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MITIGATION OF HYDROGEN BY OXIDATION USING NITROUS OXIDE AND NOBLE METAL CATALYSTS

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7. Abstract

This test studied the ability of a blend of nuclear-grade, noble-metal catalysts to catalyze a hydrogen/nitrous oxide reaction in an effort to mitigate a potential hydrogen (H_2) gas buildup in the Hanford Site Grout Disposal Facility. For gases having H_2 and a stoichiometric excess of either nitrous oxide or oxygen, the catalyst blend can effectively catalyze the H_2 oxidation reaction at a rate exceeding 380 μmoles of H_2 per hour per gram of catalyst (μmol/h/g) and leave the gas with less than a 0.15% residual H_2 concentration. This holds true in gases with up to 2.25% water vapor and 0.1% methane. This should also hold true for gases with up to 0.1% carbon monoxide (CO) but only until the catalyst is exposed to enough CO to block the catalytic sites and stop the reaction. Gases with ammonia up to 1% may be slightly inhibited but can have reaction rates greater than 250 μmol/h/g with less than a 0.20% residual H_2 concentration.

The mechanism for CO poisoning of the catalyst is the chemisorption of CO to the active catalyst sites. The CO sorption capacity (SC) of the catalyst is the total amount of CO that the catalyst will chemisorb. The average SC for virgin catalyst was determined to be 19.3 ± 2.0 μmoles of CO chemisorbed to each gram of catalyst (μmol/g). The average SC for catalyst regenerated with air was 17.3 ± 1.9 μmol/g.

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EXECUTIVE SUMMARY

This test studied the ability of a blend of nuclear-grade, noble-metal catalysts to catalyze a hydrogen/nitrous oxide reaction in an effort to mitigate a potential hydrogen (H_2) gas buildup in the Hanford Site Grout Disposal Facility. The catalyst studied was a 50-50 blend of Deoxo (a trademark of the Engelhard Corporation) nuclear catalyst type A16430 and Atomic Energy of Canada Limited hydrophobic catalyst type 85-42.

For gases having H_2 and a stoichiometric excess of either nitrous oxide (N_2O) or oxygen (O_2), this catalyst blend can effectively catalyze the H_2 oxidation reaction at a rate exceeding 380 μmoles of H_2 per hour per gram of catalyst (μmol/h/g) and leave the gas with less than a 0.15% residual H_2 concentration. This holds true in gases with up to 2.25% water vapor and 0.1% methane. This should also hold true for gases with up to 0.1% carbon monoxide (CO) but only until the catalyst is exposed to enough CO to block the catalytic sites and stop the reaction. Gases with ammonia up to 1% may be slightly inhibited but can have reaction rates greater than 250 μmol/h/g with less than a 0.20% residual H_2 concentration. Higher reaction rates with lower conversions are possible, but were not quantified in this test because the blend's catalytic ability exceeded the equipment's ability to feed the gas mixtures to the reactor.

The mechanism for this CO poisoning of the catalyst is the chemisorption of CO to the active catalyst sites. The CO sorption capacity (SC) of the catalyst is the total amount of CO that the catalyst will chemisorb. The average SC for virgin catalyst was determined to be 19.3 ± 2.0 μmoles of CO

chemisorbed to each gram of catalyst (µmol/g). The average SC for catalyst regenerated with air was 17.3 ± 1.9 µmol/g.

Because the catalyst will work effectively until it is nearly fully loaded with CO, the catalyst bed can be oversized to scavenge CO for several years. This will keep some of the catalyst available for the H_2 oxidation reaction for many years. When the catalyst is almost completely poisoned by CO, it can then be regenerated by exposure to air, either by removing the bed from the sump or by an insitu catalyst regeneration method where an airline is installed in catalyst bed and air is flushed over the catalyst without removing it from the sump.

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MITIGATION OF HYDROGEN BY OXIDATION USING NITROUS OXIDE AND NOBILE METAL CATALYSTS

1.0 INTRODUCTION

The Hanford Site Grout Disposal Facility is designed to store Hanford Site low-level radioactive waste. This grout-waste mixture is expected to generate hydrogen (H_2) as well as other gases. If the gas generation rate is too high, H_2 concentration levels in the gas spaces of the grout vaults may exceed the lower flammability limit (LFL). Hydrogen recombiner catalysts (HRC) may provide a method of reducing this flammability hazard.

This report presents data obtained from testing an HRC's performance in oxidizing H_2 using nitrous oxide (N_2O) under various conditions. This data can be used to size H_2 oxidation beds for the grout vaults as well as define operating parameters for these beds. This testing was directed by the *Hydrogen Recombiner Catalyst Performance and Durability Test Plan* (Britton 1993a) and was funded by Grout Technology in support of the *Grout Treatment Facility Safety Analysis Report* (WHC 1992).

1.1 BACKGROUND

The Hanford Site Grout Disposal Facility may be used to store Hanford Site low-level radioactive waste. Radiolysis and chemical reactions occurring in the grout are expected to cause the generation and release of H_2 and N_2O (Roblyer 1993). Other gases such as carbon monoxide (CO), methane (CH_4), and ammonia (NH_3), which are products of organic degradation, may also be in the gas stream. These gases will migrate from the vault catch basin, through the drain line, into the leachate sump, and to the atmosphere through the leachate sump vent. The driving forces for this gas migration in and out of the sump are advection, diffusion, and atmospheric pressure changes (Roblyer 1993). Gas concentrations in the sump will depend on the grout's gas generation rate and the migration rate of gases from the sump. If the H_2 generation rate is too high, the H_2 concentration level in the sump could exceed the LFL, potentially causing an unacceptable scenario. See Figures 5-5c, 5-9c, and 5-10c in Roblyer (1993). One solution is to use a HRC to lower the H_2 concentration to an acceptable range.

Two possible oxidants for the H_2 oxidation reaction in the sump are oxygen (O_2) and N_2O. The availability of O_2 for the H_2 oxidation reaction will depend on the H_2 generation rate and the migration rate of outside air into the sump. If there is not enough air supplied to the sump, an O_2 deficient atmosphere will occur and another compound will have to be used as the oxidant. It is estimated that the ratio of N_2O to H_2 produced by the grout will be a minimum of 1:1 and as high as 2.4:1 (Roblyer 1993). Therefore, N_2O will always be available as an oxidant for the reaction.

Previous work on HRCs at Hanford was performed by J. O. Henrie, D. J. Flesher, K. L. Meshako, B. D. Bullough, and others in support of the cleanup efforts at the damaged Three Mile Island (TMI) Number Two Reactor (Henrie et al. 1986, Meshako and Bullough 1985). This work studied the reaction of H_2

and O_2 in stoichiometric quantities to form water (H_2O) when catalyzed by platinum or palladium catalysts and resulted in recommendations on the type of catalyst and catalyst bed dimensions used in this test.

I. I. Tret'yakov and B. R. Shub demonstrated that a heated platinum wire, purified in a high vacuum, would catalyze both the H_2/O_2 and the H_2/N_2O reactions. Furthermore, both these reactions can be explained by similar kinetic equations and have similar reaction mechanisms (Tret'yakov et al. 1967, Tret'yakov and Shub 1970). Because of these similarities between the H_2/O_2 and H_2/N_2O reactions, some of Henrie's recommendations (Henrie et al. 1986) for catalysts and catalyst beds in H_2/O_2 atmospheres were in this test.

1.2 OBJECTIVE

The Chemical Engineering Laboratory (CEL) conducted performance and sorption capacity tests on a blend of HRCs. The primary objective of the performance test was to determine whether the catalyst blend is effective in catalyzing the H_2 oxidation reaction using N_2O as the oxidant. A second goal was to determine whether the catalyzed reaction rate is affected by the presence of several gas species that may also be produced by reactions in the grout vault. A recommendation on an appropriate catalyst bed size for the grout vault leachate sump could then be made, based on the results from this test.

The test plan (Britton 1993a) described a durability test designed to evaluate catalyst deactivation by measuring the change in the catalyst's performance over a period of one year. Conclusions on CO_2 poisoning from the performance test indicated this durability test would not provide relevant information and therefore, was not performed. The reasons for this are described in Section 5.6. Instead of the durability test, a test was designed to answer questions about CO chemisorbing onto the active catalyst sites.

The sorption capacity test was used to show the relationship between the decrease in the H_2/N_2O reaction rate and the amount of CO chemisorbed onto the catalyst. This test was then used to determine the CO sorption capacity of the catalyst, and to determine a method by which the catalyst could be regenerated for future use.

1.3 SCOPE

The performance test involved determining the rate of the H_2/N_2O reaction in the presence of a blend of two nuclear-grade catalysts. The catalyst blend was that recommended in Henrie et al. (1986) for use in shipping and storing wet radioactive waste. Because of time constraints placed on this project, the recommendation in Henrie et al. (1986) on catalyst bed composition was used and no investigation of different catalysts or blend ratios was performed.

The reaction rate is a function of many variables, two of which are H_2 and N_2O concentrations. The LFL for a 1:1 ratio of H_2 and N_2O in air is 4 volume percent H_2 (Weis 1993). The required design safety limit for H_2 concentration in the sump is 25 percent of the LFL or 1 percent (NFPA 69, 1992). For the H_2/N_2O reaction to completely consume the H_2, the ratio between N_2O and H_2 must be above one. Therefore, only reaction rates at H_2 concentration levels between 0 and 1 percent and N_2O to H_2 ratios greater than or equal to 1 were investigated.

These tests were not intended to provide a kinetic model of the reaction rate. They were designed to determine which variables have the greatest effect on the reaction rate and to define a reaction rate that could be used to size the catalyst bed for the sump.

These tests assumed the sump will act as a mixed flow reactor with a well-mixed gas. Therefore, these tests do not account for diffusion or concentration gradients in the leachate sump. Additionally, the catalysts do not function while submerged in H_2O. This should be avoided when a catalyst bed is designed and placed in the sump. The effects of submerging the catalyst in liquid were not investigated.

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2.0 TEST ENVIRONMENT AND EQUIPMENT

In the tests, a feed mixture gas was introduced into the bottom of a reactor vessel containing a bed of HRC. The gases flowed upward through the reactor vessel and out a tube at the top. Both the inlet and outlet gases were sampled to determine the gas compositions. From this, the reaction rate and the sorption capacity were determined.

2.1 CATALYST

The catalyst bed was a 50-50 blend of Engelhard Deoxo[1] nuclear catalyst type A16430 and Atomic Energy of Canada Limited (AECL) hydrophobic catalyst type 85-42 (Henrie et al. 1986). The Engelhard catalyst, a palladium-on-alumina media, effectively catalyzes the H_2/O_2 reaction, but only when the catalyst media is dry. When wet, the Engelhard media becomes very inefficient. The AECL catalyst is a hydrophobic, platinum-on-silica/alumina media. Wet or dry, the AECL media is not as effective as dry Engelhard media, but is more effective than the wet Engelhard media. When the mixed bed becomes wet, the AECL media continues to catalyze the H_2 oxidation reaction, providing enough heat to evaporate the H_2O from the adjacent Engelhard catalyst. Once dry, the Engelhard catalyst then performs the majority of the catalysis.

The Engelhard catalyst pellets are fairly uniform in shape. Each pellet is a cylinder having an average diameter of 3.25 mm and an average length of 3.6 mm. The AECL catalyst pellets are rough spheres approximately 6.5 mm in diameter. This blend of catalysts has a bulk density of approximately 1 g/mL.

2.2 ENVIRONMENT

The hydrogen recombiner catalyst tests were conducted at Westinghouse Hanford Company's (WHC) Chemical Engineering Laboratory in the 2703E Building in the 200E Area at the U.S. Department of Energy's Hanford Site. The laboratory ventilation system, which includes both heating and air conditioning, moderated the environmental temperature between 13 and 26°C.

2.3 EQUIPMENT

The flowsheet for the HRC tests is shown in Figure 2-1. All the tubing in the apparatus was ¼-in., 304L stainless steel tubing. All the valves (except V-2 and V-3) are Matheson stainless-steel, greaseless ball-valves.

Two nearly identical test apparatuses were constructed on unistrut carts. Each cart held six gas cylinders. The gases flowed through pressure regulators (PR-1 through PR-6) that reduce the gas pressure to 25 psig. Matheson series 6103 flash arrestors (FA-1 through FA-4) made of brass and butyl rubber were placed after the regulators on the H_2, CO, CH_4, and NH_3

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[1] Deoxo is a registered trademark of the Engelhard Corporation.

lines to protect the gas cylinders from a rapid burn or detonation[2] in the downstream equipment, if one should occur. These flash arrestors act as check valves under normal operating conditions. If a flashback were to occur in the downstream equipment, the flash arrestors would check the reverse flow and stop the gas supply. The flash arrestors would then need to be manually reset before operation could be continued. Flash arrestors were also situated in the line between F-1 and the reactor (FA-5), and in the offgas line as it connected to the CEL exhaust system (FA-6). These would protect the metering equipment and the reactor from a rapid burn or detonation in the downstream equipment, if one should occur.

The gas flowrates were controlled by Omega FMA-100 series mass flow controllers (FC-1 through FC-6), all of which are calibrated for air at 20°C. These flow controllers passed the gas stream through a heated tube and measured the heat required to raise the gas temperature by 18°C. By comparing the temperature change to heat input, the mass flow controller operated its magnetic valve to control the mass flowrate. Ratios between the heat capacity of the controlled gas and air were used to calculate the actual mass flowrate. The flow controllers displayed the flowrate as volumetric flowrate at standard atmosphere and pressure. Omega recommended a 138-kPa (20-psi) drop across the flow controller for optimum control.

The apparatus was designed so that after the feed gases had mixed together the feed gas mixture could then be diverted to a humidifier, where the H_2O concentration is increased by bubbling it through a column of deionized H_2O. The gas enters the humidifier at the bottom and is forced through a sintered filter to diffuse the gas into tiny bubbles. Figure 2-2 gives details of the humidifier.

The apparatus was contingently constructed with a heat exchanger. The gases could flow into the heat exchange from the flowmeters or from the humidifier. Because temperature adjustment of the feed gas was not needed, this heat exchanger was not used in these tests. Next, the temperature, pressure, and flowrate of the feed mixture were taken by a thermocouple (T-2), a pressure gauge (P-2), and a rotameter (F-1).

The feed mixture then flowed into the reactor. The reactor was a 7571-mL (2-gal), Parr series 4660 general purpose bomb. It had a 15.2-cm (6-in.) inner diameter, a 43.7-cm (17.2-in.) inner depth, and an all 316 stainless steel construction. The reactor had two ¼-inch inlet/outlet ports, a pressure gauge (P-3), a ¼-inch inconel rupture disk with a 6,900-kPa (1,000-psig) burst rating, and a thermowell. The incoming gas was directed to the bottom of the reactor by an injection tube that extended from the inlet port to within 5 cm of the bottom of the reactor.

The catalyst bed was made of two concentric cylinders of 316 stainless steel wire screen with the catalyst contained in the annular region. The catalyst bed slipped into the reactor and allowed the gas to contact the catalyst on the inside surface of the catalyst bed. The catalyst bed was 14.9 cm (5.875 in.) in outer diameter and 38 cm (15 in.) high with the

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[2] No flammable or detonable gas mixtures were used in these tests, although the test apparatus was contingently designed to operate using detonable gas mixtures.

catalyst bed 1 cm (0.39 in.) thick (see Figure 2-3). The recommended catalyst bed thickness was 1 cm with the catalyst exposed to the gas though an 8x8-mesh (8 wires/lin.in.) screen using 0.035-in.-dia. wire (Henrie et al. 1986). These catalyst beds held 44 ± 4 g of catalyst per cm of catalyst bed height. The catalyst bed in Apparatus 2 was shortened and elevated 15.2 cm (6 in.) from the bottom of the reactor. This was done so the feed mixture entering through a tube near the bottom of the reactor would have time to mix with resident gas in the bottom of the reactor vessel before flowing past the catalyst bed. This was used for the performance test runs using Apparatus 2 and all the sorption capacity test runs.

Two arrays of thermocouples were placed in the reactor. The first array consisted of four thermocouples brazed into a Cajon[3] plug, which was inserted into the reactor through the thermowell hole. These thermocouples were adjusted to slide into sheaths of tubing placed in the catalyst bed. The sheaths for thermocouples T3, T4, T5, and T6 ended 2 cm, 10 cm, 16.7 cm, and 28.7 cm from the bottom of the catalyst bed. Each thermocouple was long enough to extend past the end of its sheath by 0.5 to 1 cm when installed and was in contact with catalyst, assuming enough catalyst was placed in the bed to cover the ends of the thermocouple sheaths.

The second array of thermocouples consisted of four type K thermocouples brazed into a Swagelok[4] cap and inserted into the reactor through a tee installed between the reactor and the rupture disk. The thermocouples were adjusted to sit near the center line of the reactor and at the same levels thermocouples T3, T4, T5, and T6 were at, respectively.

Gas samples were taken on the inlet and outlet tubes from the reactor by diverting the gas flow through gas sample cylinders (GSC) using valves V-7, V-8, V-11, and V-12. The GSCs were made of 304L stainless steel and had a 150 mL internal volume. All the gas samples taken for the performance test were taken in the GSC. Most of the samples analyzed for the sorption capacity test were taken in Tedlar[5] bags.

The two apparatuses used the same Whittaker series 800 H_2 detector (HA-1), which employed a diffusion limited electrochemical cell to measure the H_2 concentration. It was used as an operational tool to assist in controlling the H_2 concentration in the reactor. Valves V-5 and V-14 allow the inlet and outlet gas streams to be diverted into HA-1. V-19 opened up a line of nitrogen (N_2) to purge the analyzed gases out of the analyzer sample chamber. Whittaker technical representatives indicated that nitrogen oxides, including N_2O, may interfere with accurate determination of the H_2 concentration and may also degrade the detector's H_2 permeable membrane, leading to the detector's failure. No interference from N_2O was observed throughout the test. Furthermore, no degradation was observed in the detector's ability to detect H_2.

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[3] Cajon is a registered trademark of the Cajon Company.

[4] Swagelok is a registered trademark of the Crawford Fitting Company.

[5] Tedlar is a registered trademark of the E. I. DuPont De Nemours and Company.

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Figure 2-1. Hydrogen Recombiner Catalyst Test Apparatus.

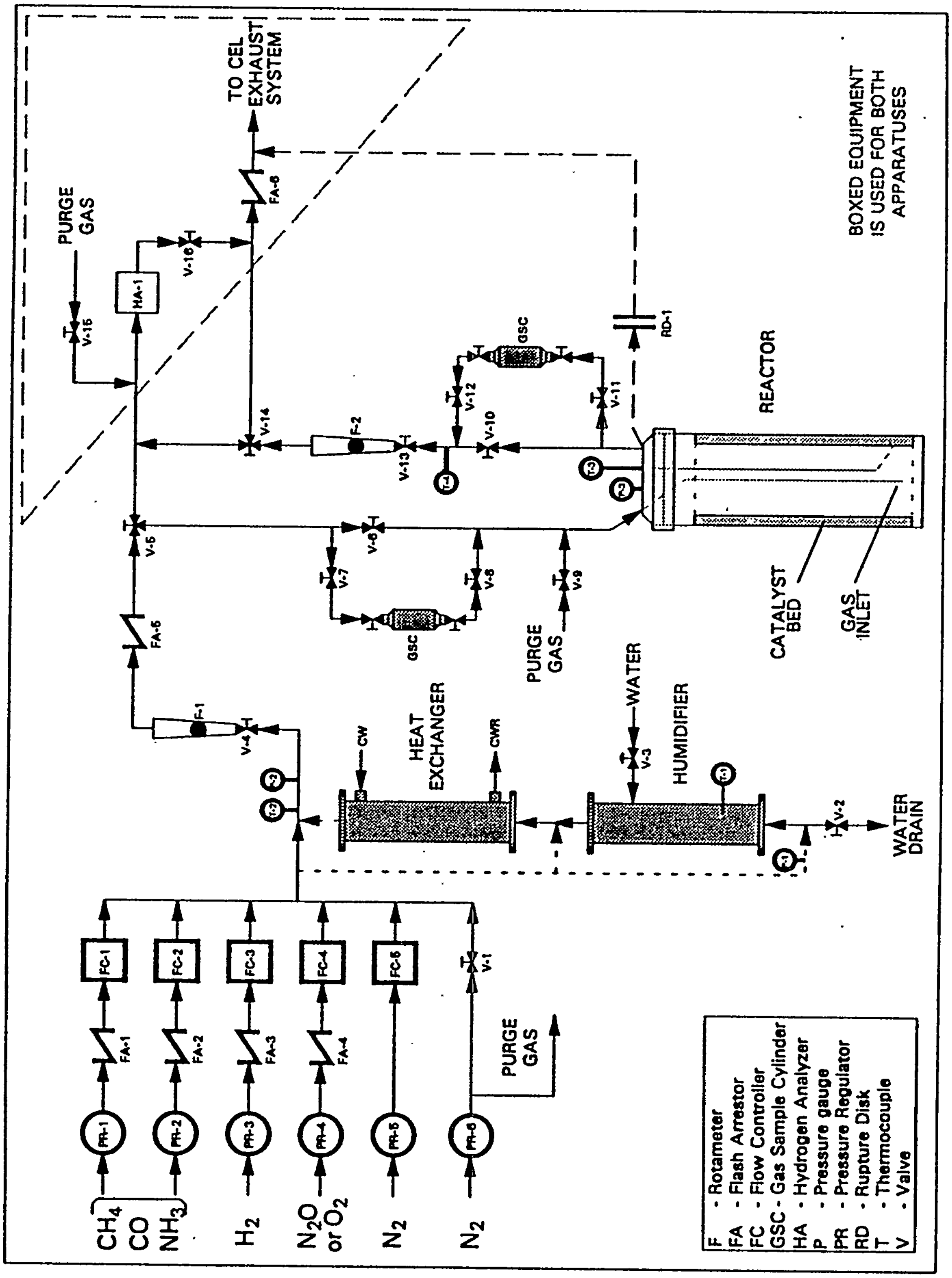


Figure 2-2. HRC Humidifier Schematic.

