CHAPTER IV
RESULTS AND DISCUSSION

Experiments were conducted at room and elevated temperatures to identify an effective barrier materials for blocking chlorine while passing hydrogen through the palladium wire with such a coating material. It may enable the sensor to respond to a change of hydrogen concentration in the H_2-Cl_2 gas mixture without interference from chlorine, oxygen and moisture.

The screening procedure

Firstly, the various materials are tested with a hydrogen gas mixture to determine if hydrogen passed readily using the breakthrough time (B/T).

- The Hydrogen B/T was determined as the first detection of H_2 on collection side.
- The Chlorine B/T was determined as the first indication of stain in the detector tube.

Secondly, the various materials were tested with a hydrogen gas mixture varying the thickness of coating materials in order to identify the acceptable thickness of coating materials.

Finally, the potential materials were tested with a hydrogen-chlorine gas mixture to determine the chlorine permeability coefficients and investigate the effectiveness of the coating for blocking chlorine.

4.1 Hydrogen Permeability Coefficients Results

In these experiments, the various materials were tested to determine their hydrogen permeability coefficients. First, a Teflon was tested at room temperature and at an elevated temperature to confirm the literature values and previous test results.

4.1.1 Teflon Test (0.15 mm thick)

Table 4.1. The permeability coefficients of hydrogen through Teflon at ambient and elevated Temperatures

Temperature(°C)	Permeability Coefficient (cm^3H_2(STP)cm/cm^2min atm)	
	Literature Value	Test Results
25 °C	4.500×10^{-6}	5.045×10^{-6}
80 °C	-	25.49×10^{-6}

From Table 4.1, the literature value and test results for hydrogen diffusion through Teflon are similar. The permeability coefficient was found to increase with increasing temperature as expected from the Arrhenius relation.

4.1.2 Coating Materials

Table 4.2 The permeability coefficients of hydrogen through the coating materials at 80 °C

Materials	Permeability Coefficient ($cm^3H_2(STP)cm/cm^2min\ atm$)
Boron Nitride Hardcoat (0.65 mm thick)	No B/T* in 6 hours
Lindron 31 (0.29 mm thick)	24.30×10^{-6}
Lindron 101 (0.26 mm thick)	46.41×10^{-6}
Fluorodyn Caulk (0.289 mm thick)	28.36×10^{-6}
Derakane Resin (0.215 mm thick)	9.026×10^{-6}

* B/T is the break through time.

Figure 4.1 shows hydrogen concentration as a function of time for coating materials at 80 °C.

As seen in Table 4.2 and Figure 4.1, Boron Nitride Hardcoat did not allow the passage of hydrogen within 6 hours.

