INVESTIGATION INTO THE POTENTIAL RELEASE OF CHLORIDE FROM THE MODERATOR COVER GAS RECOMBINER CATALYST

L. Stolberg, S. Suppiah and K. Kutchcoskie
Atomic Energy of Canada Limited, Chalk River, Ontario, Canada

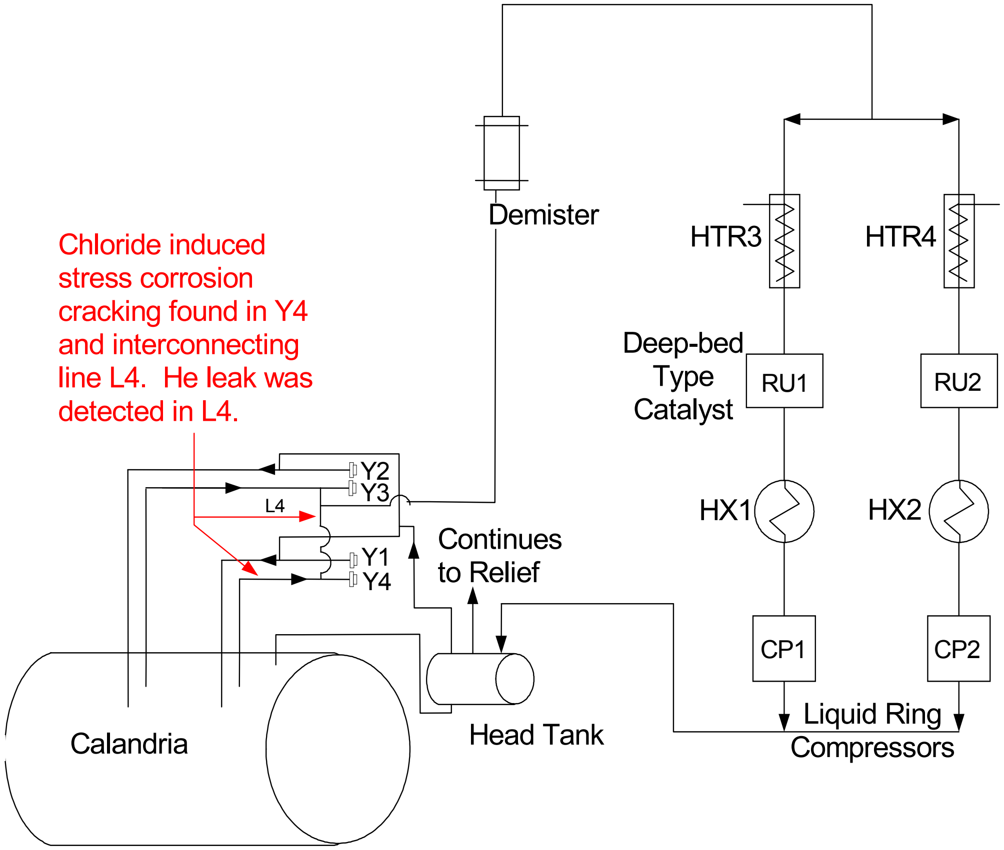
Abstract

Corrosion has been identified in the Bruce-B Unit 7 Moderator Cover Gas System. A failure analysis was able to show that chloride induced transgranular stress corrosion cracking and pitting corrosion took place. Understanding the source of the chloride that caused this corrosion is critical if this corrosion problem is to be mitigated. A number of potential chloride sources have been identified. One such source is the catalyst that is used for recombining deuterium and oxygen in the moderator cover gas recombination units. In this paper the potential for release of chloride from the recombiner catalyst is addressed.

1. Introduction

The objective of the work described in this paper is to determine if chloride could potentially be released from the moderator cover gas recombiner catalyst during deuterium-oxygen (D_2-O_2) recombination conditions found in the Moderator Cover Gas System (MCGS). This work was carried out as part of a larger effort to understand the cause(s) for corrosion that has been observed in the Bruce-B Unit 7 MCGS. A schematic of the Bruce-B MCGS is shown in Figure 1. The corrosion issues were identified in the 18-inch calandria outlet relief ducts associated with the Y3 and Y4 rupture discs. Through-wall cracks, which initiated on the inner-diameter (ID) surface, have been found adjacent to welds on a 1-inch pipe that runs between the Y3 and Y4 relief ducts. ID surface initiated cracks have also been found along both straight and bent sections of the 1-inch pipe. Cracks and pits have been observed on the 2-inch x 1-inch reducers and weld-o-lets. Chloride induced transgranular stress corrosion cracking and pitting corrosion have been identified as being responsible for this corrosion.