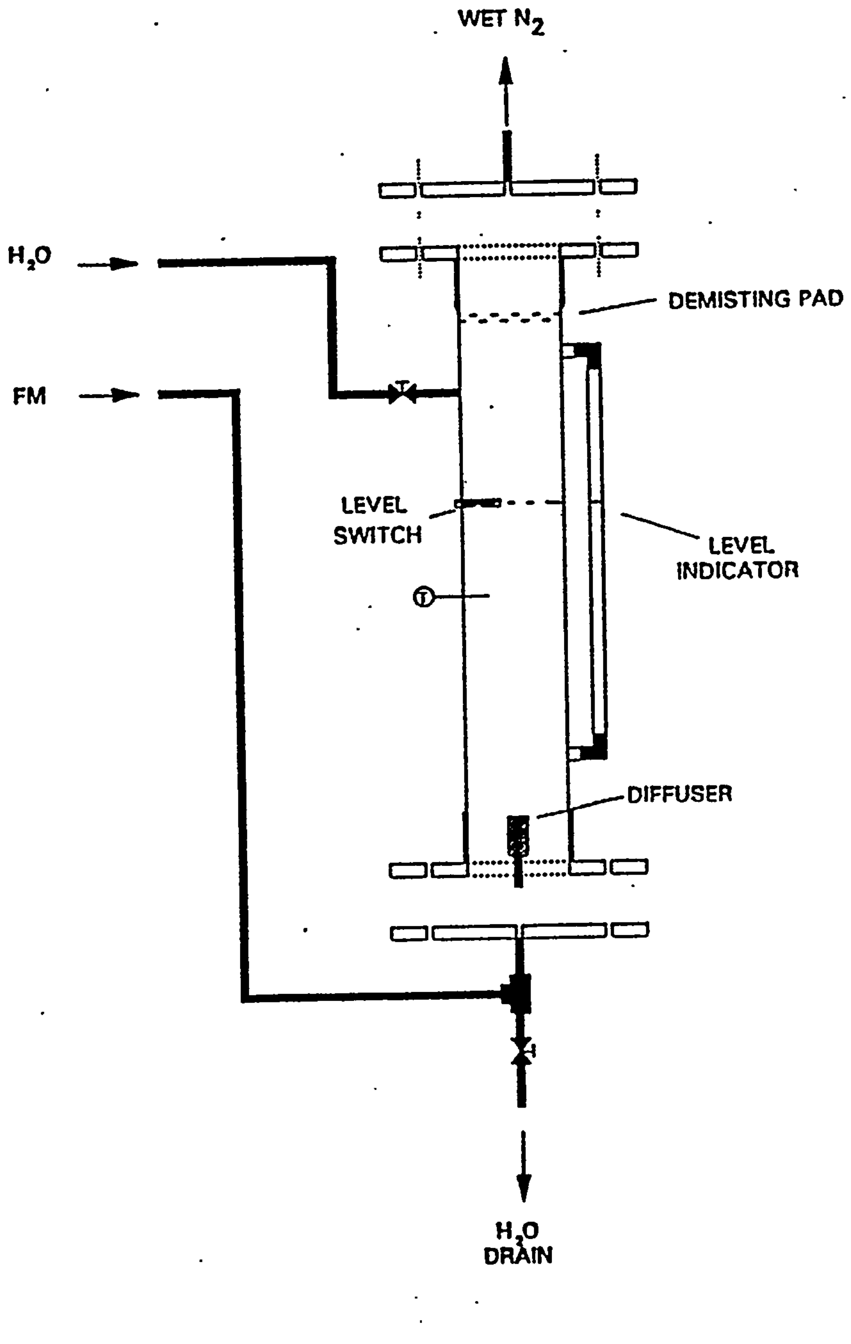
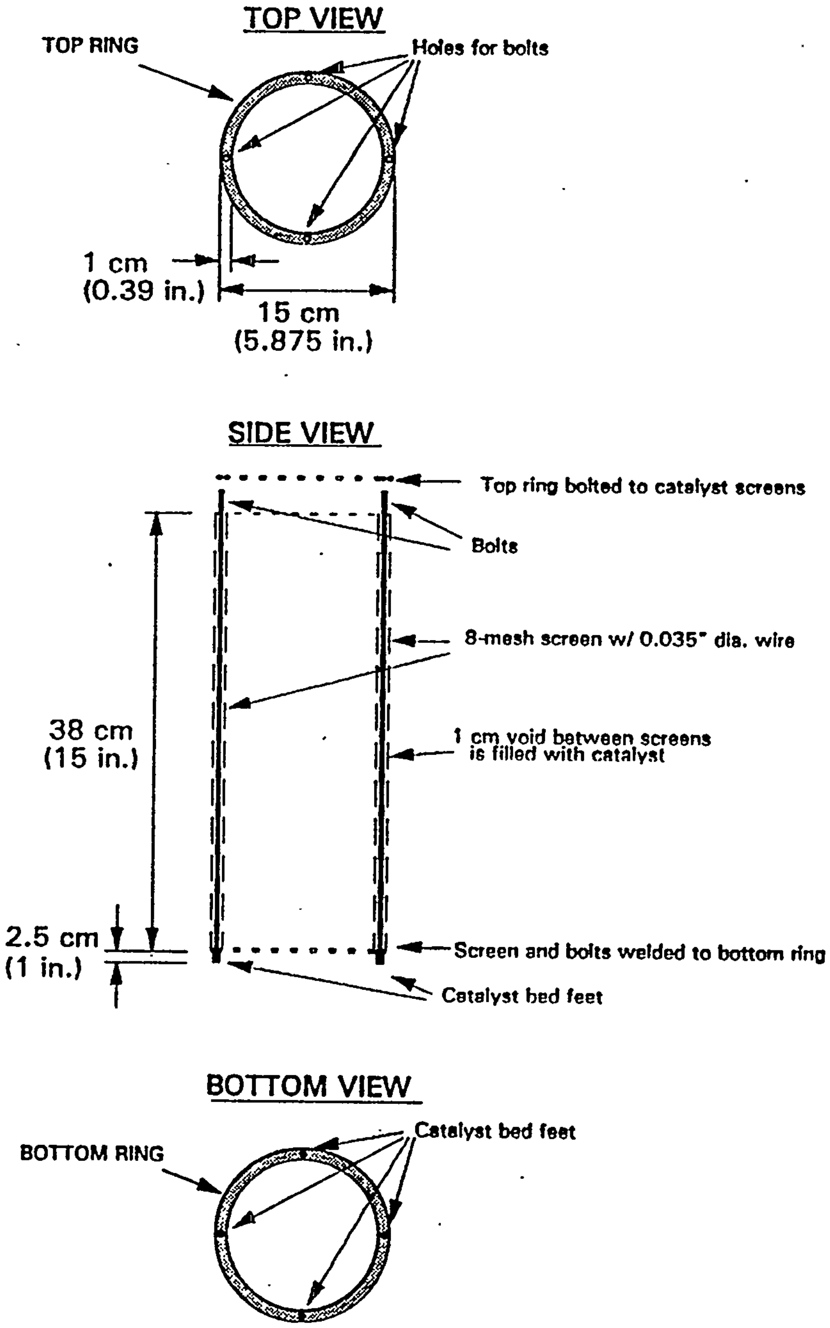


Figure 2-3. HRC Catalyst Bed Schematic.



2.4 QUALITY ASSURANCE

The feed gases were purchased with a certificate of analysis. These can be seen in Appendix G of the supporting data document (Britton 1994). The gases were certified by the vendor, Matheson Gas Products, Inc., to be the following.

- 4.07% H_2 in N_2
- 3.87% N_2O in N_2
- 2.06% O_2 in N_2
- 0.50% CO in N_2
- 0.505% CH_4 in N_2
- 5.05% NH_3 in N_2.

The N_2O was also purchased from Matheson Gas Products and had a minimum purity of 99.995 percent. The pure N_2 was purchased from WHC's general supplies warehouse as 99.997 percent pure. All the gases were analyzed individually using a mass spectrometer to ensure they met their stated purity. The Whittaker series 800 H_2 detector was calibrated using the 4.07 percent H_2 gas mixture.

The calibration of the Omega FMA-100 series mass flow controllers was checked using a Bois DC-1SC Dry Cal flow calibrator. The Bois flow calibrator was, in turn, checked by the WHC Standards Laboratory. Appendix H in the supporting data document (Britton 1994) contains the flowmeter calibration check information. Appendix I in the supporting data document (Britton 1994) contains the WHC Standards Laboratory Physical and Electrical Report on the Bios calibrator.

The accuracy of the thermocouples was checked against two calibrated mercury thermometers. These thermometers had the calibration codes: HEDL 809-79-01-017 and HEDL 809-79-01-018. The offgas thermocouples from Apparatuses 1 and 2 had a zero error at 21°C and read a lower temperature than the HEDL # 809-79-01-017 thermometer by no more than 2°C at the 68 to 74°C temperature range. The other thermocouples read a lower temperature than the HEDL # 809-79-01-018 thermometer by no more than 2°C at the ambient temperature range of 20 to 21°C and read as much as 8°C less than the HEDL # 809-79-01-018 thermometer in the 48 to 52°C range. Because the temperature in the system never rose more than a few degrees above the ambient temperature, the calibration check at ambient conditions was satisfactory.

The mass of the catalyst was measured on a Mettler AE 260 DeltaRange[6] scale. The calibration of this scale is checked annually by WHC Hanford Standards Laboratory (Standards Lab No. 815-06-01-005).

The system was checked for leaks by increasing the pressure to greater than 90 psi, valving the system off from the pressure source and all outlets, and then watching the pressure in the system decay. Pressure decays that decreased less than 2 psi in 15 minutes were considered satisfactory.

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[6] DeltaRange is a registered trademark of Mettler Instrumente AG.

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3.0 PERFORMANCE TEST DESCRIPTION

In the performance test, a feed mixture gas was metered into a reactor vessel containing a bed of HRC. Both H_2 and N_2O (or O_2) chemisorbed onto active catalytic sites, where they reacted to produce H_2O, N_2, and heat. The heat of the reaction drove the products into the gas phase and cleared the catalyst site for further chemisorption. When the gas concentrations came to equilibrium, the approximate change in H_2 concentration was measured using the online Whittaker H_2 detector. If the inlet H_2 concentration was equal to the outlet H_2 concentration, the flowrate was lowered. If the outlet H_2 concentration was zero, the flowrate was increased. When a measurable H_2 concentration change was found, samples of the inlet and outlet gas streams were taken. After the gas samples had been analyzed, a comparison of the inlet and outlet H_2 concentrations revealed the reaction rate of the H_2 oxidation.

3.1 EXPERIMENTAL DESIGN

The purpose of the performance test was to determine the maximum H_2/N_2O reaction rate the catalyst could effect. The rate of the H_2/N_2O reaction can be limited either by the catalyst's maximum reaction rate (the catalyst's kinetic ability to catalyze the reaction) or by the reactant supply rate. Therefore, to measure the catalyst's maximum reaction rate, the experiment should have supplied the reactants to the catalyst fast enough to fully use the catalyst and slow enough that the difference between the inlet and outlet concentrations was readable and the reaction rate could be calculated.

The reactant supply can be described by the specific flowrate (SF) for H_2, which is a single variable used to describe the ratio between the H_2 flowrate supplied to the reactor and the mass of the catalyst. SF has the same units as the reaction rate which are μmoles of H_2 per hour per gram of catalyst (μmol/h/g).

Because the reaction rate of the H_2/N_2O reaction was unknown, the apparatus was designed to handle a wide range of SF. The catalyst bed was designed to hold between 50 and 1,650 g of catalyst and the flowmeters could vary the feed mixture flowrate between 50 and 750 mL/min. This allowed the apparatus to operate with SFs between 0.74 and 370 μmol/h/g. With some feed mixtures, flowrates as high as 900 mL/min were achieved, allowing higher than designed SFs to be obtained. SFs between 16.5 and 454 μmol/h/g were used during the performance test. This SF operability region was chosen so that the crucial reaction rates lie within the region. If the reaction rate was slower than 0.74 μmol/h/g, the catalyst bed required for the leachate sump would be too large to be practical. And if the reaction rate exceeded 370 μmol/h/g, almost any size catalyst bed would do. For these calculations see Appendix C.

3.2 CATALYST

In the performance test, between 20 and 240 g of the 50-50 catalyst blend of Engelhard Deoxo and AECL hydrophobic catalysts was used. The catalyst bed was filled with catalyst by dropping the catalyst pellets into the bed one-by-one in an effort to get the two catalyst types well mixed in the bed.

3.3 FEED MIXTURES

The nine feed mixtures (FM) used in the performance test had different concentrations of N_2O, O_2, H_2O, CO, CH_4, and NH_3 in N_2 (refer to Table 3-1). All the gases except H_2O were supplied by compressed-gas cylinders with purities greater than 99.99 percent. H_2O was supplied, when needed, by bubbling the other gases through a column of deionized H_2O, as described in Section 2.3. Because the flowrates of H_2, O_2, CO, CH_4, and NH_3 were so low, each was supplied diluted in N_2, which made the flowrates large enough for an accurate meter reading.

The ninth feed mixture is FM 10 rather than FM 9. FM 9 was described in the test plan as the feed mixture to be used in a durability test.

The feed mixtures were chosen so that, when the test reactor came to equilibrium, the reactor concentrations resembled plausible sump concentrations. The concentrations of the feed mixtures used are listed in Table 3.1.

Table 3-1. Performance Test Feed Mixture Compositions.

Feed mixture number	Volume percent in N_2						
	H_2	O_2	N_2O	H_2O	CO	CH_4	NH_3
FM 1	1	0.5					
FM 2	1		1				
FM 3	1		10				
FM 4	1		40				
FM 5	1		40	2.25			
FM 6	1		40		0.1		
FM 7	1		40			0.1	
FM 8	1		40				1
FM 10	1		40		0.01		

- FM 9 was intended for the durability test, which was not performed.
- FM 11 and 12 were 0.01% CH_4 and 0.1% NH_3 and were to be used only if the higher levels caused the reaction to slow.
- Blank cells indicate zero percent for that component.

3.3.1 Hydrogen

The inlet H_2 concentration for all the feed mixtures in the performance test was intended to be 1 percent. The actual inlet H_2 concentrations for the completed runs ranged between 0.56 and 1.63 percent. With the exception of six runs with either high or low H_2 concentrations, the inlet H_2 concentrations averaged to 0.99 ± 0.05 percent.

The 1 percent H_2 concentration is projected to be the highest acceptable H_2 concentration in the grout vault sump, as it is 25 percent of the LFL for H_2 and N_2O in air (NFPA 69, 1992). Concentrations higher than 1 percent were not investigated because higher H_2 concentrations will increase the reaction rate, which in turn lowers the H_2 concentration. Therefore, the minimum H_2 concentration the catalyst will be required to perform adequately at is 1 percent.

3.3.2 Oxygen

The TMI work (Henrie et al. 1986, Meshako and Bullough 1985) studied the reaction of H_2 and O_2 in stoichiometric amounts to produce H_2O. Under some conditions, the sump will have enough O_2 to complete the H_2 oxidation reaction. FM 1 was designed to have stoichiometric concentrations of H_2 and O_2, making the O_2 concentration 0.5 percent. After being corrected for air contamination, the actual compositions used in the runs were: Run 4, 0.31 percent; Run 9, 0.49 percent; Run 15, 0.48 percent; Run 19, 0.36 percent; Run 31, 0.36 percent; Run 33, 1.11 percent; Run 44, 0.39 percent. With the exception of Run 33, the O_2 inlet concentrations average to 0.4 ± 0.07 percent. Appendix D contains a discussion of the method used to correct for air contamination.

3.3.3 Nitrous Oxide

Even though some air will migrate into the sump, it will not be enough to provide the O_2 needed for the H_2 oxidation under high gas generation rates. See Figures 5-5c, 5-9c, and 5-10c in Roblyer (1993). In this situation, an O_2 depletion will occur and the catalyst will need to catalyze the reaction of H_2 and N_2O. FM 2 through 8 used N_2O as the oxidant.

FM 2 had approximately stoichiometric concentrations of N_2O and H_2, making the N_2O concentration 1 percent. This is the lowest N_2O to H_2 ratio presented in Roblyer (1993). Actual N_2O concentrations in FM 2 varied between 0.93 and 1.42 percent with an average of 1.11 ± 0.19 percent. The N_2O concentrations in FM 3 ranged between 8.9 and 9.7 percent N_2O with an average of 9.39 ± 0.317 percent N_2O and represented a case of a moderate excess of N_2O. These feed mixtures were used to investigate whether low but at least stoichiometric concentrations of N_2O, which diffuses slower than H_2, would limit the reaction rate.

The nominal case presented in Roblyer (1993) used a N_2O to H_2 ratio of 2.4. This would produce a N_2O concentration greater than 40 percent in the sump. See Figure 5-5 in Roblyer (1993). FMs 4 through 10 had between 35 and 42 percent N_2O concentration. Three runs using these feed mixtures were unintentional exceptions and had N_2O concentrations between 21.0 and 32.3 percent.

3.3.4 Water Vapor

If H_2O condenses on the catalyst, the liquid will cover active catalyst sites and impede the flow of H_2 and N_2O to the catalyst sites. H_2O in the bottom of the leachate sump will create a humid atmosphere and saturate the gas in the sump.

In FM 5, the H_2, N_2O, and N_2 were mixed together and saturated with H_2O in the humidifier. FM 5 left the humidifier at 20°C with approximately 2.25 percent H_2O concentration. See Appendix C in Britton (1993a).

3.3.5 Carbon Monoxide

Carbon monoxide has been shown to inhibit the catalytic reaction of H_2 and O_2 (Meshako and Bullough 1985). This inhibiting effect occurs because the CO competitively chemisorbs to active catalyst sites. Also, the oxidation of CO, which produces carbon dioxide (CO_2), may be a competing reaction.

FM 6 was intended to be 0.1 percent CO. The actual composition varied between 0.1 and 0.3 percent. This concentration was chosen because preliminary data from investigations into the grout's gas production indicated this was a reasonable value. A lower concentration was also planned in case the 0.1 percent overwhelmed the catalyst. FM 10 was intended to be 0.01 percent CO although there is no CO analysis available to confirm this because of equipment failure during analysis.

3.3.6 Methane

Methane, a common product of organic decomposition, may enter the sump as a generated gas. Runs with approximately 0.1 percent CH_4 were performed to determine if CH_4 affects the H_2/N_2O reaction rate. Runs using FM 7 had CH_4 concentrations that varied between 0.091 and 0.101 percent.

3.3.7 Ammonia

Ammonia is another gas that may be produced by the grout in the vault. Runs with NH_3 in the 1 percent concentration range were used to determine if NH_3 has a major impact on the reaction rate of H_2 and N_2O. Because NH_3 readily sorbs to solids and interacts with H_2O, it is extremely difficult to quantitatively analyze gases for NH_3. Runs using FM 8 were estimated to have a NH_3 concentration between 0.6 and 1.1 percent. See Appendix D of the supporting data document (Britton 1994) for more details on this analysis method.

3.4 RUN ORDER

Each feed mixture was used at least five times, once in each of the five primary sets of runs performed. Within each set, all eight feed mixtures were performed in random order. Multiple sets and a random order were used to ensure that the data was not tainted with cumulative errors such as a buildup of a contaminant on the catalyst. Initially, a set of scoping runs using FMs 1 and 4 was performed. And after the primary runs, a set of CO runs and a set of extended runs were performed. Table 3-2 shows these sets of runs and their order.

3.5 PERFORMANCE TEST CONDITIONS

The sump is centered below and to the side of the grout vault and is contained within an asphalt diffusion barrier. The temperature of the barrier at this point, 10 years after filling, is expected to be 40°C (Crea 1992, Figure 32). The temperature of the sump can be increased by the heat of the reaction and by the inlet vault gas. Heat will be lost by H_2O condensing on the walls of the sump and by heated gases leaving the sump and cold gases entering the sump. The temperature in the sump is assumed to be between 20 and 40°C. The reactors were kept between 13 and 26°C during the performance test. Some of the test temperatures were lower than the expected temperature. This should give a slower reaction rate than would occur at higher temperatures. Table 3-3 lists the steady state conditions that were maintained in the reactors for the performance test.

3.6 DATA COLLECTION AND SAMPLE ANALYSIS

The mass and volume of the catalyst placed in the bed were recorded in the laboratory notebook (Britton 1993b) along with details on the catalyst bed dimensions. A list of data taken during each experiment and recorded in the laboratory notebook is listed in Table 3-4 along with the range and accuracy for each variable measured.

During each experimental run, at least one inlet and outlet gas sample was taken. Samples 93-001 through 93-157 were shipped to the Inorganic Mass Spectrometry Laboratory at Pacific Northwest Laboratories (PNL) for mass spectrometer analysis. The samples were analyzed with a Finnigan MAT-271 mass spectrometer using analytical procedure PNL-MA-299 ALO-284. This procedure is supplied in Appendix C of the supporting data document (Britton 1994). The analysis reports are located in Appendix A of the supporting data document (Britton 1994).

Samples 93-158 through 93-168 were not analyzed by mass spectroscopy. Instead they were analyzed by gas chromatography. The computer data files for these runs were lost due to a misconfigured computer program before they could be examined.

Table 3-2. Run Order.

Scoping Set Apparatus 1	
Run #	FM #
4	1
5	4
6	4

Set 1 Apparatus 1	
Run #	FM #
7	4
8	5
9	1
10	7
11	3
12	2
13	6
14	8

Set 2 Apparatus 2	
Run #	FM #
15†	1
16	7
17	3
18	6
19	1
22	8
24	4
25	2
27	5

†scoping run

Set 3 Apparatus 2	
Run #	FM #
28	5
30	2
31	1
32	6
35	4
37	8
38	3
40	7

Set 4 Apparatus 1	
Run #	FM #
21	7
23	3
26‡	3
29	6
33	1
34	8
36	4
39	2
46	5

‡Duplicate run

Set 5 Apparatus 2	
Run #	FM #
41	4
42	5
43	8
44	1
45	7
47	3
48	2
49	6

CO set Apparatus 2	
Run #	FM #
50	10
52	6
55	6
56	6
57	6
58	6

Extended runs Apparatus 1&2	
Run #	FM #
59	6
62	8
63	7
64	5

Table 3-3. Performance Test Conditions.

Variable	Range		Notes
H_2 concentration	0.01 %	1.45 %	
O_2 concentration	0.00 %	0.05 %	For runs using FM1. Run 44 was an exception and had 0.26% O_2 in the outlet gas.
N_2O concentration	0.24 %	0.57 %	For runs using FM 2.
	8.10 %	9.10 %	For runs using FM 3.
	35.80 %	40.50 %	For runs using FM 4-10. Runs 18, 49, and 32 were exceptions and had lower N_2O concentrations of 33.8%, 25.2%, and 19.2%, respectively.
H_2O concentration	0 %	3.25 %	These concentrations were estimates. See Britton 1993a, Appendix C for more detail.
CO concentration	0.1 %	0.3 %	For runs using FM 6. Run 50 using FM 10 was estimated to have 0.01 percent CO.
CH_4 concentration	0.091%	0.1 %	For runs using FM 7. Run 10 had a lower CH_4 concentration measured at 0.03%.
NH_3 concentration	0.6 %	1.07 %	For runs using FM 8. These concentrations were estimates. See Appendix D of the supporting data document (Britton 1994).
Temperature	13°C	26°C	This drifted with the ambient temperature of the laboratory.
Pressure	98.9 kPa		Average barometric pressure.

Table 3-4. Experimental Data Measurements and Accuracy.

Measurement	Equipment	Range	Accuracy
Mass flowrate	FC-1, FC-2, FC-3, FC-4	10-100 sccm[†]	± 10 sccm[†]
	FC-5	50-500 sccm[†]	± 10 sccm[†]
Volumetric flowrate	F-1, F-2	50-250 mL/min	± 25 mL/min
Temperature of: humidifier H_2O inlet gas catalyst temperature outlet gas	 T-1, T-2, T-3, T-4	 20 °C 13 °C 13-20 °C 13-18 °C	± 1 °C
Pressure	P-1, P-2, P-3	0 psig	± 2 psig
H_2 concentration	HA-1	0-1 %	± 0.2 %

[†] Equipment measured the gas flowrate of N_2 at standard pressure. This data was converted to actual flowrate data later.

4.0 SORPTION CAPACITY TEST DESCRIPTION

In the sorption capacity test, a feed mixture containing CO was metered into the reactor which contained a known quantity of the catalyst blend. When a CO molecule came in contact with a free active catalyst site, the molecule sorbed to that site. The inlet and outlet CO concentrations were measured and the amount of CO chemisorbed by the catalyst was determined by difference.

4.1 EXPERIMENTAL DESIGN

The purpose of the sorption capacity test was to determine the amount of CO the catalyst would chemisorb under conditions similar to those in the grout vault. A mixture of CO in N_2 was metered into the reactor which had an initial CO concentration of zero. The CO concentration in the reactor then rose from zero to the inlet concentration.

If the inlet gas mixed quickly with the bulk gas in the reactor, the outlet concentration would be equal to the reactor concentration. And, if no chemisorption occurred, the change in the outlet concentration could be described by the first order equation for a mixed flow reactor. Refer to Appendix D for more information on the sorption capacity equations. A comparison between the actual and theoretical outlet concentration curves over the sorption time interval reveals the extent of CO chemisorption on the catalyst.

A second goal of this test was to determine a regeneration method for the catalyst. Between runs, the catalyst in the reactor was flushed with varying amounts of N_2 or air or the catalyst was replaced with virgin catalyst. If the reactor was flushed with air or was opened to replace the catalyst, the air in the reactor was removed by purging with N_2. A comparison of the CO sorption capacities between virgin catalyst and catalyst regenerated with either N_2 or air was then made.

4.2 CATALYST

In the sorption capacity test, between 10 and 30 g of the 50-50 catalyst blend of Engelhard Deoxo and AECL hydrophobic catalyst was used. The catalyst bed was filled with catalyst by dropping the catalyst pellets into the bed one-by-one in an effort to get the two types of catalysts well mixed in the bed.

4.3 FEED MIXTURES

The feed mixtures used in the sorption capacity test are shown in Table 4-1. FM 4 nominally contained 1 percent H_2, 40 percent N_2O and no CO. This was used to show the uninhibited and unpoisoned rate of the H_2/N_2O reaction on the catalyst. After the reaction rate was established, the feed was switched to FM 14. FM 14 nominally contained 1 percent H_2, 40 percent N_2O and 0.05 percent CO and was used to show the relationship between the drop in the reaction rate and the sorption of the CO onto the catalyst.