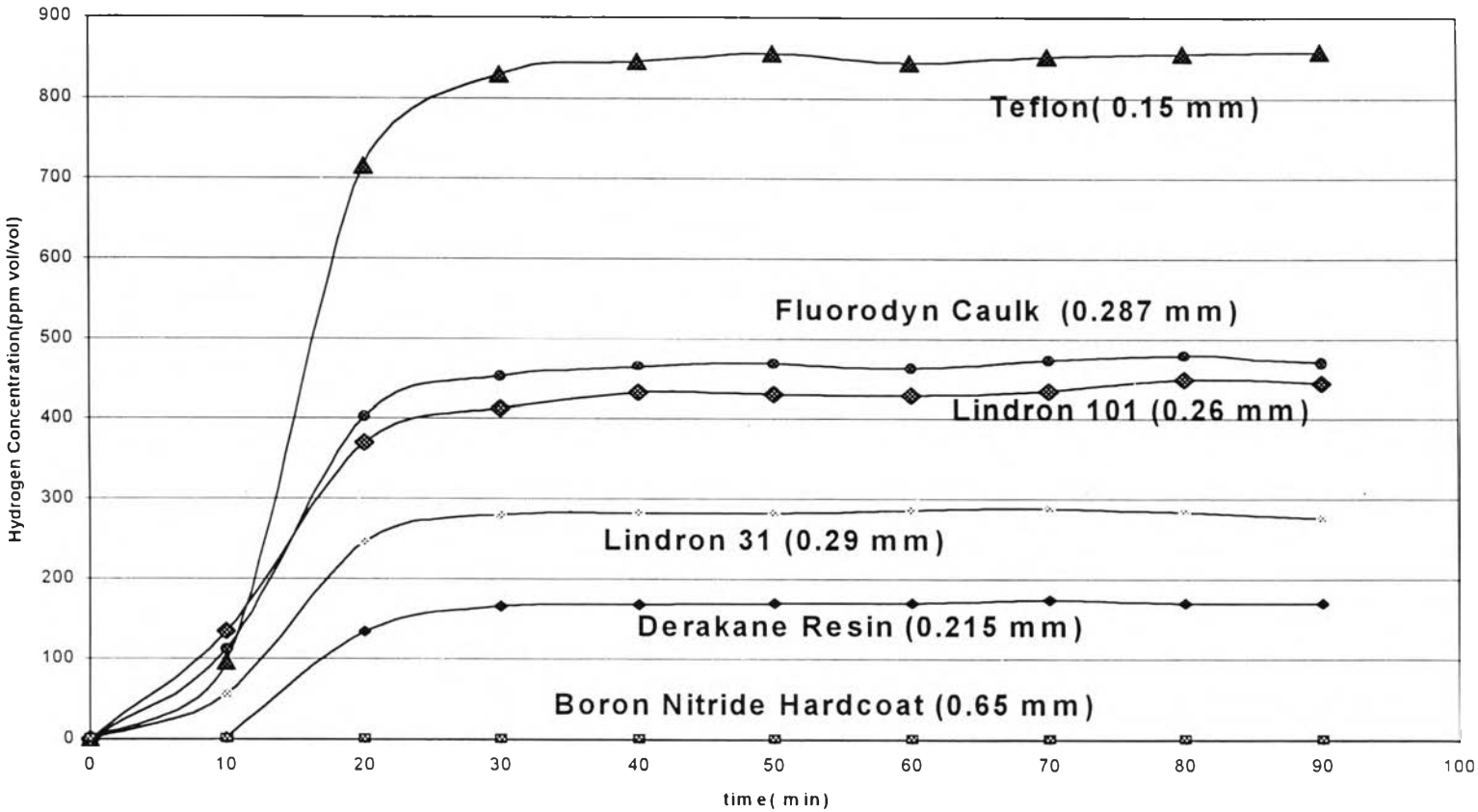

Figure 4.1 Hydrogen concentration in the collection gas as a function of time for coating materials at 80 ^{0}C

Lindron 31 and Lindron 101 allowed hydrogen to pass and the determined permeability coefficients were 24.30 x 10^{-6} and 46.41 x 10^{-6} cm^3H_2 (STP)cm/cm^2min atm, respectively. They deformed and were brittle at high temperature. Therefore, these were not suitable coating materials for a high temperature sensor. As a result, Fluorodyn Caulk and Derakane Resin were identified as the potential coating materials.

Subsequently, Fluorodyn Caulk and Derakane Resin were tested by varying the coating thickness and determining the permeability coefficient variation with thickness. For 0.289 and 0.329 mm Fluorodyn Caulk, the permeability coefficients were determined as 28.36 x 10^{-6} and 32.54 x 10^{-6} cm^3H_2 (STP) cm/cm^2 min atm. The trend for three thicknesses of Derakane Resin was similar to those of Fluorodyn Caulk, 9.026 x10^{-6} for 0.215 mm Derakane Resin, 12.76 x10^{-6} for 0.572 mm, and 1.844 x 10^{-6} for 0.959 mm Derakane Resin. This indicates that the permeability coefficient is independent of thickness (Figure 4.2 and Figure 4.3).