Analyses of corrosion deposits taken from the Y4 outlet relief duct were found to contain significant amounts of chloride. This finding is consistent with the type of corrosion damage that has been reported in the relief ducts and downstream piping. A number of possible sources for chloride contamination within the MCGS have been identified. This paper will focus on the catalyst that is used in the recombination units. The recombination units use palladium (Pd) coated alumina (γ-Al_2O_3) pellets (0.3 wt% Pd/Al_2O_3) as the catalyst to promote recombination of D_2 and O_2 to reform heavy water (D_2O). The Bruce B Recombination Unit Specification Sheet indicates that the catalyst was 0.2 wt% Pd on alumina pellets, and that the supplier was Pall Canada, which is part of the Pall Trinity Micro Corporation of New York. However, when contacted, Pall was not able to locate any information related to the supply of recombination units to Bruce. Since 1980, 3L Filters Ltd. (Cambridge, Ontario) has supplied recombination units to Pickering, Darlington, Wolsong, Point Lepreau and Qinshan. 3L Filters Ltd. has confirmed that they did not supply the Bruce recombination units. Therefore, the supplier of the Bruce recombination units has not been conclusively determined.



Chloride induced stress corrosion cracking found in Y4 and interconnecting line L4. He leak was detected in L4.

Figure 1. Simplified Bruce-B moderator cover gas system layout showing the heaters (HTR3 and HTR4), recombination units (RU1 and RU2), heat exchangers (HX1 and HX2) and the liquid ring compressors (CP1 and CP2).

Initially, recombination units supplied by 3L Filters Ltd. contained a 0.2 wt% Pd/Al_2O_3 catalyst. The change to a 0.3 wt% catalyst was introduced around the time when reactors were being planned for the Qinshan project. 3L Filters Ltd. obtain their catalyst from BASF (Seneca, S.C., USA) and have noted in a memorandum that they supplied the catalyst for the above reactors. In the present study AECL has obtained recombiner catalyst samples directly from BASF and 3L Filters Ltd. The BASF catalyst is 0.2 wt% Pd/Al_2O_3 while the 3L Filters Ltd. catalyst is 0.3 wt% Pd/Al_2O_3. Although 3L Filters Ltd. did not supply the recombination units to Bruce, we chose to use their catalyst in our study for the following reason. Corrosion products have been observed in the Darlington Unit 2 south, east and west calandria relief ducts at the rupture disk flange location. Since Darlington and Bruce have both reported corrosion related issues in similar locations, and since 3L Filters Ltd. supplied the Darlington recombination units, we concluded that if the recombiner catalyst was responsible for the corrosion observed in the relief ducts then the 3L Filters Ltd. supplied catalyst would be the best choice for our study.

Catalysts containing platinum group metals are commonly made by impregnation of oxide supports with chloride containing precursor salts [1]. A certificate of analysis obtained from

BASF shows that their catalyst may contain as much as 30 ppm of chloride. Thus, in the present study, we are interested in determining the amount of chloride that is present on the Pd/Al_2O_3 recombiner catalyst and we would also like to know if this chloride can be released to a cover gas under the conditions normally found during MCGS operation.

Degreasers and lubricants have been used in the MCGS. Degreasers may contain compounds such as dichloromethane, tetrachloroethylene and chlorobenzene as well as trichloroethane and trichloroethylene. If any of these chlorinated organic compounds enter the recombination units and come into contact with the recombiner catalyst, HCl may be formed as a product of catalytic reactions. Thus, it is also of interest to understand the interaction of HCl with the recombiner catalyst. In this paper desorption of HCl from an HCl contaminated 0.3 wt% Pd/Al_2O_3 catalyst will also be considered.