FM 13 was the primary feed mixture used in the sorption capacity test. FM 13 contained between 0.09 and 0.13 percent CO and allowed CO to be introduced to the catalyst without the effects of oxidants (O_2 or N_2O), which may produce reactions, and without effects of H_2, which may compete with the CO for active catalytic sites. This allowed the sorption capacity to be more accurately estimated than could have been done with the feed mixtures used in the performance test.

Table 4-1. Sorption Capacity Test Feed Mixture Compositions.

Feed mixture	Volume percent in N_2		
	H_2	N_2O	CO
4	0.71 - 1.77	40	
13		40	0.096 - 0.135
14	0.70 - 1.87	40	0.050 - 0.050

- Blank cells indicate zero percent for that component.

4.4 SORPTION CAPACITY TEST CONDITIONS

The sorption capacity test was performed at ambient temperature and pressure. Table 4-2 lists the conditions that were maintained in the reactor for the sorption capacity test.

4.5 DATA COLLECTION AND SAMPLE ANALYSIS

The inlet CO concentration was measured several times before and after each run. The outlet concentration was measured at 10 or 15 minute intervals until it steadied out at the inlet concentration. The gas samples were taken in Tedlar[7] bags and analyzed on an MTI Quad 400 gas chromatograph. The gas chromatography data was analyzed by WHC, Special Analytical Studies.

The total difference between the amount of CO that came out and the amount of CO that would have come out if the catalyst had not been chemisorbing CO is defined as the catalyst's sorption capacity. This data and the results are presented in Section 6.0.

Table 4-2. Sorption Capacity Test Conditions.

Variable	Range		Notes
H_2 concentration	0.01 %	1.45 %	For runs using FM 4 and 14.
N_2O concentration	~40 %		For runs using FM 4, 13, and 14.
CO concentration	0.052%	0.133%	For runs using FM 13 and 14.
Temperature	13°C	21°C	
Pressure	0.976 atm		Average barometric pressure.

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[7] Tedlar is a registered trademark of the E. I. DuPont De Nemours and Company.

5.0 RESULTS OF THE PERFORMANCE TEST

FMs 1 through 8 and 10 were metered into the reactor with the catalyst in Runs 1 through 64. Inlet and outlet gas concentrations were determined by mass spectroscopy. The analytical data for these samples is in Appendix A, Table A-1.

5.1 AIR CONTAMINATION

Some contamination of the samples with air was expected. Possible causes of this contamination were an incomplete evacuation of the line when the sample container was connected to the analytical equipment, or an air intrusion in the valves or piping in either the experimental apparatus or the analytical equipment. Because analysis of the feed gases determined there was very little argon (Ar) in any of the feed gases, any large amount of Ar in a sample was assumed to have come from air contamination. The degree of air contamination (Φ) was determined by calculating the percentage of the analyzed sample that is air rather than pure sample. Equation 5-1 shows that Φ is the ratio of the mole percent of Ar in the sample (X_{Ar}) to the mole percent of Ar in air (Y_{Ar}).

$$\Phi = \frac{X_{Ar}}{Y_{Ar}} * 100\% \qquad \text{(Eqn 5-1)}$$

As an alternate method, Φ was calculated using O_2 instead of Ar in all runs except those using O_2 feeds. The results of both Φ calculation methods can be seen in Table A-1 in Appendix A. The Φ was used to screen the sample analysis for samples and runs with poor data. The O_2 concentrations were corrected for the air contamination for the runs using FM 1. The corrected composition equation can be seen in Appendix D. Other components and runs were not corrected for the air contamination factor because in most other cases the correction was negligible.

For most of the samples, Φ was below 5 percent. In sample 93-061, Φ was 48.2 percent when calculated with the Ar method. Because the O_2 method calculated Φ to be normal and all the other gas constituents were within expected ranges, the Ar data was assumed to be faulty.

In sample 93-124, the inlet sample for Run 43, Φ was 61.8 percent and 64.0 percent for the Ar and O_2 methods, respectively. An open valve on the GSC allowed an air intrusion that resulted in this poor data. Because only one inlet sample was taken for this run, the analysis on this run was not carried further.

5.2 RUN DATA

Tables 5-1 and 5-2 display the performance test data. Table 5-1 lists run data in the sequential order in which the runs were performed while Table 5-2 displays the run data organized by feed mixtures. The runs with shaded run numbers were performed with Apparatus 1 while the remaining runs were performed in Apparatus 2.

Table 5-1. Performance Test Run Data - by Run. (Sheet 1 of 2)

Run #	Notes	FM #	Time t min	Time $\#t_r$	T °C	$X_{H,in}$ %	$X_{H,out}$ %	Q sccm	W g	Q/W mL/min / g cat	SF µmol H_2/h / g Cat	r_H µmol H_2/h / g Cat	Conversion %	Outlet Gas Composition Oxidant	Outlet Gas Composition Other
1	a		153	10	19	0.385 ±0.007	0.326 ±0.007	500	240	2.1	19.7				
2	b								240	0.0					
3	b								240	0.0					
4	c ☼	1	171	11	19	0.558 ±0.008	0.029 ±0.003	500	240	2.1	28.5	27.0 ± 0.54	94.8%	0.02 % O_2	
5	d	4	92	3	22	1.070 ±0.020	0.057 ±0.005	275	240	1.1	30.1	28.5 ± 1.04	94.7%	0.01 % N_2O	
6		4	290	10	21	0.938 ±0.009	0.017 ±0.002	250	240	1.0	24.0	23.5 ± 0.94	98.2%	39.20 % N_2O	
7		4	348	13	21	0.932 ±0.009	0.016 ±0.002	275	240	1.1	26.2	25.8 ± 0.94	98.3%	39.50 % N_2O	
8	e ☼	5	84	3	23	0.957 ±0.009	0.024 ±0.002	275	240	1.1	26.9	26.2 ± 0.95	97.5%	39.30 % N_2O	3.2 % H_2O
9	c ☼	1	245	9	20	0.912 ±0.010	0.023 ±0.002	275	240	1.1	25.6	25.0 ± 0.91	97.5%	0.12 % O_2	
10		7	939	34	21	0.926 ±0.010	0.014 ±0.001	275	240	1.1	26.0	25.6 ± 0.93	98.5%	39.60 % N_2O	0.029 % CH_4
11		3	269	10	21	0.913 ±0.010	0.016 ±0.006	275	240	1.1	25.7	25.2 ± 0.92	98.3%	8.39 % N_2O	
12		2	170	6	20	0.924 ±0.010	0.024 ±0.002	275	240	1.1	26.0	25.3 ± 0.92	97.4%	0.24 % N_2O	
13	f g	6	240	9	20	0.940 ±0.010	0.070 ±0.003	275	240	1.1	26.4	24.5 ± 0.89	92.6%	40.10 % N_2O	0.1 % CO
14		8	240	9	18	0.920 ±0.010	0.030 ±0.001	275	240	1.1	25.9	25.0 ± 0.91	96.7%	40.50 % N_2O	0.6 % NH_3
15	c ☼	1	80	10	17	0.960 ±0.010	0.313 ±0.006	900	50	18.0	424.0	285.7 ± 3.23	67.4%	0.16 % O_2	
16		7	120	11	18	1.040 ±0.010	0.103 ±0.002	700	50	14.0	357.2	321.9 ± 4.64	90.1%	36.80 % N_2O	0.1 % CH_4
17		3	120	11	19	0.985 ±0.010	0.096 ±0.002	700	50	14.0	338.4	305.4 ± 4.41	90.3%	8.13 % N_2O	
18	f i	6	489	3	21	1.550 ±0.020	1.450 ±0.020	50	50	1.0	38.0	2.5 ± 0.53	5.5%	33.80 % N_2O	0.1 % CO
19	c j k	1	338	18	18	1.050 ±0.010	0.345 ±0.007	400	50	8.0	206.1	138.4 ± 3.47	67.1%	0.01 % O_2	
20	l ☼	4	47	2				275	20	13.8					
21		7	120	4	19	0.937 ±0.009	0.109 ±0.003	275	20	13.8	316.1	279.3 ± 10.25	88.4%	40.20 % N_2O	0.1 % CH_4
22	m	8	170	15	22	1.020 ±0.010	0.312 ±0.006	650	50	13.0	325.3	225.8 ± 3.50	69.4%	37.90 % N_2O	1.0 % NH_3
23		3	105	4	23	0.896 ±0.009	0.085 ±0.004	275	20	13.8	302.3	273.6 ± 10.04	90.5%	8.56 % N_2O	
24		4	209	21	20	1.030 ±0.010	0.129 ±0.003	750	50	15.0	379.1	331.6 ± 4.47	87.5%	38.40 % N_2O	
25		2	205	20	21	1.010 ±0.010	0.407 ±0.008	750	50	15.0	371.7	221.9 ± 2.99	59.7%	0.42 % N_2O	
26		3	120	4	20	0.899 ±0.009	0.093 ±0.004	275	20	13.8	303.3	271.9 ± 9.98	89.7%	9.10 % N_2O	
27	e	5	122	12	21	1.070 ±0.010	0.126 ±0.005	750	50	15.0	393.8	347.4 ± 4.68	88.2%	39.10 % N_2O	3.3 % H_2O
28	e	5	119	14	23	1.060 ±0.010	0.139 ±0.003	888	50	17.8	461.9	401.3 ± 4.59	86.9%	38.70 % N_2O	3.2 % H_2O
28e	e	5	1249	146	23	1.060 ±0.010	0.137 ±0.003	888	50	17.8	461.9	402.2 ± 4.60	87.1%	39.00 % N_2O	3.2 % H_2O
29	i	6	1265	4	19	1.040 ±0.020	0.970 ±0.020	25	20	1.3	31.9	2.1 ± 0.93	6.7%	36.10 % N_2O	0.1 % CO
30	☼	2	130	13	21	1.020 ±0.020	0.419 ±0.008	750	50	15.0	375.4	221.2 ± 3.00	58.9%	0.43 % N_2O	
31	c	1	120	12	22	1.030 ±0.020	0.311 ±0.009	750	50	15.0	379.1	264.6 ± 3.58	69.8%	0.02 % O_2	
32	g	6	220	1	19	1.410 ±0.020	0.145 ±0.002	50	50	1.0	34.6	31.0 ± 6.21	89.7%	19.20 % N_2O	0.0 % CO
33	c n	1	120	4	19	0.871 ±0.010	0.203 ±0.004	275	20	13.8	293.8	225.4 ± 8.27	76.7%	0.05 % O_2	
34	m	8	120	4	20	0.937 ±0.009	0.154 ±0.003	275	20	13.8	316.1	264.2 ± 9.70	83.6%	40.00 % N_2O	1.0 % NH_3
35		4	120	12	23	1.040 ±0.030	0.105 ±0.003	750	50	15.0	382.8	344.1 ± 4.65	89.9%	35.80 % N_2O	
36		4	120	4	22	0.911 ±0.020	0.107 ±0.003	275	20	13.8	307.3	271.2 ± 9.96	88.3%	40.10 % N_2O	
37		8	120	10	23	1.060 ±0.010	0.201 ±0.004	650	50	13.0	338.1	274.0 ± 4.25	81.0%	35.80 % N_2O	1.1 % NH_3
38		3	140	13	21	0.970 ±0.020	0.114 ±0.003	700	50	14.0	333.2	294.0 ± 4.24	88.2%	8.51 % N_2O	
39	n	2	165	6	19	0.900 ±0.020	0.170 ±0.004	275	20	13.8	303.6	246.3 ± 9.04	81.1%	0.27 % N_2O	
40		7	155	14	22	1.040 ±0.020	0.121 ±0.003	700	50	14.0	357.2	315.7 ± 4.56	88.4%	36.10 % N_2O	0.1 % CH_4
41		4	120	12	22	1.030 ±0.020	0.116 ±0.003	750	50	15.0	379.1	336.4 ± 4.54	88.7%	36.60 % N_2O	
42	e	5	120	14	20	1.040 ±0.020	0.148 ±0.003	888	50	17.8	453.2	388.7 ± 4.45	85.8%	38.10 % N_2O	3.2 % H_2O
43	n o ☼	8	120	11	20	[illegible]	[illegible]	650	50	13.0	[illegible]	[illegible]	[illegible]		
44	c p	1	120	12	20	1.020 ±0.020	0.812 ±0.020	750	50	15.0	375.4	76.5 ± 1.75	20.4%	0.29 % O_2	

Table 5-1. Performance Test Run Data - by Run. (Sheet 2 of 2)

Run #	Notes	FM #	Time		T	$X_{H,in}$	$X_{H,out}$	Q	W	Q/W	SF	r_H	Conversion	Outlet Gas Composition	
			t min	$\#t_r$	°C	%	%	sccm	g	mL/min / g cat	µmol H_2/h / g Cat	µmol H_2/h / g Cat	%	Oxidant	Other
45		7	100	9	21	1.050 ±0.020	0.109 ±0.002	700	50	14.0	360.7	323.2 ± 4.67	89.6%	36.70 % N_2O	0.1 % CH_4
46	e	5	185	7	20	0.940 ±0.010	0.107 ±0.002	275	20	13.8	317.1	281.0 ± 10.32	88.6%	40.30 % N_2O,	3.1 % H_2O
47		3	120	11	22	1.030 ±0.020	0.102 ±0.002	700	50	14.0	353.8	318.8 ± 4.60	90.1%	8.52 % N_2O	
48		2	120	12	22	0.982 ±0.020	0:439 ±0.008	750	50	15.0	361.4	199.8 ± 2.71	55.3%	0.57 % N_2O	
49	g	6	1070	7	19	1.630 ±0.020	0.071 ±0.010	50	50	1.0	40.0	38.3 ± 7.65	95.6%	25.20 % N_2O	0.3 % CO
50	f g	10	105	10	23	1.040 ±0.010	0.178 ±0.003	750	50	15.0	382.8	317.3 ± 4.28	82.9%	36.90 % N_2O	0.01 % CO
51	b	6	1014	33	22			250	50	5.0					
52	f g ☼	6	1115	44	23	1.140 ±0.010	0.021 ±0.003	300	500	0.6	16.8	16.5 ± 0.55	98.2%	37.30 % N_2O	0.1 % CO
53	b	6			23			500	500	1.0					
54	b	6			22			750	500	1.5					
55	f g	6	75	9	23	1.010 ±0.010	0.060 ±0.006	888	500	1.8	44.0	41.4 ± 0.47	94.1%	38.60 % N_2O	0.1 % CO
56	f g	6	220	23	21	1.030 ±0.010	0.156 ±0.002	800	200	4.0	101.1	85.8 ± 1.07	84.9%	37.50 % N_2O	0.1 % CO
57	f ☼	6	975	97	19	1.050 ±0.010	1.020 ±0.010	750	100	7.5	193.2	5.5 ± 1.23	2.9%	38.30 % N_2O	0.1 % CO
58	b	6	1400	37	19			200	100	2.0					
59	i q	6	2665	176	19	0.950 ±0.070	1.000 ±0.020	500	500	1.0	23.3	-1.2 ± -2.6	-5.3%	40.16 % N_2O	0.1 % CO
60	l ☼	6			20			200	500	0.4					
61	l ☼	6			22			200	1000	0.2					
62	m q	8	1770	175	21	0.930 ±0.060	0.050 ±0.000	750	100	7.5	171.1	161.9 ± 2.29	94.6%	35.89 % N_2O	1.0 % NH_3
63	q r	7	1690	167	21	1.500 ±0.000	0.000 ±0.000	750	100	7.5	276.0	276.0 ± 3.69	100.0%	na % N_2O	0.1 % CH_4
64	e q r	5	3089	306	16	1.000 ±0.000	0.000 ±0.000	750	100	7.5	184.0	184.0 ± 2.46	100.0%	na % N_2O	na % H_2O

NOTES:

☼	Reactor opened and catalyst exposed to air prior to this run.
a	Due to a mistake, there was no oxidant in this run, only H_2 and N_2. The O_2 present in the sample is due to air contamination.
b	No samples taken during this run.
c	O_2 concentration was adjusted to account for air contamination.
d	The N_2O concentration dropped to zero over the run because the N_2O line was not pressurized correctly.
e	H_2O estimated based on the assumed initial H_2O concentration of 2.3% and the percent H_2 reduction (reacted to form H_2O).
f	CO and/or CO_2 not adequately analyzed.
g	There was not enough CO introduced to the reactor to fully load the catalyst and shut the reaction down.
i	Either partial or complete CO loading of the catalyst caused the reaction rate to slow or stop.
j	Through the run, the flowrate was lowered to the shown final value.
k	Reaction rate may have been inhibited due to CO on the catalyst from the previous run.
l	Run aborted.
m	NH_3 analysis is inadequate or its adequacy is questioned.
n	Calculated air contamination is high.
o	Valve was open on GSC, results likely to be inaccurate.
p	Stoichiometrically less oxidant than H_2. Therefore the reaction rate was limited by the lack of oxidant.
q	Analysis performed by Special Analytical Studies using gas chromatograpy.
r	GC analysis data was lost. H_2 data listed is from the on-line Whittaker H_2 detector.
na	Not Analyzed for.

Darkly shaded run numbers indicate runs performed on apparatus 1. Unshaded run numbers indicate runs performed on apparatus 2. Darkly shaded data, other than run numbers, indicates unusable data or incomplete runs. Light shading indicates estimated data.

Table 5-2. Performance Test Run Data - by Feed Mixture. (Sheet 1 of 2)

FM #	Note	Run #	Time t min	Time $\#t_r$	T °C	$X_{H,in}$ %	Q sccm	W g	Q/W mL/min / g cat	SF µmol H_2/h / g Cat	r_H µmol H_2/h / g Cat	Conversion –	Outlet Gas Composition $X_{H,out}$	Outlet Gas Composition Oxidant	Outlet Gas Composition Other
1	c ☼	4	171	11	19	0.558	500	240	2.1	28.5	27.0	94.8%	at 0.029 %	0.02 % O_2	
1	c ☼	9	245	9	20	0.912	275	240	1.1	25.6	25.0	97.5%	at 0.023 %	0.12 % O_2	
1	c ☼	15	80	10	17	0.960	900	50	18.0	424.0	285.7	67.4%	at 0.313 %	0.16 % O_2	
1	c j k	19	338	18	18	1.050	400	50	8.0	206.1	138.4	67.1%	at 0.345 %	0.01 % O_2	
1	c	31	120	12	22	1.030	750	50	15.0	379.1	264.6	69.8%	at 0.311 %	0.02 % O_2	
1	c n	33	120	4	19	0.871	275	20	13.8	293.8	225.4	76.7%	at 0.203 %	0.05 % O_2	
2		12	170	6	20	0.924	275	240	1.1	26.0	25.3	97.4%	at 0.024 %	0.24 % N_2O	
2		25	205	20	21	1.010	750	50	15.0	371.7	221.9	59.7%	at 0.407 %	0.42 % N_2O	
2	☼	30	130	13	21	1.020	750	50	15.0	375.4	221.2	58.9%	at 0.419 %	0.43 % N_2O	
2	n	39	165	6	19	0.900	275	20	13.8	303.6	246.3	81.1%	at 0.170 %	0.27 % N_2O	
2		48	120	12	22	0.982	750	50	15.0	361.4	199.8	55.3%	at 0.439 %	0.57 % N_2O	
3		11	269	10	21	0.913	275	240	1.1	25.7	25.2	98.3%	at 0.016 %	8.39 % N_2O	
3		17	120	11	19	0.985	700	50	14.0	338.4	305.4	90.3%	at 0.096 %	8.13 % N_2O	
3		23	105	4	23	0.896	275	20	13.8	302.3	273.6	90.5%	at 0.085 %	8.56 % N_2O	
3		26	120	4	20	0.899	275	20	13.8	303.3	271.9	89.7%	at 0.093 %	9.10 % N_2O	
3		38	140	13	21	0.970	700	50	14.0	333.2	294.0	88.2%	at 0.114 %	8.51 % N_2O	
3		47	120	11	22	1.030	700	50	14.0	353.8	318.8	90.1%	at 0.102 %	8.52 % N_2O	
4		6	290	10	21	0.938	250	240	1.0	24.0	23.5	98.2%	at 0.017 %	39.20 % N_2O	
4		7	348	13	21	0.932	275	240	1.1	26.2	25.8	98.3%	at 0.016 %	39.50 % N_2O	
4		24	209	21	20	1.030	750	50	15.0	379.1	331.6	87.5%	at 0.129 %	38.40 % N_2O	
4		35	120	12	23	1.040	750	50	15.0	382.8	344.1	89.9%	at 0.105 %	35.80 % N_2O	
4		36	120	4	22	0.911	275	20	13.8	307.3	271.2	88.3%	at 0.107 %	40.10 % N_2O	
4		41	120	12	22	1.030	750	50	15.0	379.1	336.4	88.7%	at 0.116 %	36.60 % N_2O	
5	e ☼	8	84	3	23	0.957	275	240	1.1	26.9	26.2	97.5%	at 0.024 %	39.30 % N_2O	3.2 % H_2O
5	e	27	122	12	21	1.070	750	50	15.0	393.8	347.4	88.2%	at 0.126 %	39.10 % N_2O	3.3 % H_2O
5	e	28	119	14	23	1.060	888	50	17.8	461.9	401.3	86.9%	at 0.139 %	38.70 % N_2O	3.2 % H_2O
5	e	28e	1249	146	23	1.060	888	50	17.8	461.9	402.2	87.1%	at 0.137 %	39.00 % N_2O	3.2 % H_2O
5	e	42	120	14	20	1.040	888	50	17.8	453.2	388.7	85.8%	at 0.148 %	38.10 % N_2O	3.2 % H_2O
5	e	46	185	7	20	0.940	275	20	13.8	317.1	281.0	88.6%	at 0.107 %	40.30 % N_2O	3.1 % H_2O
6	f g	13	240	9	20	0.940	275	240	1.1	26.4	24.5	92.6%	at 0.070 %	40.10 % N_2O	0.1 % CO
6	g	32	220	1	19	1.410	50	50	1.0	34.6	31.0	89.7%	at 0.145 %	19.20 % N_2O	<0.001 % CO
6	g	49	1070	7	19	1.630	50	50	1.0	40.0	38.3	95.6%	at 0.071 %	25.20 % N_2O	0.3 % CO
6	f g ☼	52	1115	44	23	1.140	300	500	0.6	16.8	16.5	98.2%	at 0.021 %	37.30 % N_2O	0.1 % CO
6	f g	55	75	9	23	1.010	888	500	1.8	44.0	41.4	94.1%	at 0.060 %	38.60 % N_2O	0.1 % CO
6	f g	56	220	23	21	1.030	800	200	4.0	101.1	85.8	84.9%	at 0.156 %	37.50 % N_2O	0.1 % CO
7		10	939	34	21	0.926	275	240	1.1	26.0	25.6	98.5%	at 0.014 %	39.60 % N_2O	0.03 % CH_4
7		16	120	11	18	1.040	700	50	14.0	357.2	321.9	90.1%	at 0.103 %	36.80 % N_2O	0.10 % CH_4
7		21	120	4	19	0.937	275	20	13.8	316.1	279.3	88.4%	at 0.109 %	40.20 % N_2O	0.09 % CH_4
7		40	155	14	22	1.040	700	50	14.0	357.2	315.7	88.4%	at 0.121 %	36.10 % N_2O	0.10 % CH_4
7		45	100	9	21	1.050	700	50	14.0	360.7	323.2	89.6%	at 0.109 %	36.70 % N_2O	0.10 % CH_4
8		14	240	9	18	0.920	275	240	1.1	25.9	25.0	96.7%	at 0.030 %	40.50 % N_2O	0.6 % NH_3
8	m	22	170	15	22	1.020	650	50	13.0	325.3	225.8	69.4%	at 0.312 %	37.90 % N_2O	1.0 % NH_3
8	m	34	120	4	20	0.937	275	20	13.8	316.1	264.2	83.6%	at 0.154 %	40.00 % N_2O	1.0 % NH_3
8		37	120	10	23	1.060	650	50	13.0	338.1	274.0	81.0%	at 0.201 %	35.80 % N_2O	1.1 % NH_3
8	m q	62	1770	175	21	0.930	750	100	7.5	171.1	161.9	94.6%	at 0.050 %	35.89 % N_2O	1.0 % NH_3
10	f g	50	105	10	23	1.040	750	50	15.0	382.8	317.3	82.9%	at 0.178 %	36.90 % N_2O	0.01 % CO

Table 5-2. Performance Test Run Data - by Feed Mixture. (Sheet 2 of 2)

Table 5–2 Notes and Symbols

☼	Reactor opened and catalyst exposed to air prior to this run.
c	O_2 concentration was adjusted to account for air contamination.
d	The N_2O concentration dropped to zero over the run because the N_2O line was not pressurized correctly.
e	H_2O estimated based on the assumed initial H_2O concentration of 2.3% and the percent H_2 reduction (reacted to form H_2O).
f	CO and/or CO_2 not adequately analyzed.
g	There was not enough CO introduced to the reactor to fully load the catalyst and shut the reaction down.
j	Through the run, the flowrate was lowered to the shown final value.
k	Reaction rate may have been inhibited due to CO on the catalyst from the previous run.
m	NH_3 analysis is inadequate or its adequacy is questioned.
n	Calculated air contamination is high.
q	Analysis performed by Special Analytical Studies using gas chromatograpy.