Table 4.3 The permeability coefficients of hydrogen through Fluorodyn Caulk and Derakane Resin at 80 °C

Materials	Permeability Coefficient (cm^3H_2(STP) cm/cm^2min atm)
Fluorodyn Caulk (0.289 mm thick)	28.36 x 10^{-6}
(0.329 mm thick)	32.54 x 10^{-6}
Derakane Resin (0.215 mm thick)	9.026 x 10^{-6}
(0.572 mm thick)	12.76 x 10^{-6}
(0.959 mm thick)	1.844 x 10^{-6}

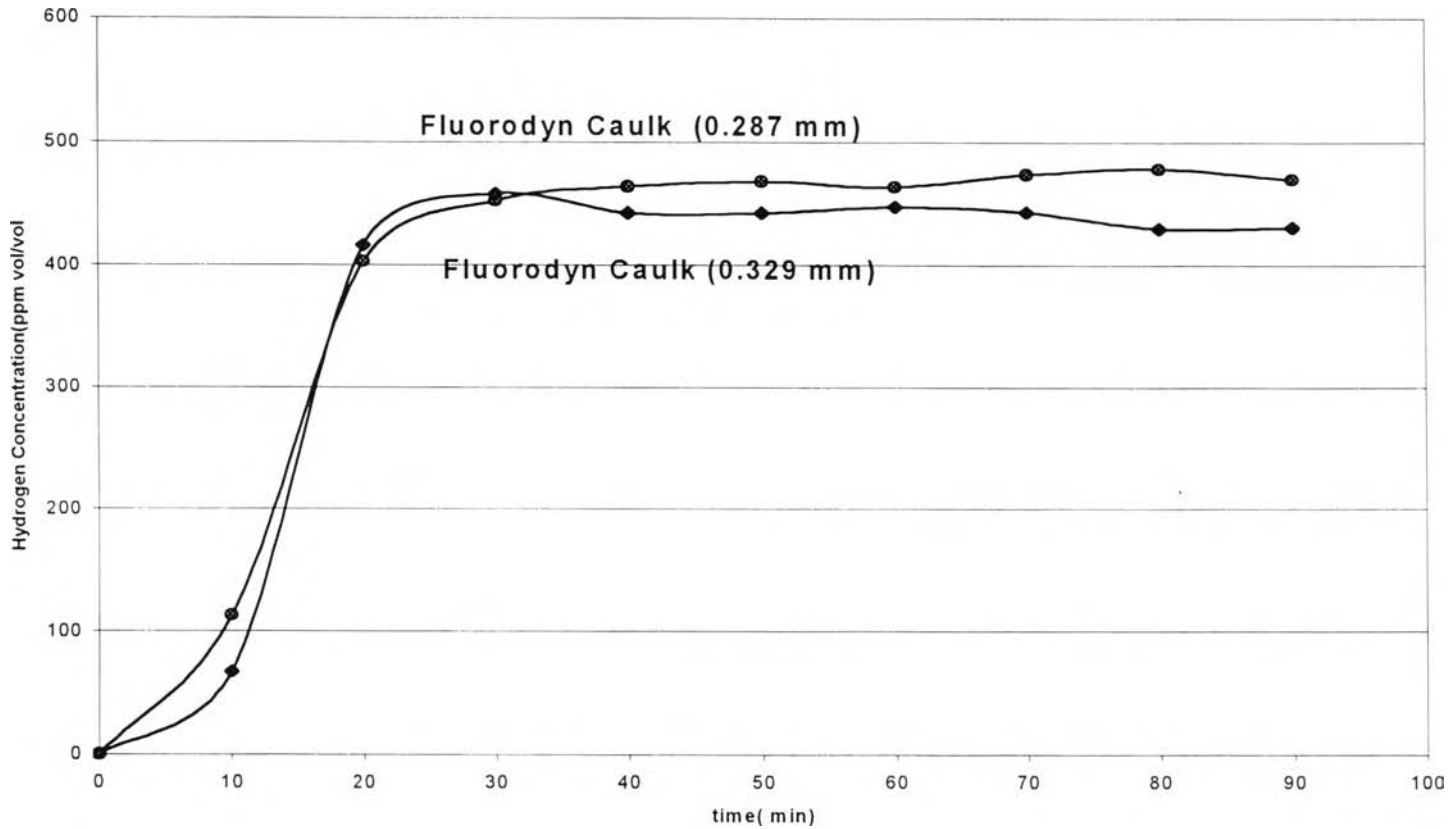

Figure 4.2. Hydrogen concentration in the collection gas as a function of time for two thicknesses of Fluorodyn Caulk at 80 ^{0}C