2. Experimental

2.1 Recombiner catalyst

The catalyst, 0.3 wt% Pd supported on 3 mm diameter by 3 mm long cylindrical γ-Al_2O_3 pellets, was obtained from 3L Filters Ltd. (Cambridge, Ontario). This catalyst was used in every experiment that is described below except for one experiment. In the one test it was not used, a catalyst supplied directly by BASF (Seneca, S.C., USA) was used. This catalyst was similar to the one described above except that it had a Pd concentration of 0.2 wt%. The chloride content in all of the catalyst samples was determined by following a proprietary procedure developed by BASF. The BASF procedure involves the extraction of the chloride present in the catalyst into aqueous solutions that are analysed for chloride content by ion chromatography.

2.2 Experiments conducted under simulated MCGS conditions

A set of three experiments was carried out to see if chloride could be removed from the 0.3 wt% Pd/Al_2O_3 recombiner catalyst (3L Filters Ltd.) under the D_2-O_2 recombination conditions found in the MCGS. The three tests are identified as Test #1, Test #2 and Test #3. In Test #1 and Test #2 the untreated catalyst was exposed to a cover gas. In Test #3 a catalyst sample treated in HCl was exposed according to the details given below.

A flow diagram of the experimental set-up used to carry out these tests is presented in Figure 2. The gas supply was either ultra high purity helium, used for purging at start-up and shutdown, hydrogen that was purified with a palladium membrane (BOC Gases) or a 1% O_2-2% H_2 mixture in N_2 (BOC Gases). A calibrated mass flow controller was used to control the flowrate of the gas at 0.436 std L/minute. The gas was humidified after passing through 69ºC de-ionized water. This is the temperature of the gaseous mixture above the moderator free surface in the relief ducts under normal reactor operating conditions. Heating tape was used to heat trace the line from the humidifier to the tube furnace in order to prevent condensation.

The humidified gas was directed to the Pyrex glass tube that contained the catalyst bed. Approximately 20 mL of catalyst was used in each test. Pyrex glass wool was placed on both ends of the bed to hold the catalyst in the middle of the glass tube. The glass tube was placed in a tube furnace. The temperature of the tube furnace was maintained at 127°C during experiments. After exiting the tube furnace the gas passed through a glass vent gas bubbler containing de-ionized water. The purpose of the vent gas bubbler was to trap any volatile chloride containing species that might be present in the flowing gas stream. This chloride, if present, would have been released from the catalyst. The vent gas bubbler was placed in a second constant temperature water bath that was sitting on top of a second hot plate. The temperature of this water bath was controlled at 67ºC to 68ºC in order to maintain a constant level of water inside the vent gas bubbler. Finally, the gas passed through polyethylene tubing to another gas washer at room temperature where most of the water vapour condensed before the gas was vented to the atmosphere.

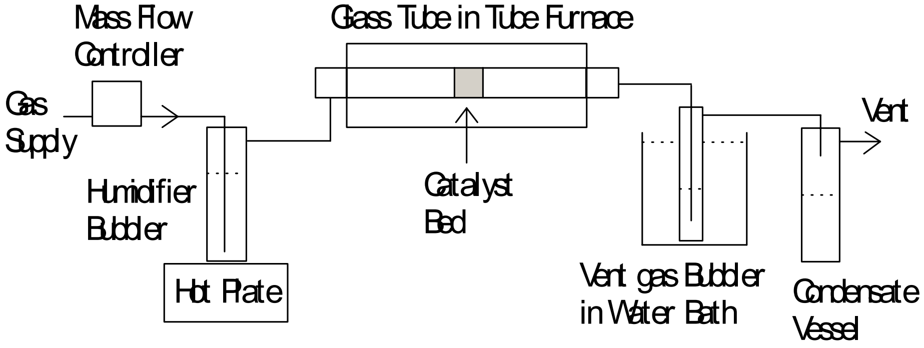


Figure 2. Flow diagram of the experiment set-up

Samples from the vent gas bubbler and the condensate vessel were collected and submitted for chloride analyses by ion chromatography (Dionex IC-DX500). De-ionized water samples were taken at the start and at the end of the experiment and submitted for chloride analysis by this same technique. The catalyst samples exposed to test conditions were analysed for chloride concentration by first treating the samples according to the BASF procedure and then analysing the samples for chloride using ion chromatography.