Light shading indicates estimated data.

The first six runs listed in Table 5-1 were used as scoping runs to functionally test the equipment and determine whether or not the reaction could be detected. Runs 7 through 49 were the performance test runs. In runs 50 through 58, the CO inhibiting phenomenon was investigated further and is discussed in Section 5.6. The last six runs, runs 59 through 64, as well as run 28e were extended runs and are discussed in Section 5.6. All the runs listed in Table 5-2 were included in the performance test analysis described in Sections 5.3 through 5.5.

The data displayed in Table 5-1 and 5-2 includes temperature (T), inlet H_2 concentration ($X_{H,in}$), volumetric flowrate (Q), catalyst mass (W), the outlet gas composition ($X_{H,out}$), and the length of time in which the run was performed in both minutes and the number of residence times (τ_r). The residence time (τ_r) is the time required for one reactor volume of fluid to flow out of the reactor. More information on the residence time is provided in Appendix D.

5.3 H_2/N_2O REACTION RATE

The inlet and outlet gases were analyzed for the H_2 concentrations (X_H) and were compared. The H_2/N_2O reaction rate (r_H) was the change in X_H times the flowrate of H_2 into the reactor divided by the mass of catalyst in the reactor. Using the ideal gas law to calculate the molar flowrate, the H_2/N_2O reaction rate (r_H) was calculated by the equation:

$$r_H = 60\frac{QP}{RTW}\left(\frac{X_{H,in} - X_{H,out}}{100}\right) \qquad \text{(Eqn 5-3)}$$

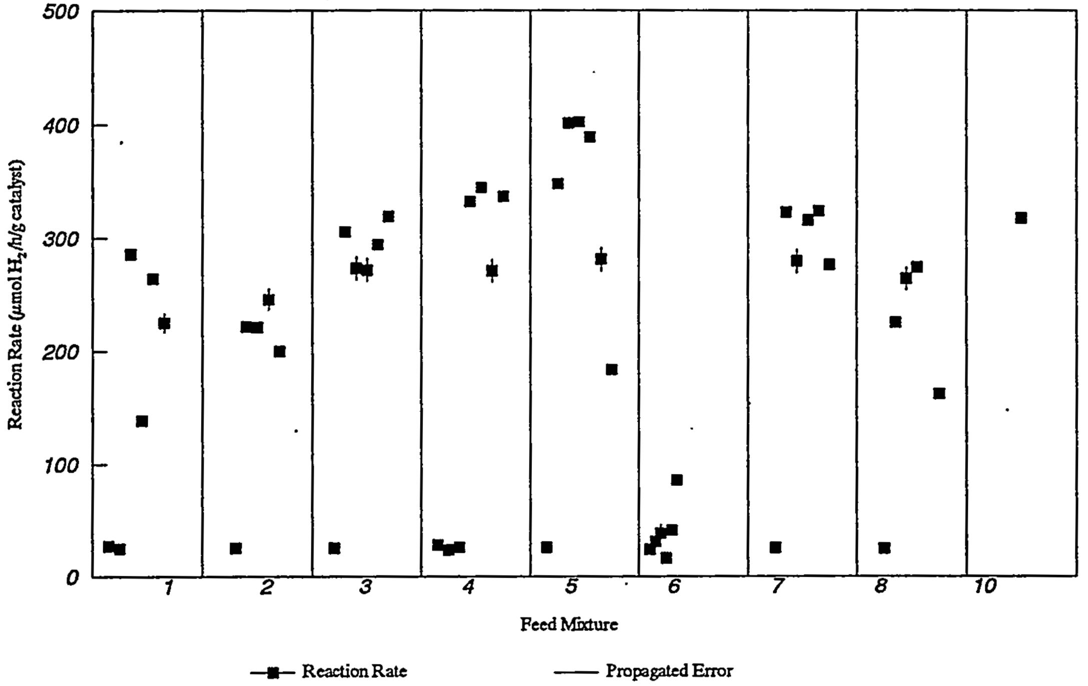
where:

r_H = Reaction rate (μmol/h/g)
Q = Total volumetric flow rate (mL/min)
P = Pressure (atm)
R = Ideal gas constant (mL·atm/μmol·K)
T = Temperature (K)
W = Mass of catalyst (g)
$X_{H,in}$ = Mole percent concentration of H_2 in inlet gas (%)
$X_{H,out}$ = Mole percent concentration of H_2 in outlet gas (%).

Tables 5-1 and 5-2 list the calculated reaction rate. The shaded data in Table 5-1 were either flawed and unusable or from runs that were not completed. The table notes explain the reasons. The data from these runs were not carried on for the rest of the analysis.

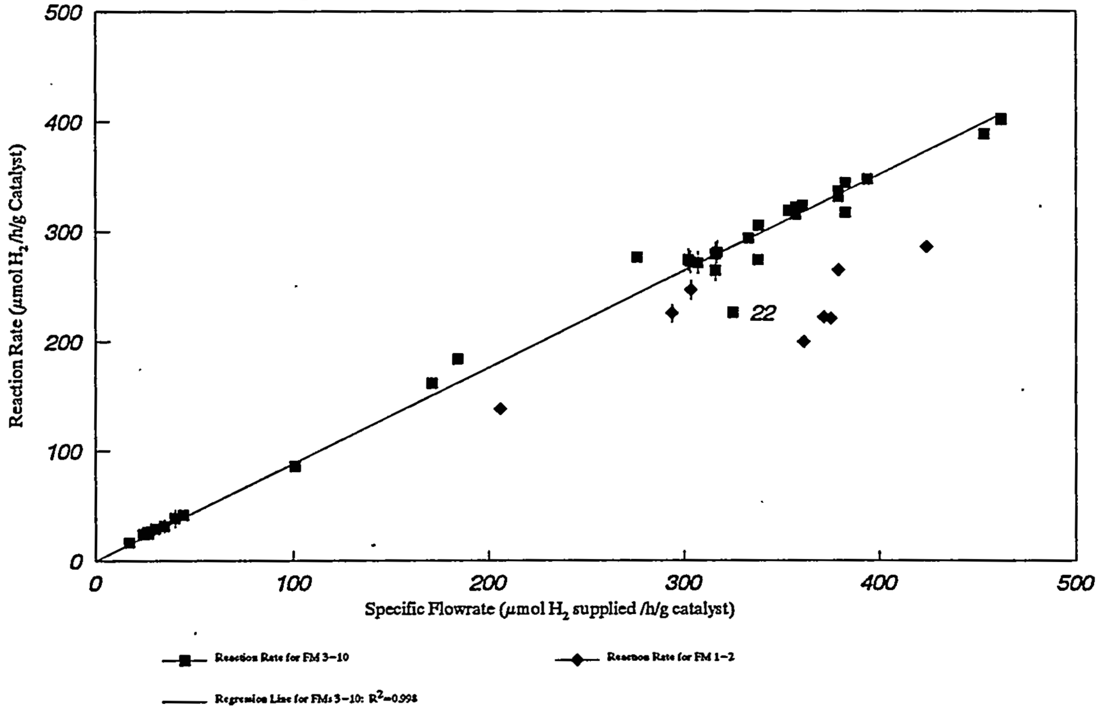
Figure 5-1 shows that the reaction rates varied widely within each of the feed mixture groups. This wide spread within each feed mixture group shows that feed mixture composition was not the only variable affecting the reaction rate. Because other factors were involved, they have to be accounted for before the feed mixture groups can be compared. However, reaction rates above 300 μmol/h/g were observed for most feed mixtures during the performance test. Lower flowrates for feed mixture groups 1, 2, 6, and 8 are discussed in Section 5.5.

Figure 5-1. Performance Test Reaction Rates



Note: Average Reaction rates for FMs cannot be compared. Reaction rate differences are due to differences in Specifc Flowrates rather than in FM composition.

Figure 5-2. Reaction Rate vs. Specific Flowrate



Run 22 is a statistical outlier from the FM 3-10 groups and is not included in regression.

5.4 SPECIFIC FLOWRATE

The SF is the rate at which H_2 was supplied to the reactor per gram of catalyst in the reactor. Because the reaction cannot oxidize more H_2 than is supplied to the reactor, the SF places an upper bound on the possible reaction rate. The SFs shown in Tables 5-1 and 5-2 were calculated from the inlet flowrate (Q) and the inlet H_2 concentration ($X_{H,in}$). The ideal gas law was then used to convert the units to match those of the reaction rate. The equation used to calculate the SF was:

$$SF = 60\frac{QP}{RTW}\left(\frac{X_{H,in}}{100}\right) \qquad \text{(Eqn 5-4)}$$

where:

SF = Specific flowrate for H_2 (μmol/h/g)
Q = Total volumetric flow rate (mL/min)
P = Pressure (atm)
R = Ideal gas constant (mL·atm/μmol·K)
T = Temperature (K)
W = Mass of catalyst (g)
$X_{H,in}$ = Mole percent of H_2 in the inlet gas (%).

If the SF is limiting the reaction rate, it is seen as a strong correlation between the r_H and the SF. Figure 5-2 graphs r_H versus the SF for all the runs listed in Table 5-2. A linear regression by the least squares method yields a squared residual error (R^2) of 0.95, which indicates a good correlation between the reaction rate and the reactant availability.

Figure 5-2 graphs the data for FM 1 and 2 with diamonds and the rest of the data with squares. This was done to show that runs using FMs 1 and 2 had reaction rates consistently lower than runs using FMs 3 through 10. Excluding FMs 1 and 2 from the linear regression yields an R^2 of 0.99, which is an excellent correlation between the reaction rate and the SF. Figures 5-3a through 5-3h graph the reaction rate versus the SF for each feed mixture. The R^2 for four of these feed mixtures is above 0.999 and all but one run have residual errors above 0.95. This indicates that the major factor in the limitation of the r_H is the reactant supply rate or SF. Therefore, reaction rates cannot be compared without first accounting for the SF.

5.5 CONVERSION

The conversion (χ) during a run is the fraction of available H_2 that reacted. The conversion can also be thought of as the ratio between the reaction rate and SF of H_2. This definition allows the reaction rates to be compared to each other with consideration of the different SFs. The conversions in Tables 5-1 and 5-2 were calculated with the equation:

$$\chi = \frac{r_H}{SF} * 100\% \ . \qquad \text{(Eqn 5-5)}$$

Figure 5-4 plots these conversions grouped by feed mixture. The FM 3, 4, 5, and 7 groups tended to have slightly better conversions at lower flowrates than at higher flowrates. Figure 5-5 shows this by graphing the χ against

Figure 5-3. Reaction Rates versus Specific Flowrate for each Feed Mixture. (Sheet 1 of 4)

Fig. 5—3a. Reaction Rate vs. Specific Flowrate for FM 1

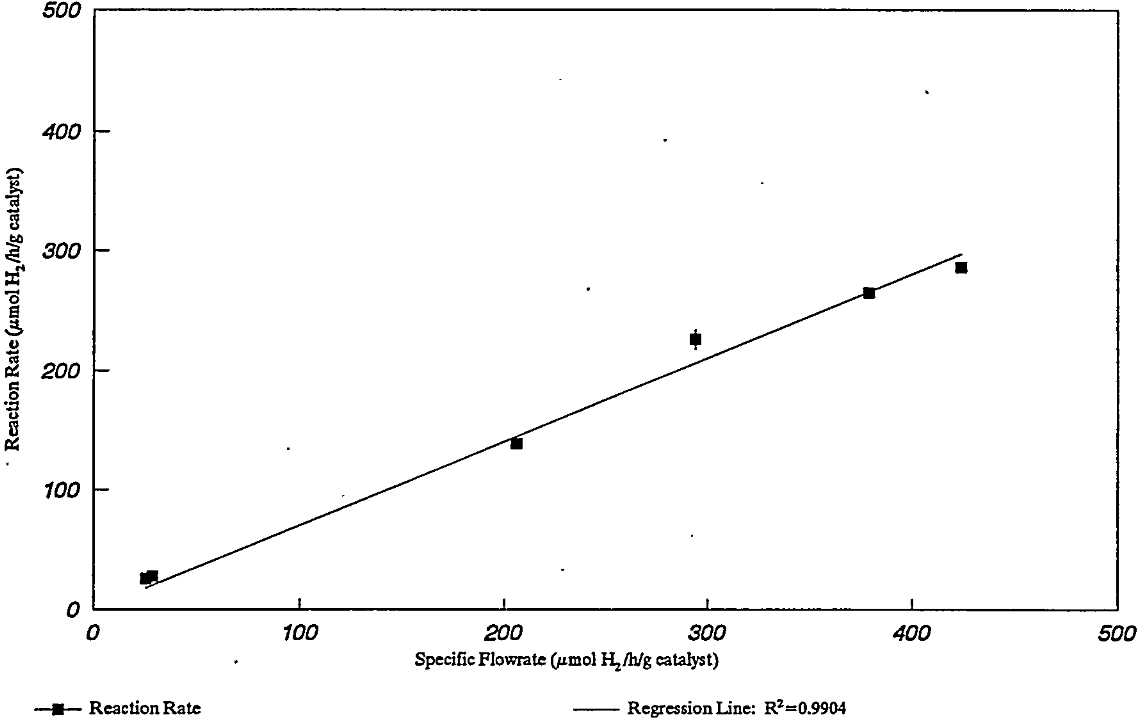


Figure 5—3b. Reaction Rate vs. Specific Flowrate for FM 2

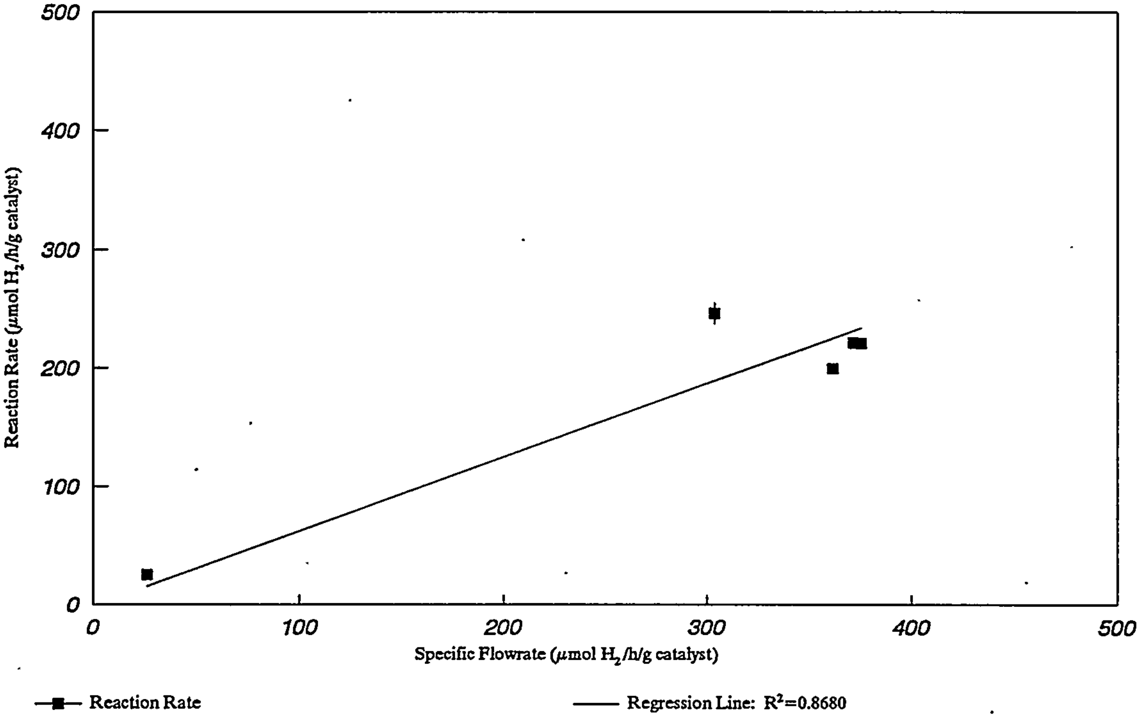


Figure 5-3. Reaction Rates versus Specific Flowrate for each Feed Mixture.
(Sheet 2 of 4)

Figure 5-3c. Reaction Rate vs. Specific Flowrate for FM 3

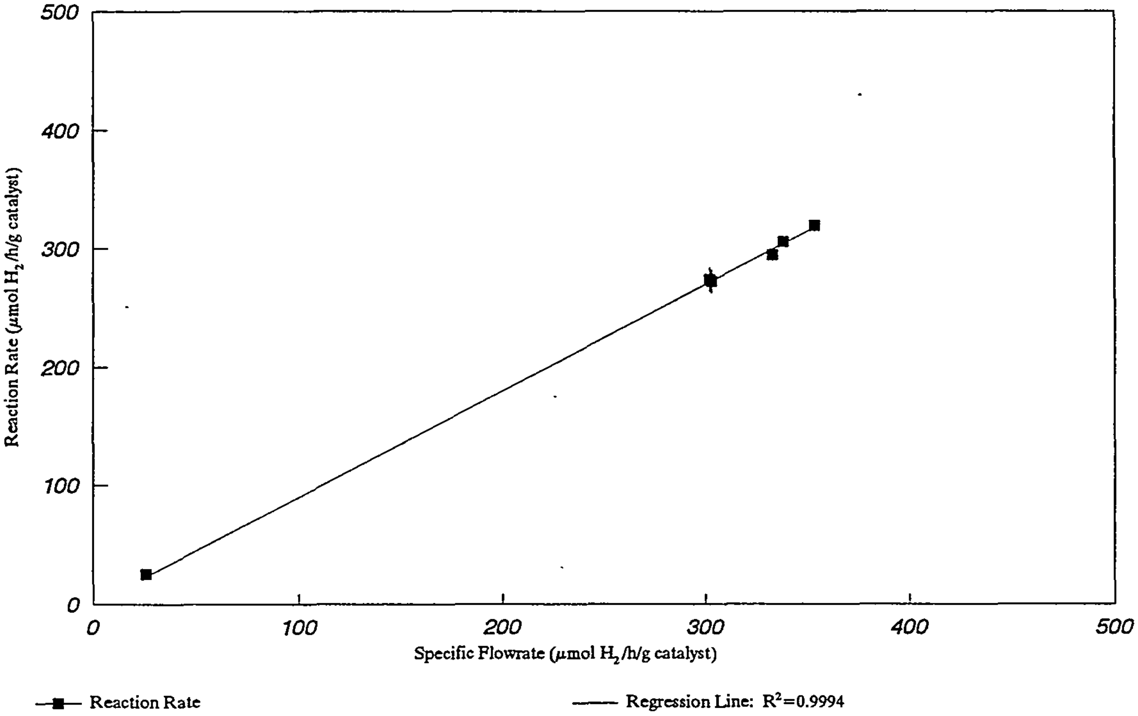


Figure 5-3d. Reaction Rate vs. Specific Flowrate for FM 4

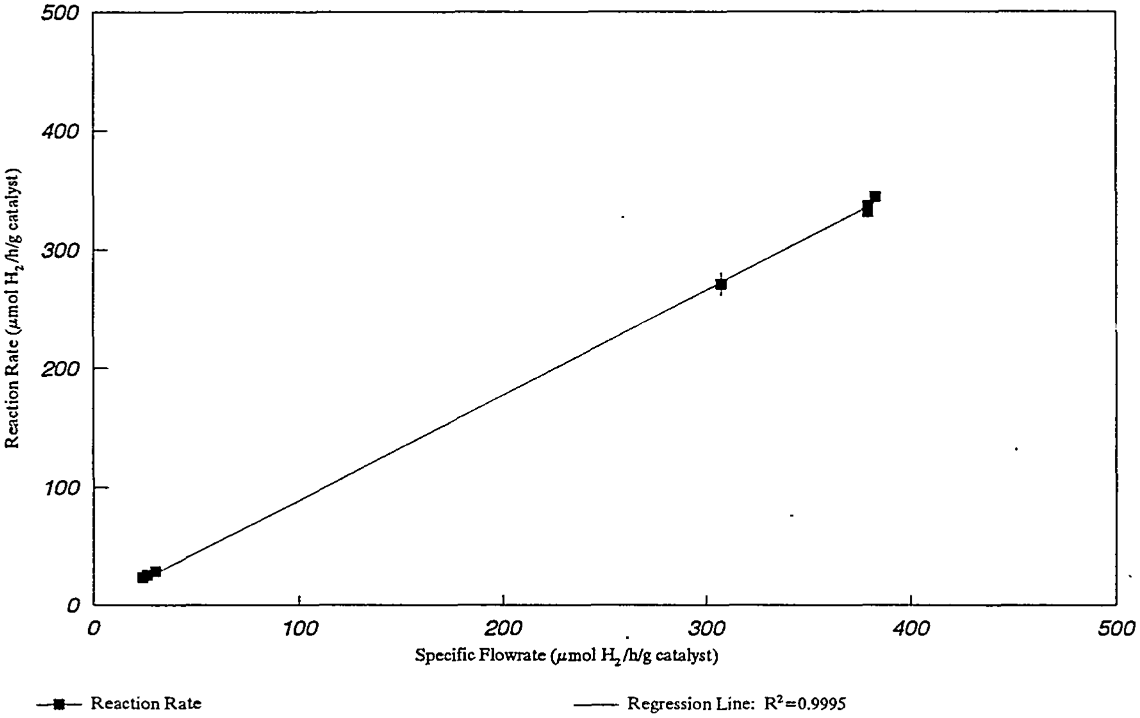


Figure 5-3. Reaction Rates versus Specific Flowrate for each Feed Mixture. (Sheet 3 of 4)

Figure 5–3e. Reaction Rate vs. Specific Flowrate for FM 5

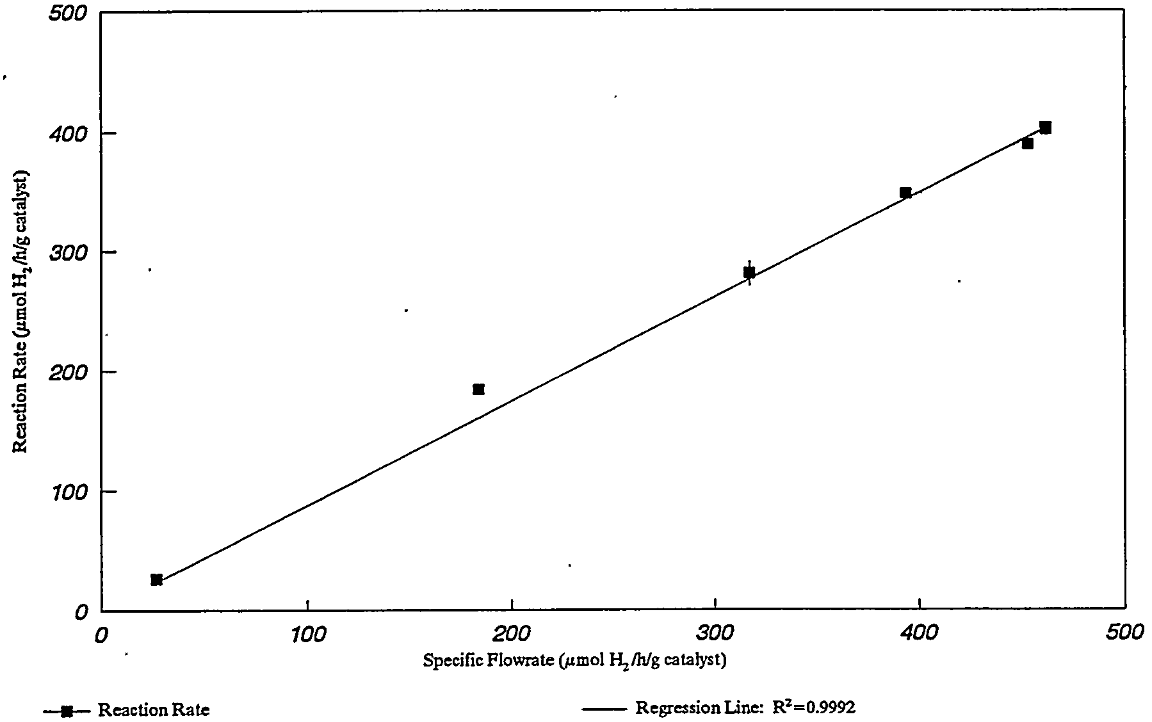
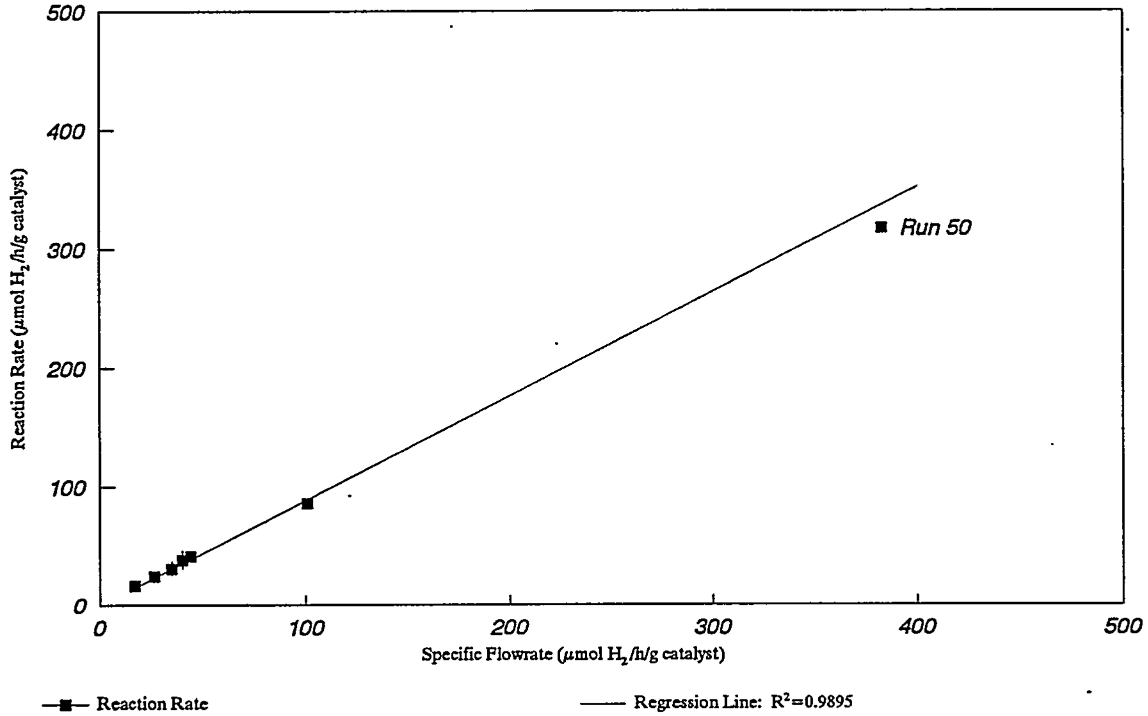


Figure 5–3f. Reaction Rate vs. Specific Flowrate for FM 6



Run 50 used FM 10 and was not included in the regression.