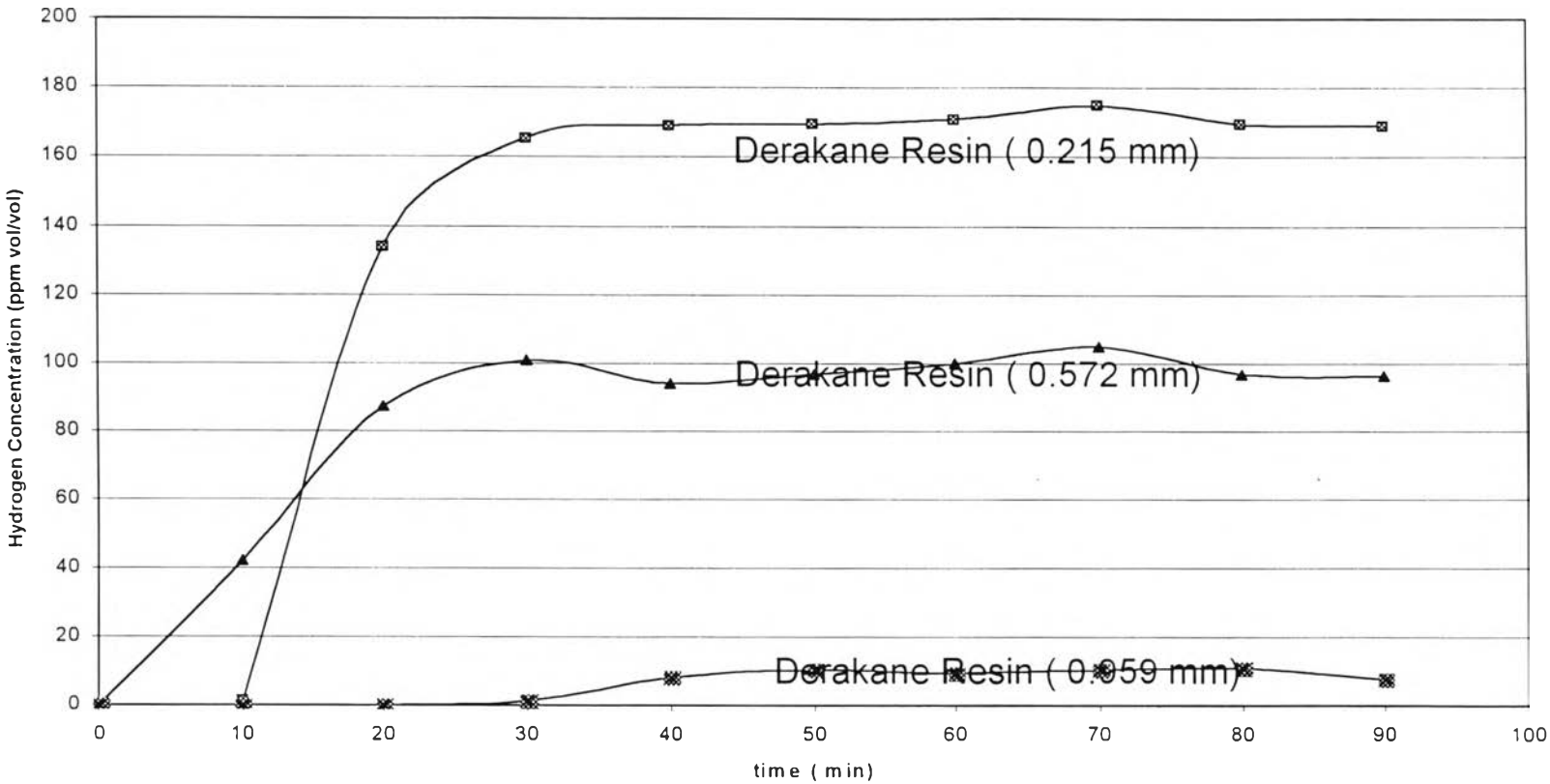

Figure 4.3 Hydrogen concentration in the collection gas as a function of time for three thicknesses of Derakane Resin at 80 ^{0}C