Test #3 was designed to determine if the Pd/Al_2O_3 catalyst, pre-exposed to HCl, would release HCl to the 1% O_2 and 2% H_2 mixture in N_2 under D_2-O_2 recombination conditions found in the MCGS. The first step in this experiment involved exposing the Pd/Al_2O_3 catalyst to HCl. The target concentration was 1000-ppm chloride. The results obtained from the analysis of two samples are 911 ppm and 876 ppm or 894 ppm on average. These values are close to the 1000-ppm target concentration. In the second part of this experiment the chloride contaminated catalyst was exposed to the 1% O_2 and 2% H_2 mixture in N_2 under D_2-O_2 MCGS recombination conditions.

In Test #4 the HCl contaminated Pd/Al_2O_3 catalyst was exposed to a 1% O_2-2% H_2 mixture in N_2 at the following temperatures: 200°C, 250°C, 300°C and 350°C. The purpose of this experiment was to see if HCl could be desorbed from the HCl contaminated catalyst at elevated temperatures.

3. Results

3.1 Chloride concentrations in the unexposed recombiner catalyst samples

The chloride concentrations in the 0.2 wt% and 0.3 wt% Pd/Al_2O_3 pellet catalysts were determined using the BASF procedure. The results are summarized below in Table 1. For each catalyst two samples were submitted for analysis. The data for each catalyst display good precision. The chloride concentration in the catalyst acquired directly from BASF is about 2.5 ppm. The chloride concentration found in the 3L Filters Ltd. catalyst is about 4.6 ppm. If both the BASF and 3L Filters Ltd. catalyst samples are fully reduced then the following explanation could account for the higher chloride concentration found in the 3L Filters Ltd. catalyst. It might be that different precursor salts were used to prepare these catalysts. According to Reference [2], the chloride content present in the catalyst displays a dependence on the nature of the precursor salt. Alternatively, the 3L Filters Ltd. catalyst is 0.3 wt% Pd while the catalyst obtained directly from BASF is 0.2 wt% Pd. It is reasonable to expect that the concentration of the chloride containing precursor salt in the impregnating solution might be higher during the manufacture of the 0.3 wt% Pd catalyst than for the manufacture of the 0.2 wt% Pd catalyst. This could explain the higher chloride concentrations observed for the 3L Filters Ltd. catalyst.

3.2 Test #1: Exposure of the Pd/Al_2O_3 catalyst to H_2 gas

The purpose of Test #1 and Test #2 is to see if the approximately 4.6 ppm chloride present in the 0.3 wt% Pd/Al_2O_3 catalyst can be released to a cover gas under simulated MCGS conditions.

Test #1 ran for a total of 33 days. The results from this test are summarized below in Table 2. In this test hydrogen flowed through the catalyst bed. As the results show, very low levels of chloride were reported in all of the water samples submitted for chloride analysis. Note that a total of four condensate water samples were submitted for chloride analysis. Only data for one sample is shown in the table. All four samples were found to have chloride concentrations that are less than 0.010 ppm. The highest concentration of chloride, 0.024 ppm, was found in the vent gas bubbler water sample. This value is just slightly larger than the value observed for the de-ionized water sample taken at the end of the experiment. These results suggest that flowing hydrogen through the catalyst bed did not remove chloride from the catalyst during the experiment. This conclusion is supported further by the following experimental data. At the completion of each test the chloride concentration in the exposed catalyst was determined using the BASF procedure. Table 3 shows the chloride concentrations determined for four catalyst samples following the completion of Tests #1, 2, 3 and 4. After Test #1, the chloride concentration in the two catalyst samples tested was found to be 5.1 ppm. This value, within experimental error, agrees well with the value of 4.6 ppm observed for the unexposed catalyst (see Table 1) indicating that no chloride was released from the catalyst to the cover gas during this experiment.