Figure 5-3. Reaction Rates versus Specific Flowrate for each Feed Mixture.
(Sheet 4 of 4)

Figure 5–3g. Reaction Rate vs. Specific Flowrate for FM 7

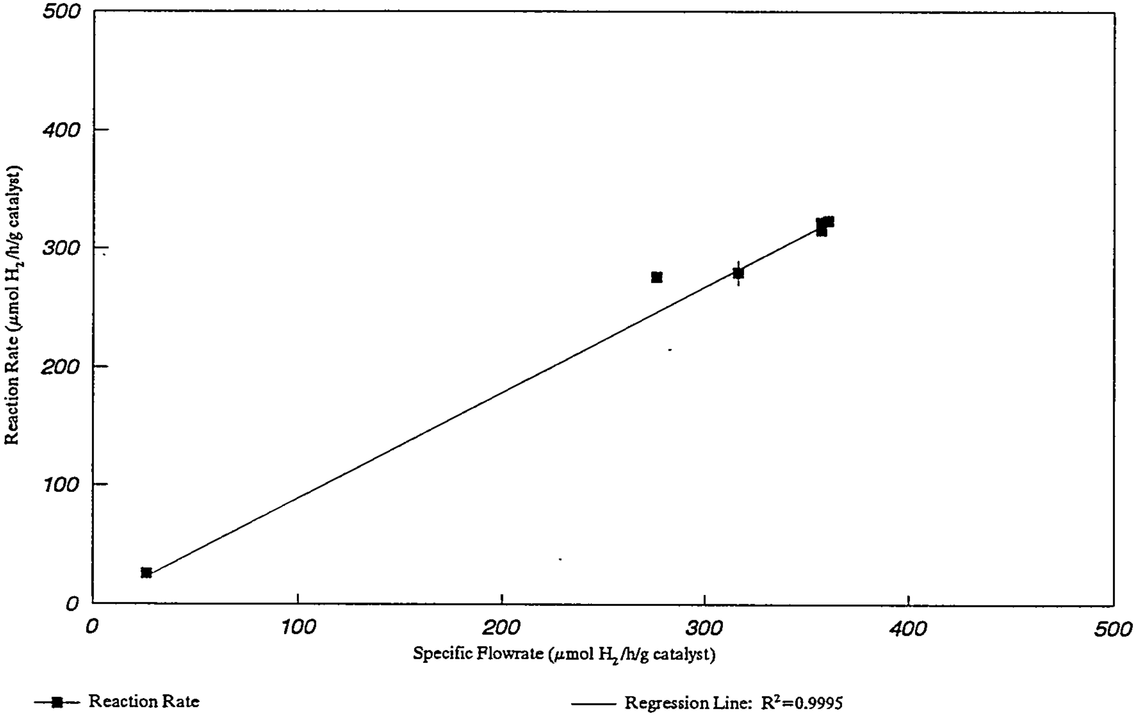


Figure 5–3h. Reaction Rate vs. Specific Flowrate for FM 8

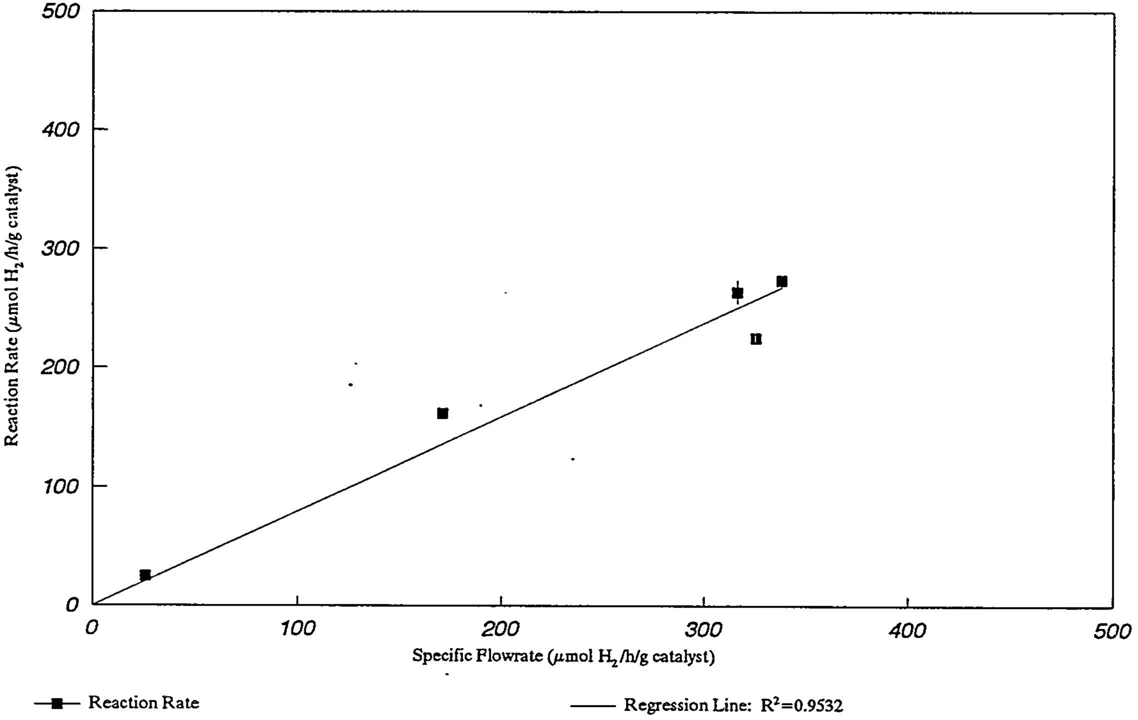
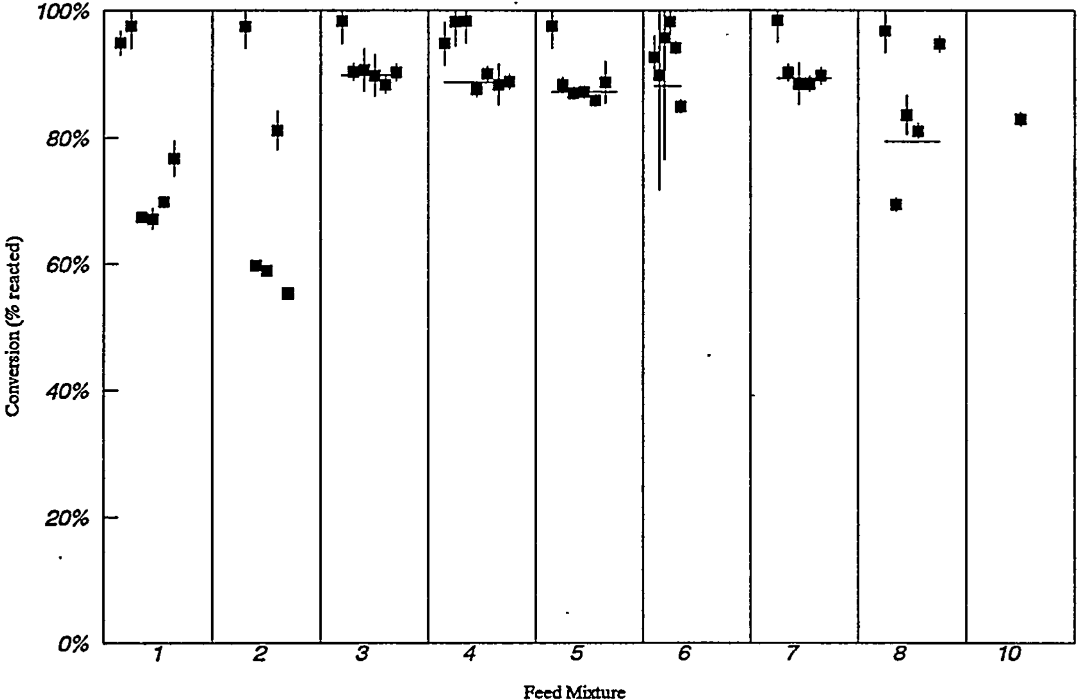


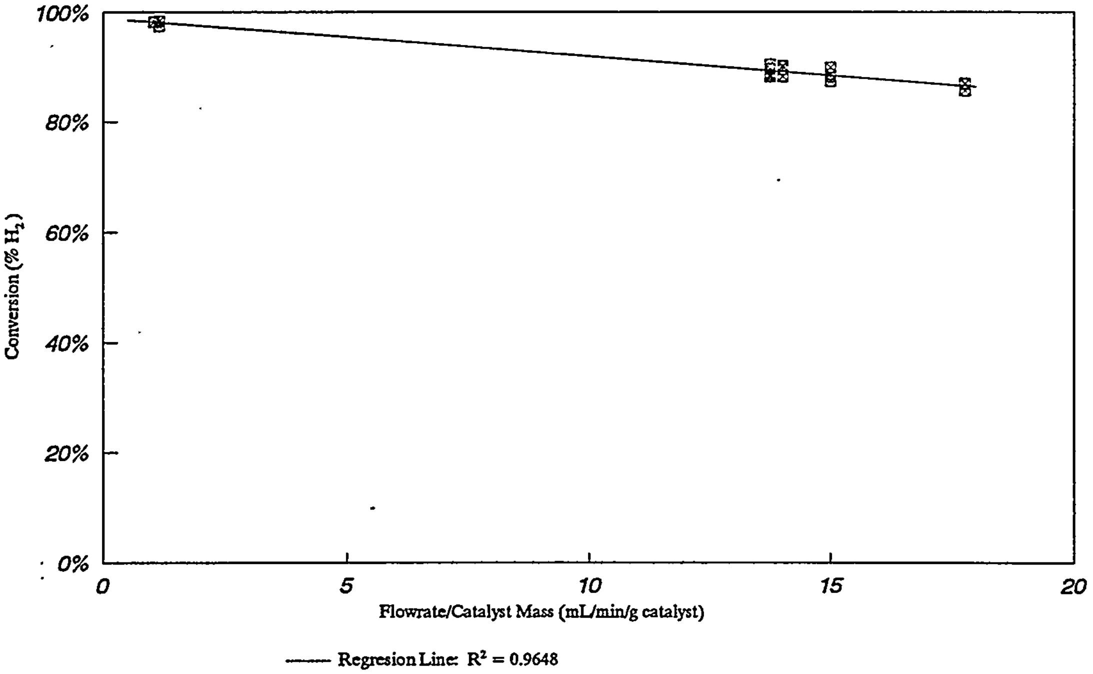
Figure 5-4. Performance Test Conversions



Runs using FM 1 or 2 may be oxidant limited.

Figure 5-5. Conversion vs. Flowrate/Catalyst Mass

Feed Mixtures 3,4,5,7



the flowrate divided by the catalyst mass (Q/W). The R^2 of the regressed line is 0.97, indicating a good correlation between χ and Q/W.

An increase in the total flowrate decreases the residence time. A shorter residence time gives the molecules less time to diffuse into the catalyst bed and less time for the reaction to take place once in the catalyst bed. At low flowrates using FM 3, 4, 5, or 7, the average SF was 25.4 ± 1.0 μmol/h/g, and the average conversion of H_2 into H_2O was 98.2 ± 0.1 percent. At higher flowrates, the average SF was 360.5 ± 50.8 μmol/h/g, and the average conversion of H_2 into H_2O was 88.7 ± 1.3 percent. Table 5-3 lists the conversions found at high and low flowrates for each feed mixture.

Table 5-3. Performance Test Conversions.

Feed Mixture	Average specific flowrate (SF) μmol/h/g	Average conversion (χ) %	Average specific flowrate (SF) μmol/h/g	Average conversion (χ) %
	Low flowrates		High Flowrates	
1	27.0 ± 2.1	96.2 ± 1.9	324.4 ± 95.9	70.3 ± 4.5
2	25.8	97.4	349.6 ± 32.1	63.8 ± 11.7
3, 4, 5 & 7	25.4 ± 1.0	98.2 ± 0.4	360.5 ± 50.8	88.7 ± 1.3
6	32.0 ± 10.8	94.0 ± 3.2	---	---
8	25.9	96.7	322.1 ± 9.3	78.0 ± 7.6
	160.0	94.6		

Run data given are averages ± the standard deviation. Data given without a standard deviation are single data points.

Runs using FM 1, 2, 6, and 8 most likely had the same type of correlation between χ and Q/W, although this was not found because it was obscured by other factors described below. FM 1 and 2 were intended to have stoichiometric concentrations of H_2 and an oxidant, O_2 or N_2O. But, because of larger than expected variances in the flowmeters, it is possible that the oxidant concentration in some of the runs using FM 1 and 2 was below the stoichiometric ratio with H_2. Also, the oxidants diffuse much slower than H_2. Between the lower oxidant feed concentrations and the oxidants diffusing slower, faster flowrates had a greater effect on the conversion in the FM 1 and 2 groups than in other groups. These conversions ranged from 55.3 to 97.5 percent.

In the grout vault, the inlet and outlet flowrate of gases will be very slow in comparison to the size of the grout vault sump and the diffusion rate of the oxidants. These conditions will allow ample time for H_2 to diffuse to the catalyst bed. Therefore, near stoichiometric concentrations of oxidant and H_2 will not cause conversion limitations due to slow diffusion.

The FM 8 conversions varied between 84 and 97 percent and did not conform to a χ versus Q/W correlation. At the higher SF ranges, runs with 0.1 percent NH_3 were slightly inhibited. While this conversion range is obviously lower than conversions using FM 3, 4, 5, and 7, runs 14 and 62 show that conversions greater than 95 percent are possible at SFs between 26 and 170 μmol/h/g.

The CO in FM 6 significantly impacted the function of the catalyst by presumably chemisorbing to the active catalytic sites and deactivating them. After being exposed to enough CO, the catalyst would no longer catalyze the H_2/N_2O reaction. In all the runs, the CO poisoning of the catalyst decreased the amount of active catalyst before the reactor achieved steady state gas concentrations. Because the reaction rate was dependent on the mass of active catalyst in the reactor, the partial deactivation of the catalyst decreases the reported reaction rates. In the runs in Table 5-2 that used FM 6 or 10, the gas samples were taken before the catalyst was completely deactivated. These runs give a conservative assessment of the catalyst's performance in a CO atmosphere before deactivation. At low SFs averaging 32.0 ± 10.8 μmol/h/g, the conversions averaged to 94.0 ± 3.2 percent.

5.6 INHIBITING AND POISONING EFFECTS

In runs using FM 6, the catalyst's performance depended on the amount of CO the catalyst had been exposed to. If the exposure was relatively low, the catalyst would function. But if the exposure was relatively high, the catalyst would not catalyze the H_2/N_2O reaction. This cumulative phenomenon is the reason the catalyst was functioning when the offgas was analyzed in some of the runs using FM 6, while in other FM 6 runs it was not.

It was seen that at times the performance runs were not long enough to allow the cumulative CO poisoning effect to kill the reaction. Therefore, extended runs were performed to determine whether cumulative poisoning effects occurred with H_2O, CH_4, or NH_3 at run times longer than allowed in the performance runs. Each extended run was over 1000 minutes long and went through more than 100 residence times (τ_r). Table 5-4 lists the runs and the effects on the reaction rate.

No cumulative poisoning effects were found using H_2O, CH_4, or NH_3. Only CO poisoned the catalyst. This shows that excess H_2O vapor, as well as CH_4 and NH_3 gases will not poison the catalyst.

The durability test described in the test plan (Britton 1993a) called for a feed mixture with CO as well as all the other gases used in the performance test. The durability test would then look at the changes in the reaction rate over a period of months. Because CO in the concentrations used in the performance test would have poisoned the catalyst and ended the durability test in a matter of hours, the durability test was not performed. Instead, a sorption capacity test was designed and performed to determine the amount of CO the catalyst could hold before becoming too poisoned to function. This sorption capacity test is described in Section 4.0 and the results are reported in Section 6.0.

Table 5-4. Extended Performance Runs.

FM	Run #	Time min	# of τ_r	SF µmol/h/g	Rxn rate µmol/h/g	Conversion %	Effect
5	28e	1249	146	454.3	396	87	none
	64	3089	306	185.2	~185[†]	~100[†]	none
6	59	2665	176	23.2	0	0	reaction killed
7	63	1690	167	273.3	~273[†]	~100[†]	none
8	62	1770	175	169.1	160	95	none

[†] The gas chromatography analytical data for runs 63 and 64 was lost due to a misconfigured computer program. The reaction rate and conversion data is estimated from Whittaker H_2 concentration measurements.

6.0 RESULTS OF THE SORPTION CAPACITY TEST

Feed mixtures of N_2, CO, H_2, and N_2O, were metered into the reactor with the catalyst in Runs 67 through 89. Inlet and outlet gas concentrations were determined by gas chromatography of samples 93-175 through 93-658. The analytical data for these samples is in Appendix B of the supporting data document (Britton 1994).

6.1 MIXED TANK REACTOR ASSUMPTION

The CO sorption capacity (SC) of the catalyst is the total amount of CO that the catalyst will chemisorb per gram of catalyst (μmol/g). This is calculated by comparing the actual CO concentration of the outlet stream to the outlet CO concentration that would exist if the catalyst was not chemisorbing CO.

The outlet CO concentration is estimated by assuming the reactor behaves like a mixed tank reactor where the inlet gas is mixed with the bulk of the gas in the reactor. The equation for the estimated outlet CO concentration is derived in Appendix D and is:

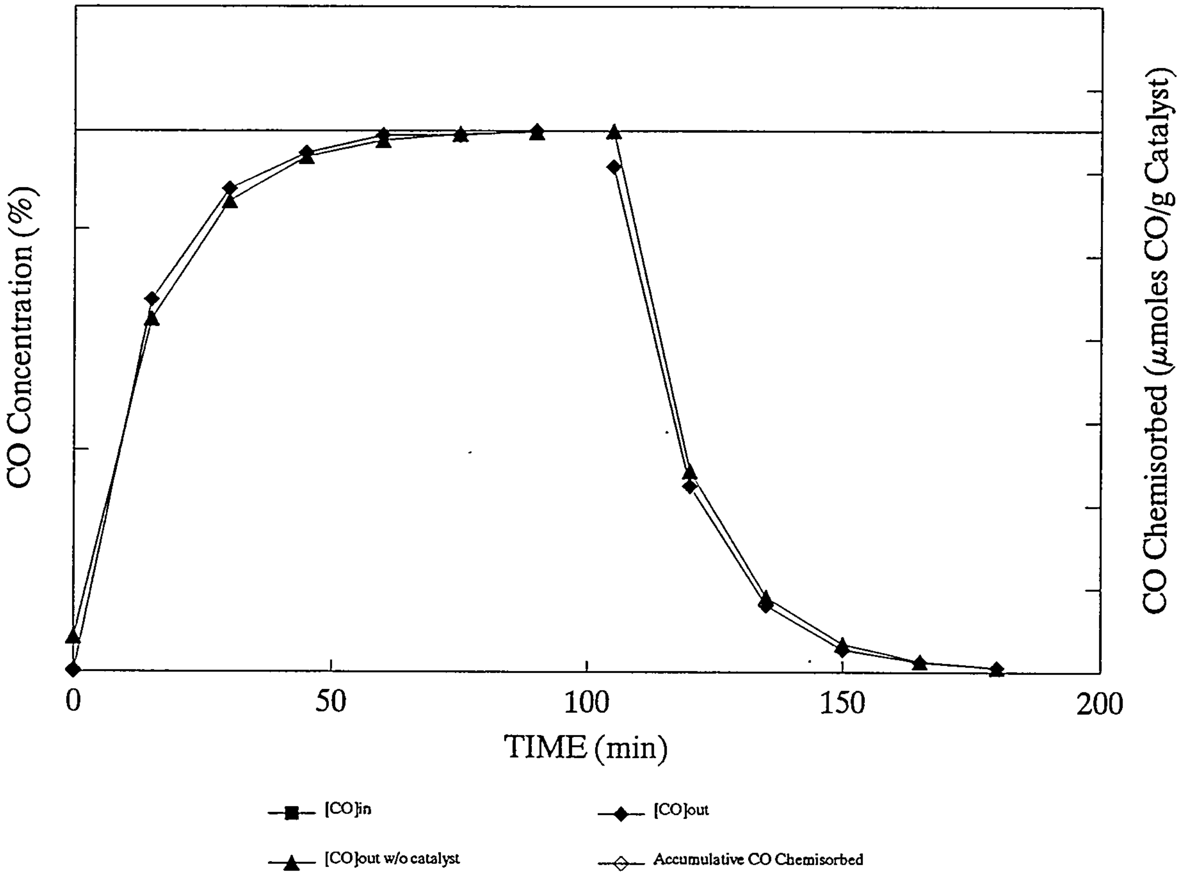
$$X_{CO,out}^{est} = X_{CO,in}\left(1 - e^{-\frac{t}{\tau_r}}\right) \qquad \text{(Eqn 6-1)}$$

where:

$X_{co,out}^{est}$ = CO concentration in the offgas assuming no CO chemisorption (%)
$X_{co,in}$ = CO concentration in the feed gas (%)
t = Time from the start of the inlet flow (min)
τ_r = Residence time for gas in the reactor (min).