4.2 Chlorine Permeability Coefficient Results.

Fluorodyn Caulk and Derakane Resin were tested with humidified (saturation at 70 ^{0}C) H_2-Cl_2 gas mixtures (99% Cl_2-1% H_2). The results are given in Table 4.4.

Table 4.4 The permeability coefficients of chlorine through Fluorodyn Caulk and Derakane Resin at 80 ^{0}C humidified (saturation at 70 ^{0}C) H_2-Cl_2 gas mixtures (99% Cl_2-1% H_2)

Materials	Breakthrough time
Fluorodyn Caulk : 0.254 mm thick	No B/T in 69 hr
: 0.347 mm thick	No B/T in 42 hr
Derakane Resin : 0.215 mm thick	No B/T in 36 hr
: 0.572 mm thick	No B/T in 19 hr
: 0.959 mm thick	No B/T in 30 hr

From Table 4.4, the potential materials were tested and could be seen that both Fluorodyn Caulk and Derakane Resin blocked the passage of Cl_2 within each breakthrough time. This breakthrough time would show the operating time for sensor where can be last in the plant. The longer breakthrough time, the better sensor.

Fluorodyn Caulk and Derakane Resin were found to be the promising materials for blocking chlorine because of no the breakthrough time (B/T).

4.3. Discussion

According to the coating material experiments, some materials allow the passage of hydrogen or chlorine, whereas some do not. One assumption for this phenomena is the molecular mechanism of molecules through coating materials. There are four diffusion mechanisms for diffusion through the polymer membrane. The feasible controlling mechanism is molecular sieving. Porous membrane contains pores of molecular dimension which is physically selective on the relative sizes of the diffusing species and the pore of each material. The function of this mechanism is to allow the smaller molecules to diffuse, while blocking the larger molecules. For H_2- Cl_2 gas mixture, the molecular size of hydrogen is 2.915 A^0 and the molecular size of chlorine is 4.115 A^0. The chlorine molecules are larger than those of hydrogen molecules. Therefore, the differences in H_2 and Cl_2 molecules were used to select suitable coating materials.

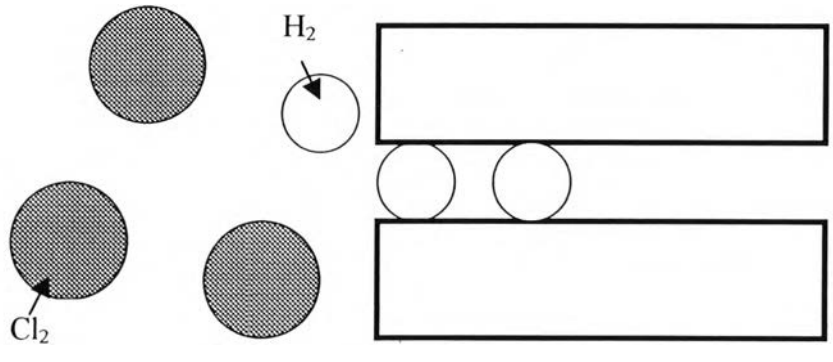

Figure 4.4 Schematic of the molecular sieving mechanism for H_2-Cl_2 gas mixture with different molecular sizes.

Some polymers such as Derakane Resin and Fuorodyn Caulk allowed the passage of hydrogen, but blocked chlorine because H_2 molecules was smaller than Cl_2 molecules. Somes allowed the passage of both hydrogen and chlorine since the pore size of that polymer was smaller than the size of the diffusing species. Both gases were able to pass through that polymer. On the other hand, some, such as Boron Nitride Hardcoat, did not allow the passage of hydrogen and chlorine molecules because of both H_2 and Cl_2 molecules were larger than pore sizes.