Table 1. Chloride concentrations in the fresh BASF and 3L Filters Ltd. recombiner catalysts

Catalyst	Sample	Catalyst Weight (g)	Solution Chloride Concentration (mg/L)	Catalyst Chloride Content (ppm)	Average Chloride Content (ppm)
BASF Catalyst - 0.2 wt% Pd/Al_2O_3	1-A	2.9253	7.4E-02	2.5	2.5
	1-B	2.8939	6.9E-02	2.4	
3L Filters Ltd. Catalyst – 0.3 wt% Pd/Al_2O_3	2-A	2.9388	1.4E-01	4.8	4.6
	2-B	2.9250	1.3E-01	4.4	

Table 2. Chloride concentrations in Test #1 water samples

Sample	Weight (g)	Chloride Concentration (mg Cl^-/L)	Chloride in Sample (mg Cl^-)
Vent Gas Bubbler	85.87	0.024	0.00206
Condensate #1	1023	<0.010	-
De-ionized Water – On Day 1		<0.010	-
De-ionized Water – On Day 33		0.016	

Table 3. Chloride concentrations in the catalyst samples used in Tests #1, 2, 3 and 4

Experimental Conditions	Sample	Catalyst Weight (g)	Solution Chloride Concentration (mg/L)	Catalyst Chloride Content (ppm)	Average Chloride Content (ppm)
Test #1, Catalyst exposed to H_2 gas for 33 days	3-A	2.9451	1.5E-01	5.1	5.1
	3-B	2.9183	1.5E-01	5.1	
Test #2, Catalyst exposed to 1% O_2 and 2% H_2 for 67 days	6-A	2.9203	1.4E-01	4.8	4.6
	6-B	2.9780	1.3E-01	4.4	
Test #3, Catalyst contaminated with HCl then exposed to 1% O_2 and 2% H_2	8-A	2.9374	2.8E+01	953	965
	8-B	2.9712	2.9E+01	976	
Test # 4, catalyst contaminated with HCl then exposed to 1% O_2 & 2% H_2 at 200°C to 350°C	9-A	2.9507	1.70E+00	58	55
	9-B	2.9403	1.50E+00	51	

3.3 Test #2: Exposure of the Pd/Al_2O_3 catalyst to a H_2-O_2 gas mixture

The chloride concentrations obtained from Test #2, a 67 day exposure of the 0.3 wt% Pd/Al_2O_3 catalyst to a 1% O_2 and 2% H_2 gas mixture in N_2, are presented in Table 4. Under the conditions described O_2 and H_2 will recombine to form H_2O. In this experiment, 12 water samples, taken at various stages during the experiment, were submitted for chloride analysis by ion chromatography. Two vent gas bubbler water samples, seven condensate water samples and three de-ionized water sample were submitted. The results for condensate water samples #2, #3, #4 and #5 are not given in the table but are identical to the results given for condensate water sample #1. The results are very similar to those reported above for Test #1 (Table 2) where the catalyst was exposed to H_2 gas. As the Test #2 data show, it is evident that the chloride that is present in the catalyst is not released during the experiment. At the completion of this experiment the chloride concentration in the exposed catalyst was determined using the BASF procedure. The results from two catalyst samples are given above in Table 3. The average concentration of chloride present in the catalyst is 4.6 ppm. This number is identical to the value reported above for the unexposed catalyst (Table 1), which shows that chloride was not removed from the catalyst during Test #2.

After running Test #2 for 40 days, the concentration of H_2 in the inlet and outlet gas streams was determined by gas chromatography. The inlet gas stream was found to contain 21,200 ppm H_2 while the outlet gas stream was found to contain 320 ppm H_2. This means that 98.5% of the H_2 initially present on the inlet side reacted with O_2 to form H_2O when it passed through the catalyst bed. This result for the conversion implies that the catalyst has not undergone deactivation during this experiment. The temperature rise that was measured across the catalyst bed was only 9°C. This is much lower than the expected temperature rise of approximately 170ºC that theoretically results from the recombination of 2% H_2 in N_2. It appears that most of the heat of reaction (equivalent to about 1.6 W) was lost to the glass tube and tube furnace walls.