Figure 6-1 displays the actual and estimated CO outlet concentrations from Run 68. This data is presented without a scale because the data used was preliminary data and was taken before the gas chromatograph was correctly calibrated. It is nonetheless presented because run 68 was performed minutes after the catalyst had been loaded with CO in run 67 and the catalyst was not given the opportunity to desorb any of the CO. Therefore, the reactor functioned like it would without the catalyst. Figure 6-1 shows the actual outlet concentration matches very closely to the outlet concentrations that would be expected from an ideal mixed-tank reactor. This supports the assumption that the reactor behaves as a mixed tank reactor. More detail on the equations for a mixed tank reactor can be found in Appendix D.

Figure 6-1. Sorption Capacity Test Run 68.



10 g Catalyst (5 g Englehard Deoxo Type 18467, 5 g AECL Hydrophobic Type 85–42)
Reactor Volume 7571 mL, 1 atm, 20°C
500 sccm 0.122% CO in Nitrogen
Regeneration Method: None

6.2 CARBON MONOXIDE SORPTION CAPACITY CALCULATION

After applying the ideal gas law to the difference between the estimated and actual outlet concentrations and summing the data over the entire run, the equation for the SC becomes:

$$SC = \frac{PQ}{RTW} \frac{\sum_i \left[I_i \left(X^{est}_{CO,out\,i} - X^{act}_{CO,out\,i} \right) \right]}{100} \qquad \text{(Eqn 6-3)}$$

where:

SC = Sorption capacity of CO on the catalyst (μmol/g)
P = Pressure (atm)
Q = Flowrate of the inlet gas stream. (mL/min)
R = Ideal gas constant
T = Temperature (K)
W = Mass of catalyst (g)
n = Number of time intervals used
I = Length of time interval between X_{CO} measurements (min)
$X^{est}_{CO,out}$ = Estimated CO concentration in the offgas (%)
$X^{act}_{CO,out}$ = Actual CO concentration in the offgas (%).

Figure 6-2 displays, on the left Y-axis, the actual and estimated CO outlet concentrations from Run 84. The accumulated CO chemisorbed to the catalyst is on the right Y-axis, the final value of which is the SC. The SC graphs for the other runs are in Appendix B. Table B-1 in Appendix B contains the run data for the all the runs in the sorption capacity test.

Any deviation in the actual concentration from the expected concentration after the outlet concentrations had leveled off at the inlet concentration was considered a random fluctuation and its contribution to the SC was ignored. In run 84, the total SC was reached in 90 minutes. All the contributions from random fluctuations past 90 minutes were ignored.

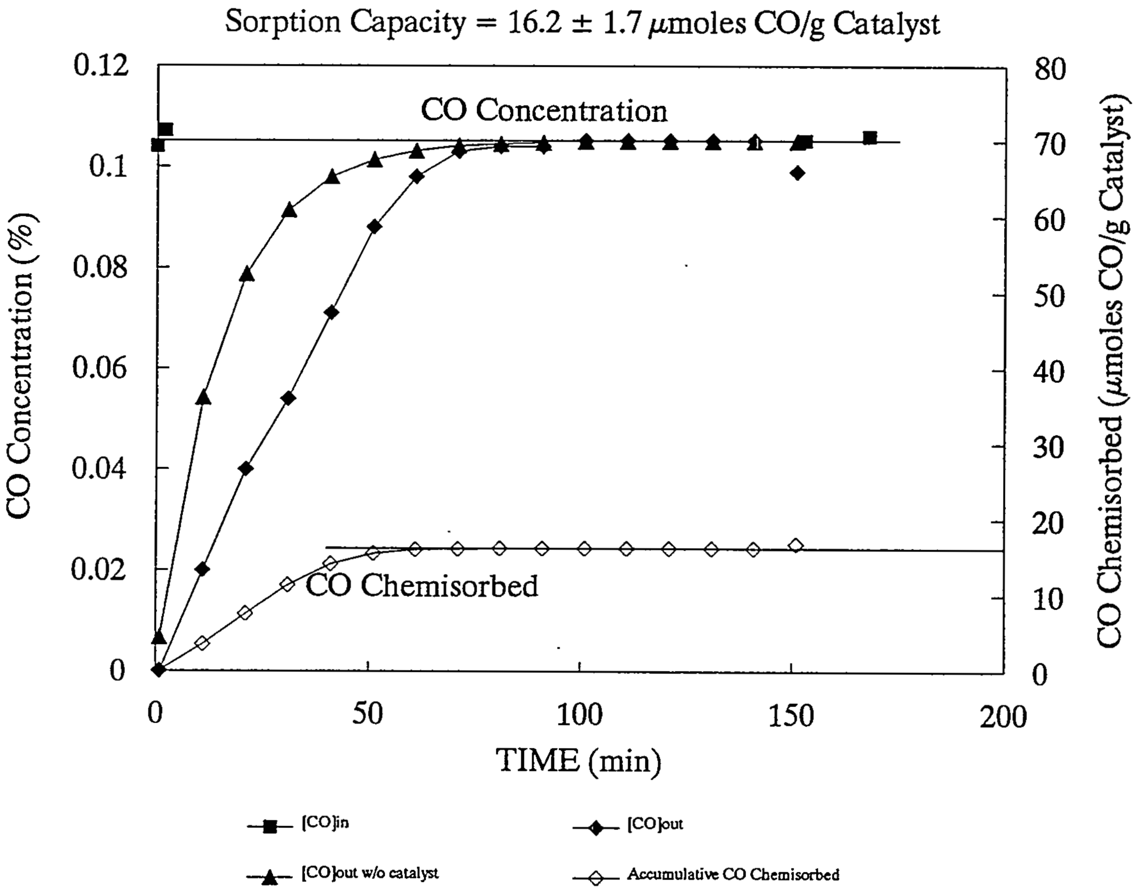
6.3 DISPLAY OF CO POISONING/INHIBITION

In run 82, FM 4, which contained H_2 and N_2O but no CO, was used to show the uninhibited and unpoisoned rate of the H_2/N_2O reaction on the catalyst. Figure 6-3 is the graphed data from run 82. The uninhibited reaction rate of 435.8 ± 36.8 μmol/h/g was determined using FM 4 which had no CO. After 105 minutes, the feed mixture was switched to FM 14 which had a nominal 0.055 percent CO concentration. Over the next 90 minutes, the reaction rate fell to zero as the amount of CO chemisorbed to the catalyst increased to 14.9 ± 21 μmol/g catalyst. This shows the relationship between the drop in the reaction rate and the sorption of the CO onto the catalyst.

6.4 CATALYST REGENERATION

Two different methods were used to regenerate the catalyst. The methods involved metering volumes of N_2 or air over the catalyst. A third scenario was replacement of the used catalyst with virgin catalyst. A comparison of the different regeneration methods was made by comparing the SC determined after each regeneration. Table 6-1 contains a summary of the sorption

Figure 6-2. Sorption Capacity Test - Run 84.



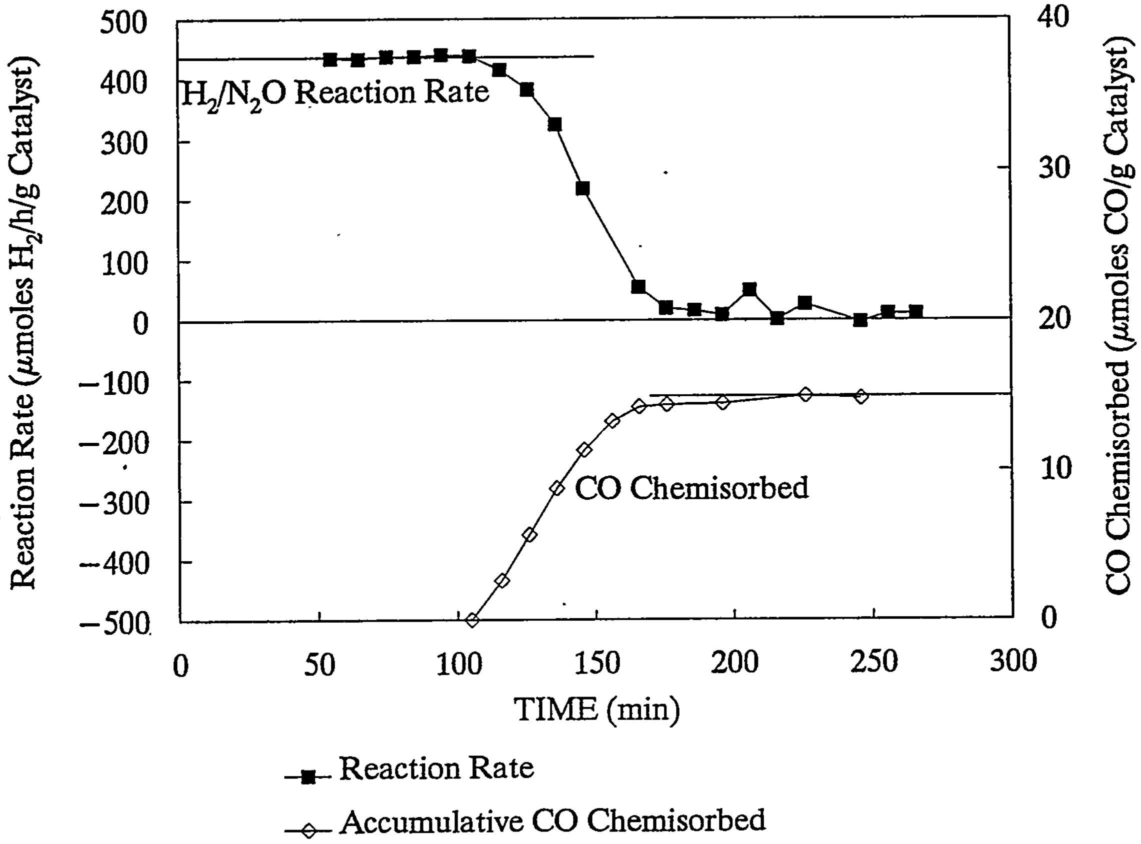
20 g Catalyst (10 g Englehard Deoxo Type 18467, 10 g AECL Hydrophobic Type 85–42)
Reactor Volume 7571 mL, 1 atm, 16°C
500 sccm 0.105% CO in Nitrogen
Regeneration Method: Air Flush
30 L/min @ 7 psi for 10 min
300 L of Air, Total
15.0 L air/g catayst

capacity test results. The five columns under the heading of regeneration method are (1) the type of gas used, (2) the flush rate (Q_f) in liters per minute, (3) the total flush time (t_f) in minutes, (4) the total volume (V_f) of gas flushed over the catalyst in liters, and (5) the ratio of flush gas volume to the mass of catalyst in liters of flush gas per gram of catalyst. The SC in the last column is given with its standard deviation.

6.4.1 Nitrogen Regenerated Catalyst

Runs 72, 73, 75, and 76 flushed the 20 grams of catalyst with between 10 and 600 L of N_2 at rates ranging from 0.5 to 30 L/min. The resulting SCs ranged from 0.0 to 2.6 μmol/g. These values are very small and the variability in this data may be noise. The longest time used to regenerate the catalyst was 984 minutes or 16.4 hours. Even in this length of time, no more than 20 percent of the CO desorbed from the catalyst.

Figure 6-3. Reaction Rate Decline - Run 82.



20 g Catalyst (10 g Englehard Deoxo Type 18467, 10 g AECL Hydrophobic Type 85−42)
Reactor Volume 7571 mL, 1 atm, 17°C
595 sccm 0.711% H_2 in Nitrogen
595 sccm 0.701 H_2 and 0.055% CO in Nitrogen
Regeneration Method: Air Flush
30 L/min @ 10 psi for 15 min
450 L of air, Total
22.5 L air/g catalyst

6.4.2 Virgin Catalyst

Runs 69, 74, and 85 were performed with 20 or 30 g of virgin catalyst. The resulting SCs ranged from 17.9 to 21.5 μmol/g with an average of 19.3 ± 2.0 μmol/g.

6.4.3 Air Regenerated Catalyst

Runs 80, 82 through 84, and 86 through 89 flushed 20 or 30 g of catalyst with between 30 and 840 L of air at rates ranging from 0.5 to 20 L/min. The resulting SCs ranged from 13.8 to 19.8 μmol/g with an average of 17.3 ± 1.9 μmol/g. This is only slightly smaller than the average SC of the virgin catalyst and shows that the catalyst can be effectively regenerated

Table 6-1. Carbon Monoxide Sorption Capacity Test Run Data.

Run #	Catalyst Mass g	Regeneration Method					% CO	Sorption Capacity µmoles CO / g Catalyst
		Gas	Q_f L/min	t_f min	V_f L	L gas / g Catlyst		
Nitrogen Regenerated Catalyst								
72	20.0	N_2	0.5	20	10	0.5	0.117	1.8 ± 0.7
73	20.0	N_2	0.5	984	492	24.6	0.123	3.7 ± 0.7
75	20.0	N_2	12	17	204	10.2	0.135	1.8 ± 0.4
76	20.0	N_2	30	20	600	30.0	0.132	0.8 ± 0.1
							Average SC	2.0 ± 0.5
Virgin Catalyst								
69	20.0	–	–	–	–	–	0.090	18.5 ± 2.0
74	20.0	–	–	–	–	–	0.121	17.9 ± 1.9
85	30.0	–	–	–	–	–	0.100	21.5 ± 2.3
							Average SC	19.3 ± 2.0
Air Regenerated Catalyst								
80	20.0	Air	17.0	10	170	8.5	0.096	13.8 ± 1.4
82	20.0	Air	30.0	18	540	27.0	0.056	14.9 ± 2.1
83	20.0	Air	30.0	28	840	42.0	0.123	19.5 ± 2.2
84	20.0	Air	30.0	10	300	15.0	0.105	16.2 ± 1.7
86	30.0	Air	0.5	900	450	15.0	0.101	18.5 ± 1.9
87	30.0	Air	37.7	20	754	25.1	0.103	19.8 ± 2.1
88	30.0	Air	0.6	418	241	8.0	0.101	18.7 ± 1.9
89	30.0	Air	0.5	60	30	1.0	0.102	17.0 ± 1.8
							Average SC	17.3 ± 1.9

with a small amount of air. The most likely mechanism for this regeneration of the catalyst is the oxidation of the CO by the O_2 in the air. The sorption capacities listed in Table 6-1 are graphed in Figure 6-4.

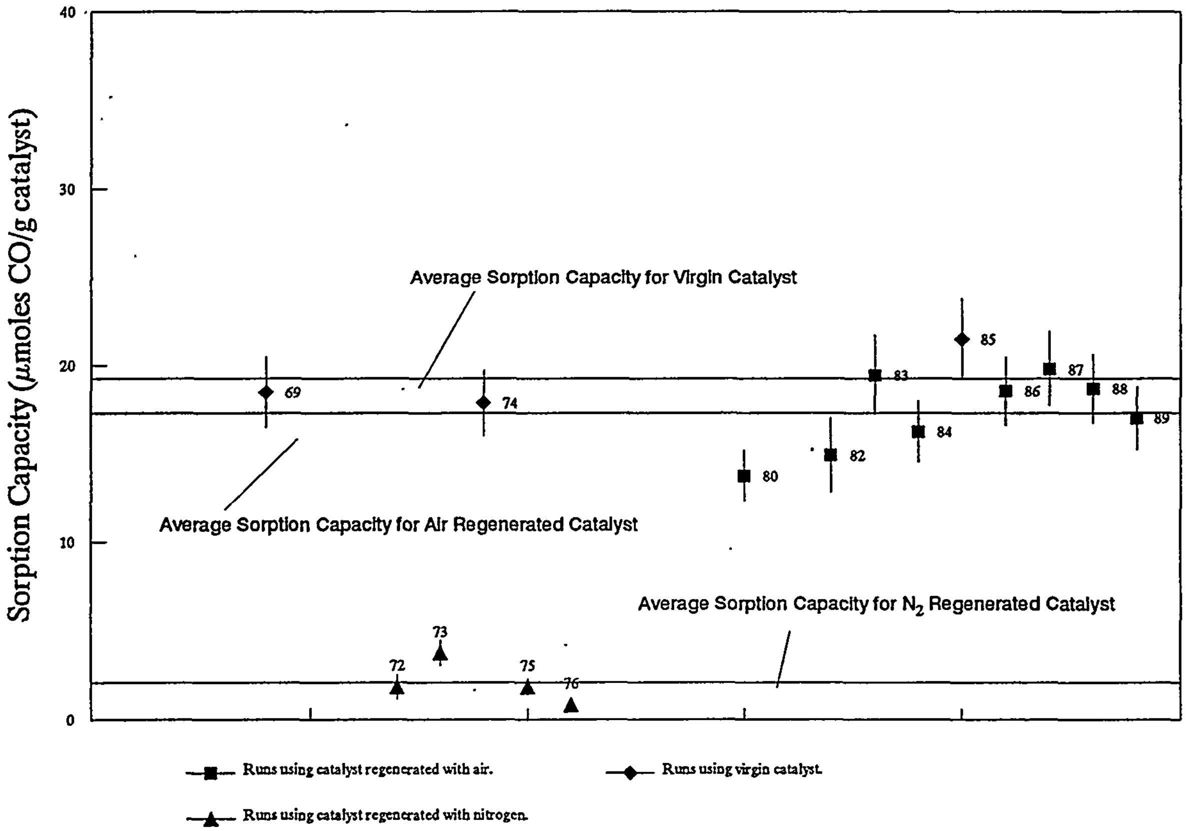
6.4.4 Lost Runs

Runs 65 through 68, 70, 71, 77, 78, 79, and 81 were either aborted, the data was lost due to a misconfigured computer program, or gave very poor and unreliable data and, therefore, were not included in Table 6-1.

6.5 ANALYSIS DIFFICULTIES- NITROUS OXIDE INTERFERENCE

During the sorption capacity test, the samples were taken in Tedlar® bags and quickly analyzed with a nearby gas chromatograph. In the analysis, the N_2O was partitioned from the other sample components by a molesieve column. But because the concentration was so high, the column overloaded. The N_2O peak then stretched out over a considerable time period and appeared as a deviation of the expected baseline. The elution of the N_2O from the column

Figure 6-4. Sorption Capacity.



Average Sorption Capacity for Nitrogen Regenerated Catalyst = 2.0 ± 0.5 μmoles CO/g Catalyst.
Average Sorption Capacity for Air Regenerated Catalyst = 17.3 ± 1.9 μmoles CO/g Catalyst.
Average Sorption Capacity for Virgin Catalyst = 19.3 ± 2.0 μmoles CO/g Catalyst.

was over a long enough period that it was initially perceived as an instrumental error. Several runs gave useless data or were aborted because of this erratic baseline. After identifying the problem, an erratic baseline, and its cause, an extended N_2O elution, analyses were spaced further apart to compensate for the N_2O elution (Pingel 1994).

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7.0 CONCLUSIONS AND RECOMMENDATIONS

The catalyst studied in this test was a 50-50 blend of Engelhard Deoxo type 18467 and AECL hydrophobic catalyst type 85-42. For gases having H_2 and a stoichiometric excess of either N_2O or O_2, this catalyst blend can effectively catalyze the H_2 oxidation reaction at a rate exceeding 380 µmol/h/g and leave the gas with less than a 0.15 percent residual H_2 concentration. This should hold true in gases with up to 2.25 percent H_2O and 0.1 percent CH_4. Higher reaction rates with slightly lower conversions are possible, but were not quantified in this test because the blend's catalytic ability exceeded the equipment's ability to feed the gas mixtures to the reactor.

This test limited the amount of time the H_2 and oxidants were given to diffuse to the catalyst bed and therefore limited the extent of the conversion. This was seen in the differences between conversions at low flowrates and those at high flowrates. This was also seen in the lower conversion with feed mixtures that did not have excess oxidant. The grout vault will have a much longer residence time than the reactor vessel in this test. This will allow more time for gases to diffuse to the catalyst bed and will result in conversions near 98 percent.

The reaction rates observed with feed mixtures having up to 1.0 percent NH_3 tended to be slower than those of other feed mixture groups possibly because of a slight inhibition. The inhibition mechanism may be an easily reversed adsorption of NH_3 to the active catalyst sites. A less likely mechanism would be oxidation of NH_3. No cumulative effect was noted with this NH_3 inhibition and no increase of the effect with prolonged exposure. Reaction rates greater than 250 µmol/h/g were measured. These left a residual H_2 concentration less than 0.20 percent H_2. This lower reaction rate and conversion with NH_3 present should not be a problem for actual operation in the sump.

The catalyst blend should also work at reaction rates exceeding 380 µmol/h/g in gases with up to 0.1 percent CO but only until the catalyst is exposed to enough CO to block the catalytic sites and stop the reaction. Rates this high were not observed in the test because, when using feed mixtures with 1 percent H_2 and 0.1 percent CO, the CO poisoned the catalyst before the reactor could come to equilibrium. However, rates as high as 310 µmol/h/g were observed in the test in gases with 0.01 percent CO.

The mechanism for this poisoning of the catalyst is the chemisorption of CO to the active catalyst sites. Under operating conditions, moderate temperature and no O_2, this chemisorption is not reversible. However, the chemisorbed CO will readily oxidize when exposed to O_2, leaving the catalyst fully functional.

The average SC for virgin catalyst was determined to be 19.3 ± 2.0 µmol/g. The average SC for catalyst regenerated with air was 17.3 ± 1.9 µmol/g. The lowest SC measured for air regenerated catalyst was 13.8 ± 1.4 µmol/g. This number is conservative and can be used in calculating the mass of catalyst required in the sump for a given period of time. If air migrates into the sump due to barometric pressure changes or diffusion, the O_2 in the air will oxidize the CO thereby regenerating the catalyst and extending the operating life of the catalyst.

Because the catalyst will work effectively until it is nearly fully loaded with CO, the catalyst bed could be oversized to scavenge CO for several years. This will keep some of the catalyst available for the reaction for many years. When the catalyst is nearly completely poisoned by CO, it can then be regenerated by exposure to air, either by removing the bed from the sump or by an insitu catalyst regeneration method where an airline is installed in catalyst bed and air is flushed over the catalyst without removing it from the sump.

8.0 NOMENCLATURE

d	= Reactor inn diameter	cm
i	= Number of X_{CO} measurements taken	---
I	= Time interval between X_{CO} measurements	min
P	= Pressure	atm
Q	= Volumetric flowrate (at 20°C)	mL/min
R	= Ideal gas constant, $8.206*10^{-5}$	$\frac{mL \cdot atm}{\mu mole \cdot K}$
r_H	= Reaction rate	µmol/h/g
SC	= CO sorption capacity on the catalyst	µmol/g
SF	= Specific flowrate	µmol/h/g
t	= Run time from the start of the inlet flow	min
T	= Gas temperature	°C or K
$\underline{V}$	= Volume of reactor	mL
V	= Linear velocity (adjusted for temp)	cm/min
W	= Mass of catalyst	g
X_i	= Concentration of i in sample as analyzed	mole %
Y_i	= Concentration of i in air	mole %
τ_r	= Residence time of the gas in the reactor	min
Φ	= Air contamination	% of total
χ	= Conversion	% reacted

Subscripts
in = inlet conditions
out = outlet or reactor conditions
f = regeneration flush during the sorption capacity test

Superscripts
act = actual
est = estimated

Other symbols
cat = catalyst
Δ = standard deviation

9.0 REFERENCES

Britton, M. D., 1993a, *Hydrogen Recombiner Catalyst Performance and Durability Test Plan*, WHC-SD-WM-TP-159, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Britton, M. D., 1993b, *Hydrogen Recombiner Catalyst*, Laboratory Notebook number WHC-N-734, 1, Westinghouse Hanford Company, Richland, Washington.

Britton, M. D., 1994, *Hydrogen Recombiner Catalyst Test Supporting Data Document*, WHC-SD-WM-TRP-212, Rev. 0., Westinghouse Hanford Company, Richland, Washington.

