membrane and also reduces the cost, thus making the process economically feasible.

$$J_{H_2} = \frac{K}{t}\left(P^n{}_{high} - P^n{}_{low}\right) \qquad (1)$$

In the case where the Pd-based membrane is totally dense and free of any defects such as cracks and pinholes, the hydrogen permeation flux is determined by the solution-diffusion mechanism in the bulk metal and the exponential factor in Equation (1) takes the value n = 0.5, denoting the equation as Sieverts' law [1]. In our reconfigured metallic membrane, the value of n was equal to1.0 indicating non-Sieverts' dependence resulting in a higher JH2 at an identical temperature and transmembrane pressure drop than in the Sieverts' law case.

MATERIALS AND METHODS

All chemicals used for plating ($PdCl_2$, $AgNO_3$, NaEDTA, and N_2H_4) were obtained from Sigma Aldrich, UK. Ceramic supports for membrane preparation were purchased from Ceramiques Techniques et Industrielles (CTI SA) France and have 45% porosity and 15nm. Pore size. The dip coating method wasused for the palladium deposition [**1,2**]. The apparatus and method used for hydrogen permeation test islike that described in US Granted Patent, GOBINA [**3**].

RESULTS AND DISCUSSION

Figure 2 shows permeate component concentration from a feed stream consisting of dry water gas shifted (WGS) dry reformate mixture (ca.67% H_2, 32% CO_2, 0.1% CO, 0.9% CH_4) at 250 ^OC, 300 ^OC, and 400^OC respectively. The highest hydrogen purity was obtained as the Δ_{PH2} (transmembrane partial pressuredifference of H_2) was increased to 0.80 bars. Experimental factors however, limited the maximum pressure difference, but extrapolation indicates that a H_2 purity of 99.99% was achievable at Δp_{H2} 1.5 bars. Theideal separation factor obtained was about 200 over this range of Δ_{PH2} hence the n value of 1. It is notedthat 100% selectivity (∞ separation factor) can only be achieved in practice if there are no defects or pinholes in the membrane and all sealing leaks inherently present are eliminated.

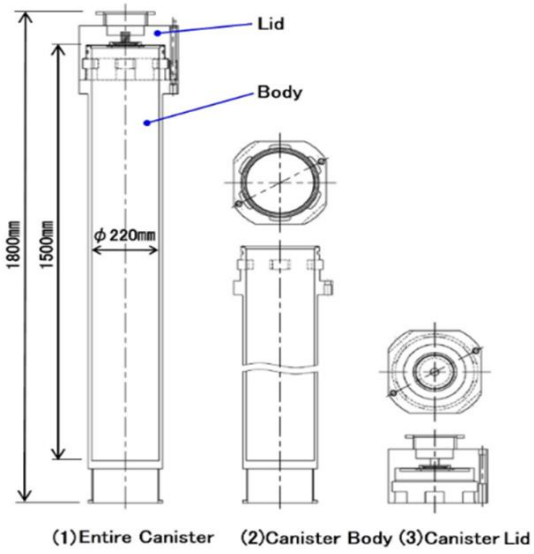

Figure 1. Fuel debris canister design TEPCO)

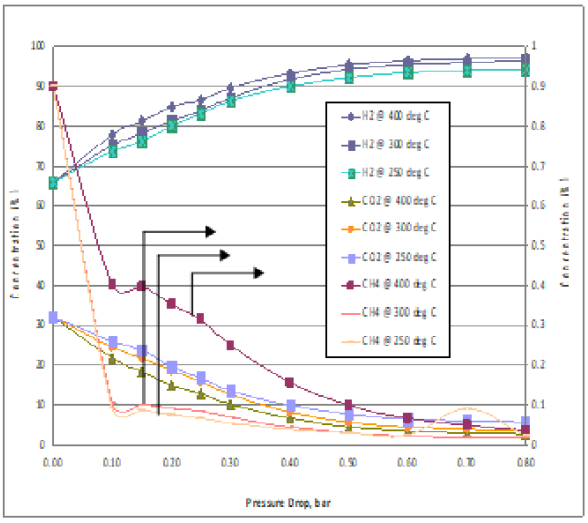

Figure 2. Permeate Purity versus pressure drop for WGS-shifted Dry Reformate Feed (ca.67% H_2, 32% CO_2, 0.1% CO, and 0.9% CH_4) at 250 ^{O}C, 300 ^{O}C, and 400 ^{O}C respectively.

CONCLUSIONS AND FURTHER WORK

By considering a reconfigured palladium membrane we have reproduced the conditions of experimentaldata of a specific metallic membrane, with a transport model that allowed for predicting the canister valvemolar fraction profiles in the reactor, and thus the performance of the membrane as a hydrogen separation device. The results are very useful for calculating the optimal area and mechanical design of the permeator, in which the concentration polarization close to the membrane surface is not a limitation forthe hydrogen permeation. Notwithstanding, a more detailed mechanistic description of the hydrogen transport is required to better understand the contribution of each underlying step, which even involves considering the presence of inhibiting species within the canister, such as steam. Future efforts will bedirected towards implementation of a more rigorous transport mathematical description of these membranes, in which the feed side and permeate side of the palladium film are noticeably different because of its composite structure. Nowadays, this simplified hydrogen transport model can reproducethe H_2 flux through composite Pd-based membranes formed by diverse stacked layers of ceramic and metallic thin-film with reasonable accuracy, forming the basis in evidencing future work.

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