Table 4. Chloride concentrations in Test #2 water samples

Sample	**Sample Weight (g)**	**Chloride Concentration (mg Cl^-/L)**	**Amount of Chloride in Sample (mg Cl^-)**
Vent Gas Bubbler #1	79.3	0.024	0.0019
Vent Gas Bubbler #2	79.62	<0.010	
Condensate #1	960.88	<0.010	-
Condensate #6	2315.7	<0.010	-
Condensate #7	4217.7	0.045	0.19
De-ionized Water – On Day 1		<0.010	-
De-ionized Water – On Day 30		<0.010	-
De-ionized Water – On Day 56		0.013	

3.4 Test #3: Exposure of the HCl contaminated Pd/Al_2O_3 catalyst to a H_2-O_2 gas mixture

The goal of Test #3 was to contaminate the recombiner catalyst with enough HCl to give a chloride concentration of 1000 ppm and then to see if this chloride could be desorbed from the catalyst by exposing it for 32 days to a 1% O_2-2% H_2 gas mixture in N_2 at 127°C. Presented in Table 5 are the chloride concentrations that were measured in the vent gas bubbler, condensate and de-ionized water samples by ion chromatography. The results show that the chloride concentration in the submitted samples is below the detection limit of the analytical instrumentation.

Table 5. Chloride concentrations in Test #3 water samples

Sample	**Sample Weight (g)**	**Chloride Concentration (mg Cl^-/L)**	**Amount of Chloride in Sample (mg Cl^-)**
Vent Gas Bubbler # 1	67.93	<0.010	-
Vent Gas Bubbler # 2	46.44	<0.010	-
Vent Gas Bubbler # 4	77.38	<0.020	-
Condensate # 1	1388.9	<0.010	-
Condensate # 2	1288.1	<0.010	-
Condensate # 4	2107.7	<0.020	-
De-ionized Water – On Day 1		<0.010	-
De-ionized Water – On Day 7		<0.010	-

At the completion of the experiment two samples of the exposed recombiner catalyst were treated according to the BASF procedure. The chloride concentrations for the two samples, as determined by ion chromatography, are presented in Table 3. The average chloride concentration is 965 ppm. This value is 71 ppm higher than the average chloride concentration of 894 ppm that was reported earlier for the unexposed catalyst sample. This implies that HCl contamination of the recombiner catalyst was not uniform.

The chloride concentrations presented in Table 5 for the water samples collected during Test #3 together with the chloride concentrations found on the exposed catalyst samples show that chloride was not desorbed from the recombiner catalyst during Test #3.

3.5 Test #4: Effect of temperature on the removal of HCl from the HCl contaminated recombiner catalyst

The experimental results from Test #3, carried out at 127°C showed that, the HCl contaminated recombiner catalyst did not release chloride during the time it was exposed to a 1% O_2-2% H_2 gas mixture in N_2. There are studies in the open literature which have demonstrated that HCl desorption from alumina surfaces is temperature dependent [3-5]. Thus, it was of interest to see if the chloride present on the contaminated recombiner catalyst could be removed at elevated temperatures. To study the effect of temperature Test #4 was carried out at the following temperatures: 200°C, 250°C, 300°C and 350°C.

Table 6: Chloride concentrations in Test #6 water samples

Temperature (°C)	Time at Temperature (Days)	Vent Gas Bubbler Water		Condensate Water	
		Weight (g)	Chloride Concentration (mg Cl^-/L)	Weight (g)	Chloride Concentration (mg Cl^-/L)
200	3	65.15	<0.0020	305.19	<0.0020
250	2	82.77	<0.0020	200.28	<0.0020
300	2	75.83	0.077	198.42	<0.0020
350	3	74.58	2.5	302.46	<0.0020

The chloride concentrations in the vent gas bubbler and condensate water samples are presented in Table 6 for the four temperatures studied. The chloride concentrations in these samples, as determined by ion chromatography suggest that, chloride was not released from the recombiner catalyst at the two lowest temperatures studied, 200°C and 250°C. At both of these temperatures the chloride concentration in the vent gas bubbler and condensate water samples are below the detection limit of the ion chromatography instrumentation. According to the results presented in Table 6, chloride was released from the recombiner catalyst at the two highest temperatures investigated. The chloride concentration in the vent gas bubbler water samples at 300°C and 350°C are 0.077 mg L^{-1} and 2.5 mg L^{-1}, respectively. This corresponds to a catalyst chloride content of 0.6 ppm and 18.5 ppm, respectively. For each temperature reported in Table 6, the chloride concentration in the condensate water was found to be below the detection limit of the analytical instrumentation. Even at the two highest temperatures, where chloride was observed in the vent gas bubbler water samples, no chloride was found in the condensate water samples. This shows that the vent gas bubbler is efficient at removing chloride from the gas stream.