Crea, B. A., 1992, *Grout Vault Heat Transfer Results*, WHC-SD-WM-ER-143, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Henrie, J. O., D. J. Flesher, G. J. Quinn, and J. Greenborg, 1986, *Hydrogen Control in the Handling, Shipping and Storage of Wet Radioactive Waste*, RHO-WM-EV-9, Rev. 1 P, Rockwell Hanford Operations, Richland, Washington.

Levenspiel, Octave, 1972, *Chemical Reaction Engineering*, Second Edition, John Wiley & Sons, Inc., New York, New York.

NFPA 69, 1992, *Standard on Explosion Prevention Systems*, National Fire Prevention Association, Chapter 3-3, Design and Operating Requirements.

Meshako, K. L. and B. D. Bullough, 1985, *Carbon Monoxide Poisoning of Selected* H_2/O_2 *Recombiner Catalysts*, SD-WM-TRP-007, Rockwell Hanford Operations, Richland, Washington.

Pingel, L. A., 1994, *Grout Program Gas Chromatograph Spread Sheets*, (internal memo 12920-SAS94-083 to M. D. Britton, April 6), Westinghouse Hanford Company, Richland Washington. (See WHC-SD-WM-TRP-212, Appendix B)

Roblyer, S. P., 1993, *Grout Disposal Facility Gas Concentrations*, WHC-SD-WM-ER-151, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Tret'yakov, I. I., B. R. Shub, and S. Z. Roginskii, 1967, *Hydrogen Oxidation by Nitrous Oxide on Platinum Purified in an Ultravacuum*, Doklady Akademii Nauk SSSR, Vol. 176, No. 3, pp. 641-644.

Tret'yakov, I. I., and B. R. Shub, 1970, *Oxidation of Hydrogen by Nitrous Oxide on Platinum Purified in High Vacuum*, Probl. Kinet. Katal., Vol. 14, pp 202-210. (Refer to Appendix F of Britton 1993a for the English translation.)

Weis, M. P., 1993, *Hydrogen Gas Mix Burn Analysis for the Grout Disposal Facility*, WHC-SD-WM-ER-162, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

WHC, 1992, *Grout Treatment Facility Safety Analysis Report*, WHC-SD-SAR-042 Rev. 0, Westinghouse Hanford Company, Richland, Washington.

APPENDIX A

PERFORMANCE TEST SAMPLE ANALYSIS DATA

Table A-1. Performance Test Sample Analysis Data. (Sheet 1 of 5)

Sample #	Run #	Note	FM & i/o	Sample Composition (as analyzed) (Mole %)											Air Contamination (Mole %)	
				N_2	Ar	H_2	O_2 †	N_2O	CO	CO_2	CH_4	H_2O ‡	NH_3 ‡	NO_x	Ar Method	O_2 Method
93-001	FG1		FG	95.720	0.035	3.550	0.683	<0.001	<0.005	0.004	<0.001	na	na	<0.001	3.7	3.3
93-002	FG1		FG	95.980	0.013	3.810	0.198	<0.001	<0.005	0.003	<0.001	na	na	<0.001	1.4	0.9
93-003	FG1	n	FG	94.870	0.072	3.550	1.500	<0.001	<0.005	0.006	<0.001	na	na	<0.001	7.7	7.2
93-004	FG1		FG	95.660	0.030	3.720	0.582	<0.001	<0.005	0.003	<0.001	na	na	<0.001	3.2	2.8
93-005	FG2		FG	98.880	0.029	0.005	0.536	<0.001	0.530	0.003	<0.001	na	na	<0.001	3.1	2.6
93-006	FG3		FG	97.700	0.015	0.0004	2.280	<0.001	<0.005	0.003	<0.001	na	na	<0.001	1.6	
93-007	FG4		FG	99.290	0.013	0.0004	0.198	<0.001	<0.005	0.003	0.497	na	na	<0.001	1.4	0.9
93-008	FG5		FG	95.930	0.022	0.0003	0.398	3.640	<0.005	<0.005	0.003	na	na	<0.001	2.4	1.9
93-009	FG6		FG	8.930	0.021	0.0003	0.052	90.530	<0.005	<0.005	0.004	na	na	<0.005	2.2	0.2
93-010	1	a	1 out	99.360	0.020	**0.326**	0.283	<0.001	<0.001	0.016	<0.001	na	na	<0.001	2.1	
93-011	1	a	1 in	99.350	0.018	**0.385**	0.212	<0.001	<0.001	0.003	0.032	na	na	<0.001	1.9	
93-012	4		1 out	99.670	0.016	**0.029**	0.244	<0.001	<0.001	0.013	0.029	na	na	<0.001	1.7	
93-013	4		1 in	98.830	0.020	**0.558**	0.591	<0.001	<0.001	0.004	<0.001	na	na	<0.001	2.1	
93-014	5	d	4 out	99.712	0.016	**0.057**	0.191	0.007	<0.001	0.012	<0.001	na	na	<0.001	1.7	0.9
93-015	5		4 in	66.400	0.013	**1.070**	0.212	32.300	<0.001	<0.001	0.002	na	na	<0.01	1.4	1.0
93-016	6		4 out	60.400	0.018	**0.017**	0.343	39.200	<0.001	<0.001	0.0008	na	na	0.020	1.9	1.6
93-017	6		4 in	58.800	0.013	**0.938**	0.221	40.100	<0.001	<0.001	0.0006	na	na	0.020	1.4	1.1
93-018	7		4 out	60.100	0.011	0.018	0.164	39.700	<0.001	<0.001	0.0005	na	na	0.020	1.2	0.8
93-019	7		4 out	60.200	0.014	**0.016**	0.250	39.500	<0.001	<0.001	0.0012	na	na	0.003	1.5	1.2
93-020	7		4 in	59.100	0.017	**0.932**	0.304	39.700	<0.001	<0.001	0.0013	na	na	0.0098	1.8	1.5
93-021	8	e	5 out	0.284	0.017	0.020	0.284	39.300	<0.001	<0.001	0.0012	3.2	na	0.001	1.8	1.4
93-022	8	e	5 in	57.600	0.010	0.960	0.134	41.300	<0.001	<0.001	0.0018	2.3	na	0.010	1.1	0.6
93-023	8	e	5 out	58.800	0.012	**0.024**	0.180	40.900	<0.001	<0.001	0.0018	3.2	na	<0.001	1.3	0.9
93-024	8	e	5 in	57.500	0.011	**0.957**	0.159	41.400	<0.001	<0.001	0.0018	2.3	na	<0.001	1.2	0.8
93-025	9		1 out	99.400	0.029	**0.023**	0.525	0.025	<0.001	<0.001	<0.001	na	na	<0.005	3.1	
93-026	9		1 in	98.320	0.018	**0.912**	0.744	0.006	<0.001	<0.001	<0.001	na	na	<0.001	1.9	
93-027	10		7 out	59.930	0.017	**0.014**	0.334	39.600	<0.001	<0.001	0.029	na	na	<0.005	1.8	1.6
93-028	10		7 in	58.170	0.026	**0.926**	0.052	40.270	<0.001	<0.001	0.091	na	na	<0.005	2.8	0.2
93-029	11		3 out	90.980	0.031	**0.0157**	0.584	8.390	<0.001	<0.001	<0.001	na	na	<0.005	3.3	2.8
93-030	11		3 in	89.500	0.015	**0.913**	0.208	9.370	<0.001	<0.001	<0.001	na	na	<0.001	1.6	1.0
93-031	12		2 out	99.140	0.039	0.028	0.702	0.094	<0.001	<0.001	<0.001	na	na	0.0012	4.2	3.4
93-032	12		2 out	99.600	0.012	**0.024**	0.119	0.242	<0.001	<0.001	<0.001	na	na	0.001	1.3	0.6
93-033	12		2 in	97.970	0.014	**0.924**	0.166	0.930	<0.001	<0.001	<0.001	na	na	<0.001	1.5	0.8
93-034	13	f	6 out	59.500	0.013	0.049	0.211	40.270	<0.001	<0.001	0.0014	na	na	<0.001	1.4	1.0
93-035	13	f	6 out	59.500	0.015	**0.070**	0.253	40.100	<0.001	<0.001	0.001	na	na	<0.001	1.6	1.2
93-036	13	f	6 in	58.100	0.011	**0.940**	0.162	40.800	<0.001	<0.001	0.001	na	na	<0.001	1.2	0.8
93-037	14		8 out	59.300	0.021	0.027	0.387	40.200	<0.001	<0.001	0.0012	na	na	<0.001	2.2	1.8
93-038	14		8 out	58.640	0.012	**0.030**	0.199	40.500	<0.001	<0.001	<0.001	na	0.6	<0.001	1.3	1.0
93-039	14		8 in	57.320	0.025	**0.920**	0.474	40.500	<0.001	<0.001	<0.001	na	0.8	<0.001	2.7	2.3

Table A-1. Performance Test Sample Analysis Data. (Sheet 2 of 5)

Sample #	Run #	Note	FM & i/o	Sample Composition (as analyzed) (Mole %)											Air Contamination (Mole %)	
				N_2	Ar	H_2	O_2†	N_2O	CO	CO_2	CH_4	H_2O‡	NH_3‡	NO_x	Ar Method	O_2 Method
93-040	15		1 out	99.040	0.028	**0.313**	0.545	0.055	<0.001	0.019	<0.001	na	na	<0.001	3.0	
93-041	15	h	1 in	98.010	0.025	**0.960**	0.831	0.181	<0.001	<0.001	<0.001	na	0.0016	0.0016	2.7	
93-042	16	h	7 out	62.800	0.007	0.100	0.059	36.900	<0.001	<0.001	0.101	1.5	na	<0.001	0.8	0.3
93-043	16	h	7 out	62.800	0.013	**0.103**	0.202	36.800	<0.001	<0.001	0.100	na	<0.001	<0.001	1.4	1.0
93-044	16	h	7 in	61.100	0.010	**1.040**	0.099	37.600	<0.001	<0.001	0.100	<0.1	na	<0.001	1.0	0.5
93-045	17	h	3 out	91.590	0.022	0.094	0.315	7.980	<0.001	<0.001	<0.001	1.3	na	<0.001	2.4	1.5
93-046	17	h	3 out	91.560	0.017	**0.096**	0.196	8.130	<0.001	<0.001	<0.001	0.8	na	<0.001	1.8	0.9
93-047	17	h	3 in	89.810	0.021	**0.985**	0.302	8.880	<0.001	<0.001	<0.001	<0.1	na	<0.001	2.2	1.4
93-048	18	s														
93-049	18	f	6 out	66.600	0.007	1.440	0.045	31.900	<0.001	<0.001	<0.001	na	na	<0.01	0.7	0.2
93-050	18	f	6 out	64.500	0.015	**1.450**	0.214	33.800	<0.001	<0.001	<0.001	na	na	<0.01	1.6	1.0
93-051	18	f	6 in	63.100	0.007	**1.550**	0.040	35.300	<0.001	<0.001	<0.001	na	na	<0.01	0.7	0.2
93-052	19		1 out	99.470	0.009	0.351	0.143	0.022	<0.001	<0.001	<0.001	na	na	<0.001	1.0	
93-053	19		1 out	99.510	0.010	0.335	0.108	0.031	<0.001	0.001	<0.001	na	na	<0.001	1.1	
93-054	19		1 out	99.400	0.014	**0.345**	0.202	0.040	<0.001	<0.001	<0.001	na	na	<0.001	1.5	
93-055	19		1 in	98.370	0.015	**1.050**	0.564	0.003	<0.001	<0.001	<0.001	na	na	<0.001	1.6	
93-056	21		7 out	59.900	0.010	0.152	0.101	39.700	<0.001	<0.001	0.089	na	na	<0.001	1.1	0.5
93-057	21		7 out	59.400	0.012	**0.109**	0.158	40.200	<0.001	<0.001	0.092	na	na	<0.001	1.3	0.8
93-058	21		7 in	57.800	0.009	**0.937**	0.109	41.000	<0.001	<0.001	0.093	na	na	<0.001	1.0	0.5
93-059	22	m	8 out	61.500	0.009	0.232	0.114	38.100	<0.01	<0.01	0.004	na	<0.001	<0.001	1.0	0.5
93-060	22	m	8 out	61.400	0.019	**0.312**	0.354	37.900	<0.01	<0.01	0.015	na	<0.001	<0.001	2.0	1.7
93-061	22	m t	8 in	60.200	0.450	**1.020**	0.410	37.900	<0.01	<0.01	0.013	na	<0.001	<0.001	48.2	2.0
93-062	23		3 out	91.370	0.032	0.096	0.475	8.020	<0.01	<0.01	<0.001	na	<0.001	<0.001	3.4	2.3
93-063	23		3 out	90.840	0.029	**0.085**	0.493	8.560	<0.01	<0.01	<0.001	na	<0.001	<0.001	3.1	2.4
93-064	23		3 in	89.060	0.025	**0.896**	0.420	9.600	<0.01	<0.01	<0.001	na	<0.001	<0.001	2.7	2.0
93-065	24		4 out	62.400	0.029	0.133	0.519	36.900	<0.01	<0.01	<0.001	na	<0.001	<0.001	3.1	2.5
93-066	24		4 out	61.500	0.006	**0.129**	0.017	38.400	<0.01	<0.01	<0.001	na	<0.001	<0.001	0.6	0.1
93-067	24		4 in	60.700	0.018	**1.030**	0.288	37.900	<0.01	<0.01	<0.001	na	<0.001	<0.001	1.9	1.4
93-068	25		2 out	99.180	0.008	0.399	<0.001	0.408	<0.01	<0.01	<0.001	na	<0.001	<0.001	0.9	0.0
93-069	25		2 out	99.170	0.008	**0.407**	<0.001	0.417	<0.01	<0.01	<0.001	na	<0.001	<0.001	0.9	0.0
93-070	25		2 in	97.960	0.008	**1.010**	<0.001	1.020	<0.01	<0.01	<0.001	na	<0.001	<0.001	0.9	0.0
93-071	26		3 out	90.780	0.019	0.096	0.215	8.880	<0.01	<0.01	<0.001	na	<0.001	<0.001	2.0	1.0
93-072	26		3 out	90.710	0.011	**0.093**	0.084	9.100	<0.01	<0.01	<0.001	na	<0.001	<0.001	1.2	0.4
93-073	26		3 in	88.940	0.027	**0.899**	0.435	9.700	<0.01	<0.01	<0.001	na	<0.001	<0.001	2.9	2.1
93-074	27	e	5 out	61.100	0.010	0.125	0.091	38.600	<0.01	<0.01	0.0021	3.3	<0.001	<0.001	1.1	0.4
93-075	27	e	5 out	60.710	0.010	**0.126**	0.079	39.100	<0.01	<0.01	<0.001	3.3	<0.001	<0.001	1.1	0.4
93-076	27	e	5 in	59.300	0.011	**1.070**	0.098	39.500	<0.01	<0.01	<0.001	2.3	<0.001	<0.001	1.2	0.5
93-077	28	e	5 out	61.100	0.012	0.143	0.120	38.600	<0.01	<0.01	<0.001	3.2	<0.001	<0.001	1.3	0.6
93-078	28	e	5 out	61.100	0.009	**0.139**	0.064	38.700	<0.01	<0.01	0.004	3.2	<0.001	<0.001	1.0	0.3
93-079	28	e	5 in	59.200	0.010	**1.060**	0.092	39.600	<0.01	<0.01	<0.001	2.3	<0.001	<0.001	1.1	0.4
93-080	28e	e	5 out	60.700	0.013	**0.137**	0.136	39.000	<0.01	<0.01	0.001	3.2	<0.001	<0.001	1.4	0.6

Table A-1. Performance Test Sample Analysis Data. (Sheet 3 of 5)

Sample #	Run #	Note	FM & I/O	Sample Composition (as analyzed) (Mole %)											Air Contamination (Mole %)	
				N_2	Ar	H_2	O_2 †	N_2O	CO	CO_2	CH_4	H_2O ‡	NH_3 ‡	NO_x	Ar Method	O_2 Method
93-081	30		2 out	99.257	0.011	0.301	0.008	0.422	<0.01	<0.01	<0.001	na	<0.001	<0.001	1.2	0.0
93-082	30		2 out	99.140	0.009	**0.419**	0.007	0.429	<0.01	<0.01	<0.001	na	na	0.001	1.0	0.0
93-083	30		2 in	97.930	0.008	**1.020**	0.005	1.030	<0.01	<0.01	<0.001	na	na	0.005	0.9	0.0
93-084	31		1 out	99.520	0.009	0.324	0.147	0.003	<0.01	<0.01	<0.001	na	<0.001	<0.001	1.0	
93-085	31		1 out	99.550	0.008	**0.311**	0.127	0.004	<0.01	<0.01	<0.001	na	<0.001	<0.001	0.9	
93-086	31		1 in	98.472	0.009	**1.030**	0.486	<0.001	<0.01	<0.01	<0.001	na	na	0.004	1.0	
93-087	29		6 out	62.900	0.006	**0.970**	0.005	36.100	0.120	<0.01	0.002	na	na	<0.001	0.6	0.0
93-088	29		6 in	62.800	0.006	**1.040**	0.026	36.100	0.110	<0.01	<0.001	na	<0.001	<0.001	0.6	0.1
93-089	33		1 out	99.660	0.008	0.197	0.113	0.016	<0.01	<0.01	<0.001	na	na	<0.001	0.9	
93-090	33		1 out	99.140	0.013	**0.203**	0.234	0.409	<0.01	<0.01	<0.001	na	na	<0.001	1.4	
93-091	33	n	1 in	96.300	0.114	**0.871**	2.700	0.012	<0.01	<0.01	<0.001	na	<0.001	<0.001	12.2	
93-092	32		6 out	80.800	0.009	0.074	0.006	19.100	<0.001	0.090	<0.001	na	<0.001	<0.001	1.0	0.0
93-093	32		6 out	80.000	0.028	**0.145**	0.501	19.200	<0.001	0.144	0.003	na	<0.001	<0.001	3.0	2.4
93-094	32		6 in	77.200	0.011	**1.410**	0.107	21.000	0.180	<0.001	<0.001	na	<0.001	<0.001	1.2	0.5
93-095	34	m	8 out	60.000	0.008	0.151	0.062	39.700	<0.01	<0.01	<0.001	na	<0.01	<0.001	0.9	0.3
93-096	34	m	8 out	59.400	0.023	**0.154**	0.418	40.000	<0.01	<0.01	0.016	na	<0.01	<0.001	2.5	2.0
93-097	34		8 in	57.300	0.008	**0.937**	0.075	40.900	<0.01	<0.01	<0.001	na	0.81	<0.001	0.9	0.4
93-098	35		4 out	63.500	0.009	0.119	0.059	36.300	<0.01	<0.01	<0.001	na	<0.01	<0.001	1.0	0.3
93-099	35		4 out	63.900	0.013	**0.105**	0.157	35.800	<0.01	<0.01	0.002	na	<0.01	<0.001	1.4	0.7
93-100	35		4 in	62.200	0.009	**1.040**	0.071	36.700	<0.01	<0.01	0.002	na	<0.001	<0.001	1.0	0.3
93-101	36		4 out	60.300	0.022	0.190	0.304	39.200	<0.01	<0.01	0.002	na	<0.001	<0.001	2.4	1.5
93-102	36		4 out	59.600	0.010	**0.107**	0.098	40.100	<0.01	<0.01	0.002	na	<0.001	<0.001	1.1	0.5
93-103	36		4 in	58.700	0.024	**0.911**	0.438	40.000	<0.01	<0.01	0.004	na	na	<0.001	2.6	2.1
93-104	37		8 out	63.900	0.054	0.183	1.020	34.000	<0.01	<0.01	<0.001	na	0.83	<0.001	5.8	4.9
93-105	37		8 out	62.800	0.011	**0.201**	0.129	35.800	<0.01	<0.01	<0.001	na	1.07	<0.001	1.2	0.6
93-106	37		8 in	61.800	0.010	**1.060**	0.123	36.100	<0.01	<0.01	<0.001	na	0.91	<0.001	1.1	0.6
93-107	38		3 out	90.960	0.032	0.114	0.486	8.410	<0.01	<0.01	<0.001	na	<0.01	<0.001	3.4	2.3
93-108	38		3 out	91.370	0.009	**0.114**	0.0004	8.510	<0.01	<0.01	<0.001	na	<0.01	<0.001	1.0	0.0
93-109	38	n	3 in	89.200	0.052	**0.970**	0.408	9.400	<0.01	<0.01	<0.001	na	<0.01	<0.001	5.6	1.9
93-110	39		2 out	99.040	0.015	0.093	0.088	0.763	<0.01	<0.01	<0.001	na	<0.01	<0.001	1.6	0.4
93-111	39	n	2 out	97.740	0.085	**0.170**	1.740	0.269	<0.01	<0.01	<0.01	na	<0.01	<0.001	9.1	8.3
93-112	39		2 in	97.510	0.014	**0.900**	0.151	1.420	<0.01	<0.01	<0.01	na	<0.01	<0.001	1.5	0.7
93-113	40		7 out	63.000	0.005	0.124	0.0013	36.800	<0.01	<0.01	0.099	na	<0.01	<0.001	0.5	0.0
93-114	40		7 out	63.500	0.012	**0.121**	0.151	36.100	<0.01	<0.01	0.097	na	<0.01	<0.001	1.3	0.7
93-115	40		7 in	61.500	0.005	**1.040**	0.002	37.300	<0.01	<0.01	0.098	na	<0.01	<0.001	0.5	0.0
93-116	41		4 out	63.300	0.006	0.121	0.0004	36.600	<0.01	<0.01	<0.001	na	<0.01	<0.001	0.6	0.0
93-117	41		4 out	63.300	0.006	**0.116**	0.0002	36.600	<0.01	<0.01	<0.001	na	<0.01	<0.001	0.6	0.0
93-118	41		4 in	61.700	0.006	**1.030**	<0.0005	37.200	<0.01	<0.01	<0.001	na	<0.01	<0.001	0.6	0.0
93-119	42	e	5 out	61.600	0.006	0.148	0.0009	38.300	<0.01	<0.01	<0.001	3.2	<0.01	<0.001	0.6	0.0
93-120	42	e	5 out	61.700	0.007	**0.148**	0.0016	38.100	<0.01	<0.01	<0.001	3.2	<0.01	<0.001	0.7	0.0
93-121	42	e	5 in	60.200	0.007	**1.040**	0.0018	38.800	<0.01	<0.01	<0.001	2.3	<0.01	<0.001	0.7	0.0

Table A-1. Performance Test Sample Analysis Data. (Sheet 4 of 5)