At the end of this experiment when the recombiner catalyst was removed from the Pyrex glass tube it was treated according to the BASF procedure and two samples were submitted for chloride analysis by ion chromatography. The results from the analysis are presented above in Table 3. The chloride concentration present in the two samples is similar with the average value being 55 ppm. The chloride concentration on the HCl contaminated recombiner catalyst was found to be as low as 876 ppm and as high as 976 ppm. According to the experimental data obtained from Test #4, the total amount of chloride released from the recombiner catalyst is 19 ppm. Based on the HCl concentration range given above there is an inventory of at least 802 ppm to 902 ppm chloride that is not accounted for in this experiment.

It was suggested that the missing HCl inventory might have been consumed in a chemical reaction or adsorbed onto components of the experimental apparatus that are downstream of the recombiner catalyst bed. The components that are downstream from the catalyst are all fabricated from Pyrex glass. This would include the glass wool used to hold the catalyst bed in place, the glass tube furnace, glass thermowell and glass vent gas bubbler. All of these components were rinsed with de-ionized water. The rinse water was collected in a beaker and samples taken and submitted for chloride analysis by ion chromatography.

The results from ion chromatography confirmed the presence of chloride. The chloride concentration in the rinse water was found to be 70 mg L^{-1}. This value can account for 952 ppm of chloride in the catalyst. Adding this value to the 19 ppm reported to be in the vent gas bubbler water and the 55-ppm remaining in the catalyst following the experiment, gives the total chloride concentration in the catalyst as 1026 ppm. This value agrees well with the target HCl concentration of 1000 ppm. However, it does lie outside of the HCl concentration range that was identified above. The fact that it lies outside of this range is further support for the view that HCl contamination of the recombiner catalyst was not uniform.

The wash water sample submitted for chloride analysis by ion chromatography was also submitted for Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) in order to identify the cationic species that is associated with the chloride. According to the ICP-AES analysis, the dominant species present in the rinse water sample is Na. Sodium is present at a concentration of 49 ±4 mg L^{-1}. If sodium chloride, NaCl, is the compound that was present on the glass components of the experimental apparatus then this value can be used to calculate the chloride concentration that would be expected based on the chemical formula for sodium chloride. The experimental error associated with the Na concentration is reported to be ±4 mg L^{-1} which suggests the sodium concentration lies within the range 45 mg L^{-1} to 53 mg L^{-1}. This gives the chloride concentration range as 69 mg L^{-1} to 82 mg L^{-1}. The chloride concentration from ion chromatography was found to be 70 mg L^{-1}. The value of 69 mg L^{-1} reported for the lower limit of the sodium concentration range is in excellent agreement with the chloride concentration of 70 mg L^{-1} consistent with the formation of NaCl during the experiment.

The experimental results presented in this section show that HCl was almost completely desorbed from the recombiner catalyst at elevated temperatures. It is being tentatively suggested that most of the HCl that desorbed from the recombiner catalyst reacted with the high surface area Pyrex glass wool that held the catalyst bed in the middle of the glass tube furnace. The reaction with HCl resulted in the formation of NaCl.

4. Discussion

The experimental results have shown that chloride is present on the 0.3 wt% Pd/Al_2O_3 recombiner catalyst, received from 3L Filters Ltd., at a concentration approximately equal to 4.6 ppm. On the catalyst obtained directly from BASF, 0.2 wt% Pd/Al_2O_3, the chloride concentration was found to be 2.5 ppm. This chloride is present as an impurity in both catalyst samples. It was introduced during the impregnation process. The results from Test #1 and Test #2, which were carried out by exposing the recombiner catalyst to H_2 gas and to a 1% O_2-2% H_2 in N_2 gas mixture, respectively, at 127°C, have shown that this chloride is not removed from the catalyst under the experimental conditions employed. Before the chloride could be transferred to the gas stream, it would have to undergo a reaction to form a volatile molecular species. In Test #1 it was thought that chloride might be removed from the catalyst as HCl following a reaction with hydrogen gas. This reaction was not observed to take place since in this test, and in Test #2, chloride was not observed in the water samples that were collected during the experiments. It can be concluded that in both tests the catalyst was able to retain chloride.

There is reason to believe that the MCGS operating conditions under which Test #1 and Test #2 were carried out at may not have been aggressive enough in terms of temperature to remove the chloride impurities that remain on the catalyst following the impregnation process. For example, in Reference [2] it was reported that when a reduced sample of a Pd/Al_2O_3 catalyst was heated at

300°C under wet flowing argon the chloride content of the catalyst decreased by two-thirds of the initial value. Here a temperature of 300°C was required to cause a change in the chloride concentration. The work of Roth et al. [6] also demonstrates the need for elevated temperatures to remove chloride. These authors reported that chloride could be completely removed from a Pd/Al_2O_3 catalyst in the form of HCl at 600^oC. The data in References [2, 6] show that chemical reactions at high temperatures are required in order to remove the chloride impurity from a Pd/Al_2O_3 catalyst. Thus, it can be concluded that, under normal MCGS conditions, chloride should be retained by the recombiner catalyst and not carried over to the moderator cover gas.

In Test #3 the 0.3 wt% Pd/Al_2O_3 recombiner catalyst was contaminated with HCl. This contaminated catalyst was exposed to the same experimental conditions as the catalyst used in Test #2. The results were the same showing that the recombiner catalyst was able to retain chloride (HCl) during the experiment.

HCl can be desorbed from alumina surfaces over a wide temperature range [5]. In order to confirm this experimental observation Test #4 was carried out. In this experiment a fresh sample of the HCl contaminated catalyst was exposed to a 1% O_2-2% H_2 gas mixture in N_2 at 200°C, 250°C, 300°C and 350°C. The water samples collected at 200°C and 250°C did not contain any chloride. However, chloride was found to be present in the vent gas bubbler water samples collected during the experiments carried out at 300°C and 350°C.

The results from Test #4 also showed that most of the chloride that was released from the catalyst was not collected in the vent gas bubbler water but reacted with the Pyrex glass components of the experimental apparatus downstream from the catalyst bed. It was tentatively suggested that the HCl reacted with the Pyrex glass wool resulting in the formation of NaCl.

Apparently there is very little increase in temperature observed across the recombiners despite the fact that the recombination reaction is exothermic. It has been suggested that the energy released by the recombination reaction is being consumed by the evaporation of water that may be present in the recombiners. Condensate from the demister could be the source of this water. A rise in temperature of 69°C is expected for each 1% of D_2, 100% recombination of D_2 assumed. Although stations report very little temperature rise across the recombiners, experiments carried out at AECL have shown that there could still be local heating of the dry catalyst bed during the recombination reaction. A direct measurement of the catalyst bed temperature during the recombination reaction is not taken at stations. At Bruce-B the inlet temperature is measured between the flame arrester and the recombination units while the outlet temperature is measured between the recombination units and the heat exchangers. In a test carried out at AECL the temperature of the catalyst bed was measured during the 1% O_2-2 % H_2 recombination reaction. The largest rise in temperature that was recorded is 45°C. This temperature was recorded at the edge of the catalyst bed and is considerably smaller than the approximately 170°C temperature rise that is theoretically predicted for the recombination of a 1% O_2-2 % H_2 mixture in N_2. Based on this finding it is evident that the recombination reaction does not produce significant local heating of the recombiner catalyst. There is therefore no reason to believe that temperatures approaching 300°C will be observed in the recombination units in service at Bruce-B or other CANDU stations. It is being suggested that if HCl is absorbed onto the recombiner catalyst it will not be desorbed but retained by the catalyst under normal MCGS operating conditions.

5. Conclusions

The experimental results from this study demonstrate that chloride present in the Pd/Al_2O_3 pellet catalyst as a result of the impregnation process is not carried over to a cover gas under normal MCGS operating conditions.

HCl has been identified as a chloride containing species that may be found as a contaminant in the MCGS. In addition, HCl could be produced in the recombination units by catalytic decomposition reactions of organic chlorine containing compounds found in degreasers. It was shown in the present study that adsorbed HCl can be desorbed from the catalyst and carried over to a cover gas if the catalyst temperature is 300°C or higher. During normal MCGS operation the temperature of the recombiner catalyst does not reach such a high value. Therefore, HCl that is picked up by the catalyst will be retained and not carried over to the moderator cover gas under normal MCGS conditions.

6. References

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