Sample #	Run #	Note	FM & i/o	Sample Composition (as analyzed) (Mole %)											Air Contamination (Mole %)	
				N_2	Ar	H_2	O_2†	N_2O	CO	CO_2	CH_4	H_2O‡	NH_3‡	NO_x	Ar Method	O_2 Method
93-122	43		8 out	62.400	0.005	0.170	0.0009	36.600	<0.01	<0.01	<0.001	na	0.78	<0.001	0.5	0.0
93-123	43		8 out	62.500	0.005	0.168	0.004	36.400	<0.01	<0.01	<0.001	na	1.00	<0.001	0.5	0.0
93-124	43	n o	8 in	70.000	0.577	0.017	13.400	15.900	<0.01	<0.01	0.004	na	na	<0.001	61.8	64.0
93-125	44		1 out	98.770	0.008	0.822	0.388	0.0128	<0.01	<0.01	<0.001	na	na	0.002	0.9	
93-126	44		1 out	98.770	0.008	0.812	0.397	0.0062	<0.01	<0.01	<0.001	na	na	0.003	0.9	
93-127	44		1 in	98.460	0.008	1.020	0.505	0.008	<0.01	<0.01	<0.001	na	na	0.004	0.9	
93-128	45		7 out	63.200	0.005	0.111	0.0007	36.600	<0.01	<0.01	0.102	na	na	<0.001	0.5	0.0
93-129	45		7 out	63.100	0.004	0.109	0.0012	36.700	<0.01	<0.01	0.101	na	na	<0.001	0.4	0.0
93-130	45		7 in	61.600	0.005	1.050	0.0017	37.300	<0.01	<0.01	0.101	na	na	<0.001	0.5	0.0
93-131	46	e	5 out	58.700	0.013	0.116	0.183	41.000	<0.01	<0.01	<0.001	3.1	na	<0.001	1.4	0.9
93-132	46	e	5 out	58.900	0.034	0.107	0.676	40.300	<0.01	<0.01	<0.001	3.1	na	<0.001	3.6	3.2
93-133	46	e	5 in	57.200	0.011	0.940	0.159	41.700	<0.01	<0.01	<0.001	2.3	na	<0.001	1.2	0.8
93-134	47		3 out	91.310	0.014	0.099	0.140	8.430	<0.01	<0.01	<0.001	na	na	<0.001	1.5	0.7
93-135	47		3 out	91.230	0.014	0.102	0.140	8.520	<0.01	<0.01	<0.001	na	na	<0.001	1.5	0.7
93-136	47		3 in	89.600	0.010	1.030	0.064	9.300	<0.01	<0.01	<0.001	na	na	<0.001	1.1	0.3
93-137	48		2 out	98.740	0.014	0.435	0.156	0.657	<0.01	<0.01	<0.001	na	na	<0.001	1.5	0.7
93-138	48		2 out	98.760	0.016	0.439	0.210	0.574	<0.01	<0.01	<0.001	na	na	0.0010	1.7	1.0
93-139	48		2 in	97.470	0.023	0.982	0.355	1.170	<0.01	<0.01	<0.001	na	na	0.0007	2.5	1.7
93-140	49	f	6 out	74.600	0.025	0.066	0.457	24.900	<0.01	<0.01	<0.001	na	na	<0.001	2.7	2.2
93-141	49		6 out	74.300	0.011	0.071	0.138	25.200	0.295	<0.01	0.003	na	na	<0.001	1.2	0.7
93-142	49	u f	6 in	70.600	0.015	1.630	0.216	26.100	1.435	<0.01	0.010	na	na	<0.001	1.6	1.0
93-143	50	f	10 out	62.500	0.039	0.158	0.673	36.600	na	na	<0.001	na	<0.001	0.034	4.2	3.2
93-144	50	f	10 out	62.300	0.032	0.178	0.543	36.900	na	na	<0.001	na	<0.001	0.024	3.4	2.6
93-145	50	f	10 in	61.200	0.014	1.040	0.235	37.500	na	na	<0.001	na	<0.001	0.053	1.5	1.1
93-146	52		6 out	63.200	0.009	0.025	0.109	36.600	na	na	<0.001	na	<0.001	0.036	1.0	0.5
93-147	52		6 in	61.400	0.010	1.140	0.146	37.500	na	na	<0.001	na	<0.001	0.034	1.1	0.7
93-148	52		6 out	62.600	0.005	0.021	0.001	37.300	na	na	<0.001	na	<0.001	0.026	0.5	0.0
93-149	55		6 out	61.800	0.044	0.052	0.942	36.900	na	na	<0.001	na	<0.001	0.013	4.7	4.5
93-150	55		6 in	60.000	0.005	1.010	0.001	39.000	na	na	<0.001	na	<0.001	0.063	0.5	0.0
93-151	55		6 out	61.200	0.005	0.060	0.002	38.600	na	na	<0.001	na	<0.001	0.001	0.5	0.0
93-152	56		6 out	61.900	0.028	0.007	0.508	37.400	na	na	<0.001	na	<0.001	<0.01	3.0	2.4
93-153	56		6 in	60.200	0.011	1.030	1.030	38.500	na	na	<0.001	na	<0.001	<0.01	1.2	4.9
93-154	56		6 out	61.900	0.013	0.156	0.156	37.500	na	na	<0.001	na	<0.001	<0.01	1.4	0.7
93-155	57		6 out	60.500	0.006	1.030	1.030	38.300	na	na	<0.001	na	<0.001	<0.01	0.7	4.9
93-156	57		6 out	60.400	0.010	1.020	1.020	38.300	na	na	<0.001	na	<0.001	<0.01	1.0	4.9
93-157	57		6 in	60.400	0.006	1.050	1.050	38.500	na	na	<0.001	na	<0.001	<0.01	0.6	5.0
93-158	59	q	6 out	na	na	1.00	na	40.16	0.08	na	na	na	na	na	na	na
93-159	59	q	6 in	na	na	0.95	na	36.62	0.08	na	na	na	na	na	na	na
93-160	62	q	8 out	na	na	0.05	na	31.33	0.02	na	na	na	na	na	na	na
93-161	62	f q	8 out	na	na	0.05	na	35.89	na	na	na	na	na	na	na	na
93-162	62	q	8 in	na	na	0.93	na	27.75	0.02	na	na	na	na	na	na	na

Table A-1. Performance Test Sample Analysis Data. (Sheet 5 of 5)

Sample #	Run #	Note	FM & i/o	Sample Composition (as analyzed) (Mole %)											Air Contamination (Mole %)	
				N_2	Ar	H_2	O_2†	N_2O	CO	CO_2	CH_4	H_2O‡	NH_3‡	NO_x	Ar Method	O_2 Method
93–163	63	r v	7 out	na	na	0.0	na	na	na	na	0.1	na	na	na	na	na
93–164	63	r v	7 out	na	na	**0.0**	na	na	na	na	0.1	na	na	na	na	na
93–165	63	r v	7 in	na	na	**1.5**	na	na	na	na	0.1	na	na	na	na	na
93–166	64	r	5 out	na	na	0.0	na	na	na	na	na	na	na	na	na	na
93–167	64	r	5 out	na	na	**0.0**	na	na	na	na	na	na	na	na	na	na
93–168	64	r e	5 in	na	na	**1.0**	na	na	na	na	na	2.3	na	na	na	na

Table A–1 Notes and Symbols

NOTES:

a	Due to a mistake, there was no oxidant in this run, only H_2 and N_2. The O_2 present in the sample is due to air contamination.
d	The N_2O concentration dropped to zero over the run because the N_2O line was not pressurized correctly.
e	H_2O estimated based on the assumed initial H_2O concentration of 2.3% and the percent H_2 reduction (reacted to form H_2O).
f	CO and CO_2 not adequately analyzed.
h	H_2O and/or NH_3 concentrations estimated by PNL using alternate analysis method.
m	NH_3 analysis is inadequate or its adequacy is questioned.
n	Calculated air contamination is high.
o	Valve was open on GSC, results likely to be inaccurate.
q	Analysis perfomed by Special Analytical Studies using a gas chromatograpy.
r	GC analysis data was lost. H_2 data listed is from the on–line Whittaker H_2 detector.
s	Sample lost.
t	Argon concentration appears to be in error.
u	The CO source was only 0.5% CO in N_2. The reported CO composition is impossible. The $X_{CO,in}$ on run 49 was approximately 0.3% CO.
v	CH_4 inlet concentration based on assumed gas composition.

SYMBOLS:

†	All O_2 concentrations are high due to small amounts of air contamination.
‡	All H_2O and NH_3 concentrations for the samples are estimates.
na	Not Analyzed for.

FEED GASES (FG):

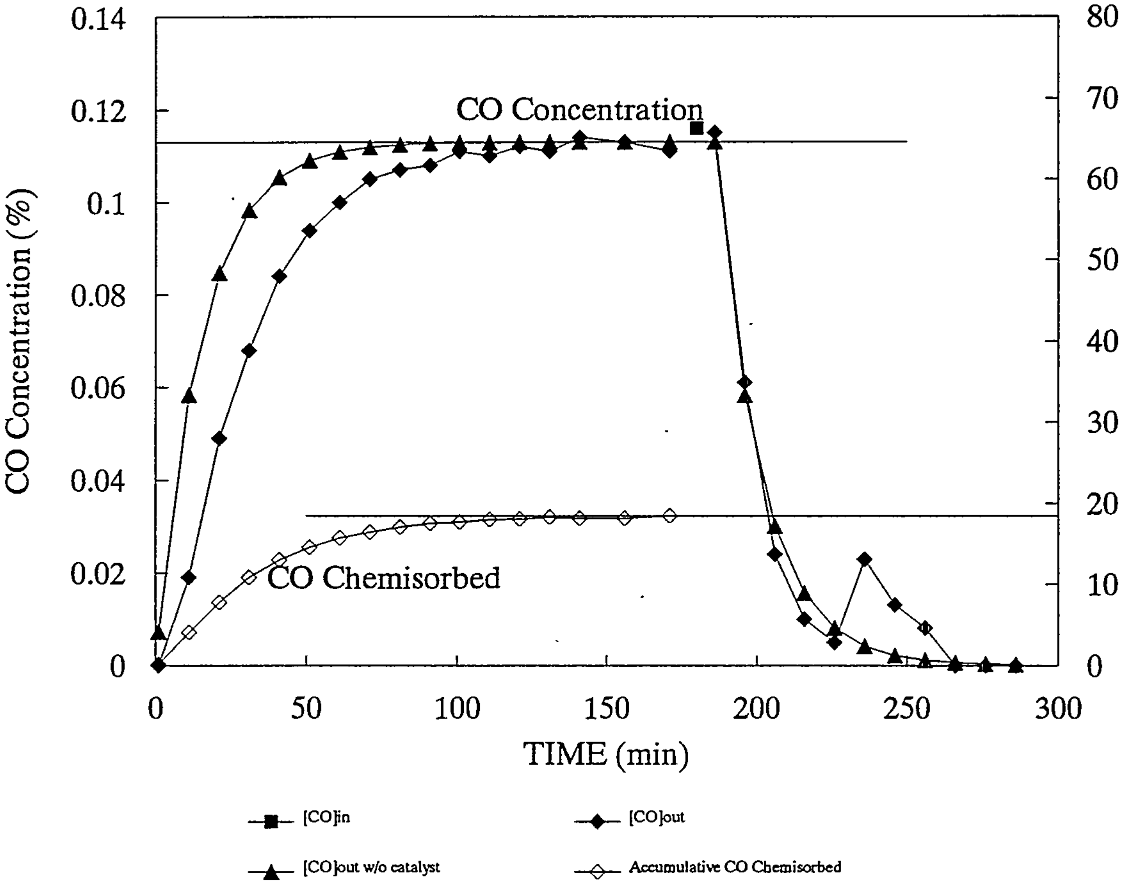
FG1	4% H_2
FG2	0.5% CO
FG3	2.0% O_2
FG4	0.5% CH_4
FG5	4% N_2O
FG6	100% N_2O

OTHER: Bolded H_2 Concentrations were used for calculation of r_H and SF.

APPENDIX B

SORPTION CAPACITY TEST DATA

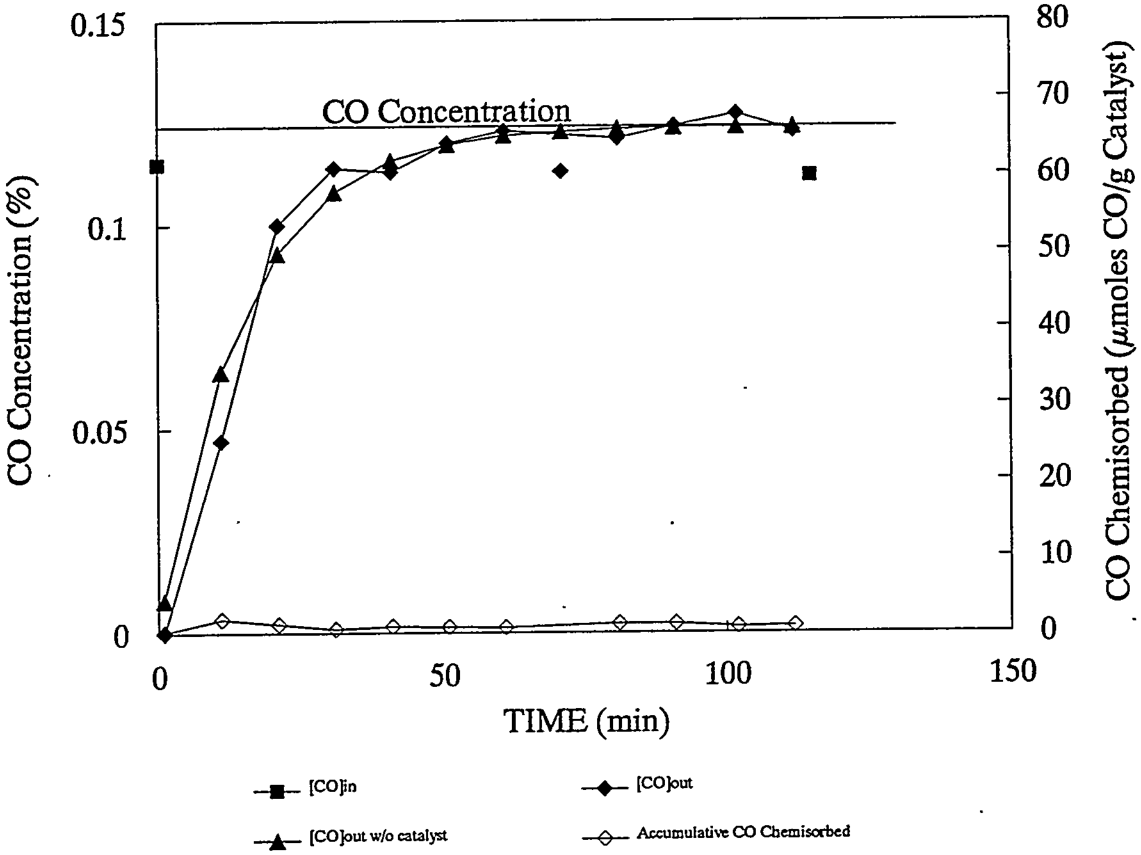
Figure B-1. Sorption Capacity Test - Run 69.



20 g Catalyst10 g Englehard Deoxo Type 1846710 g AECL Hydrophobic Type 85−42
Reactor Volume 7571 mL, 1 atm, 16°C
500 sccm 0.113% CO in Nitrogen
Regeneration Method: Virgin Catalyst

Figure B-2. Sorption Capacity Test - Run 72.

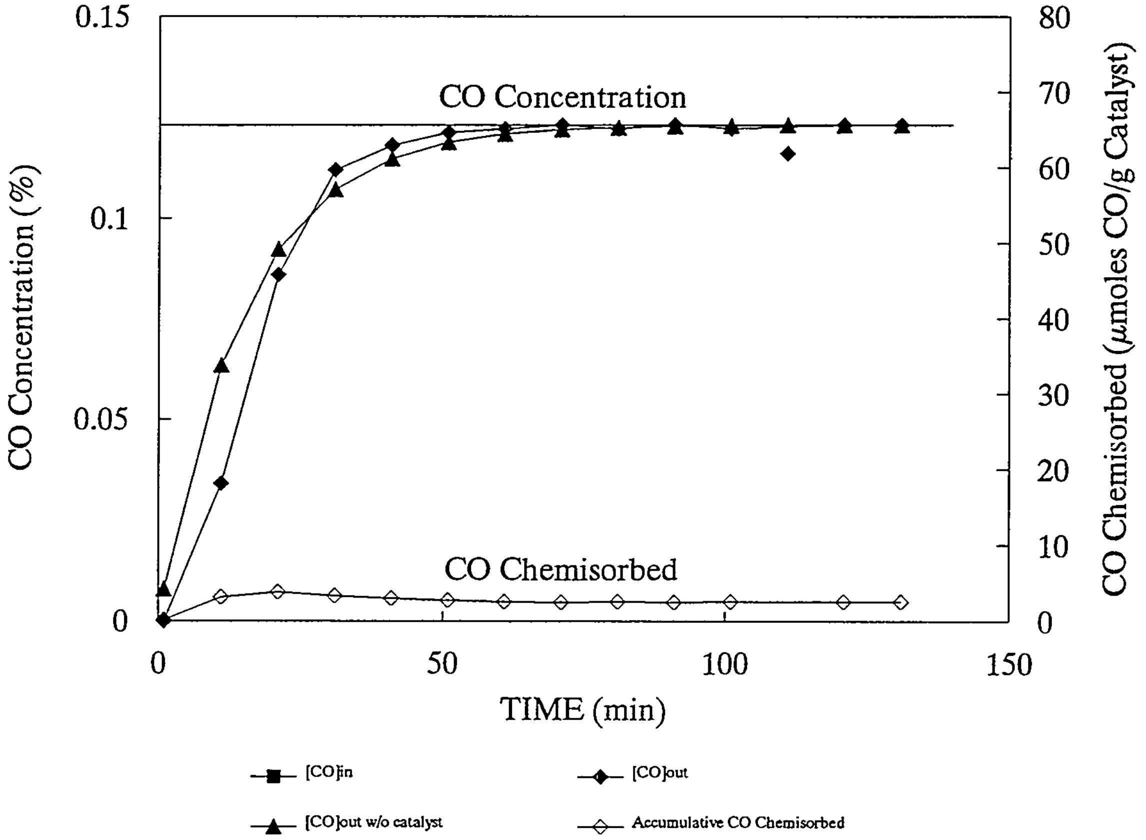
Sorption Capacity = 1.8 ± 0.7 μmoles CO/g Catalyst



20 g Catalyst (10 g Englehard Deoxo Type 18467, 10 g AECL Hydrophobic Type 85−42)
Reactor Volume 7571 mL, 1 atm, 18°C
500 sccm 0.124% CO in Nitrogen
Regeneration Method: Nitrogen
0.5 L/min for 20 min
10 L of air, Total
0.5 L air/g catalyst

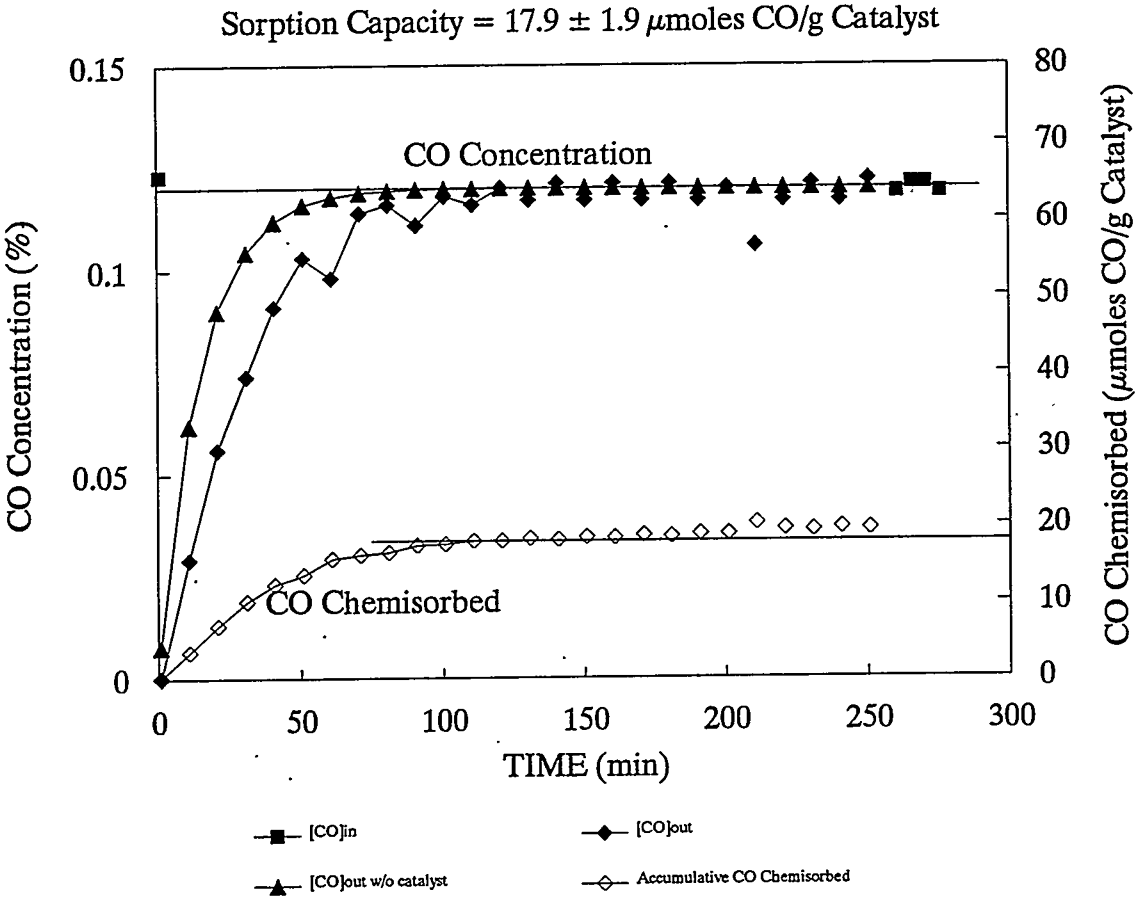
Figure B-3. Sorption Capacity Test - Run 73.

Sorption Capacity = 3.7 ± 0.7 μmoles CO/g Catalyst



20 g Catalyst (10 g Englehard Deoxo Type 18467, 10 g AECL Hydrophobic Type 85–42)
Reactor Volume 7571 mL, 1 atm, 14°C
500 sccm 0.123% CO in Nitrogen
Regeneration Method: Nitrogen Flush
0.5 L/min for 984 min
492 L of air, Total
24.6 L air/g catalyst

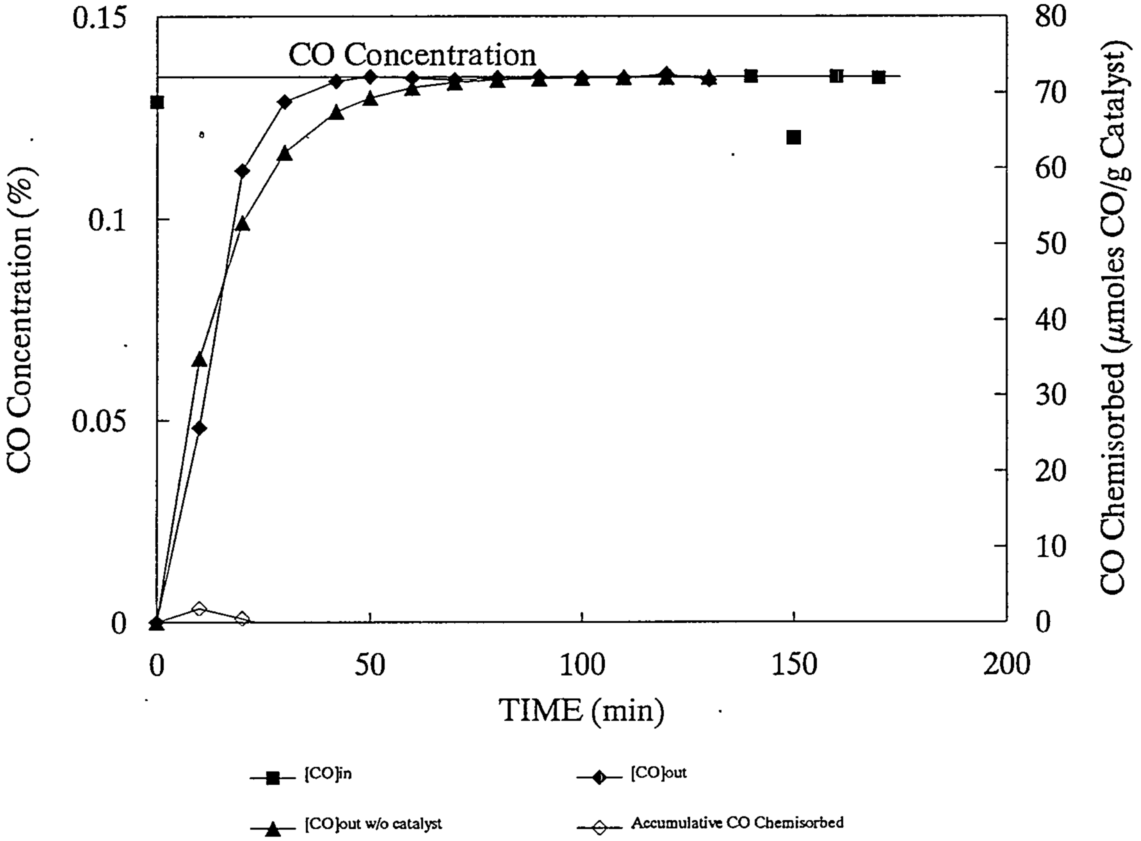
Figure B-4. Sorption Capacity Test - Run 74.



20 g Catalyst (10 g Englehard Deoxo Type 18467, 10 g AECL Hydrophobic Type 85–42)
Reactor Volume 7571 mL, 1 atm, 17°C
500 sccm 0.120% CO in Nitrogen
Regeneration Method: Virgin Catalyst

Figure B-5. Sorption Capacity Test - Run 75.

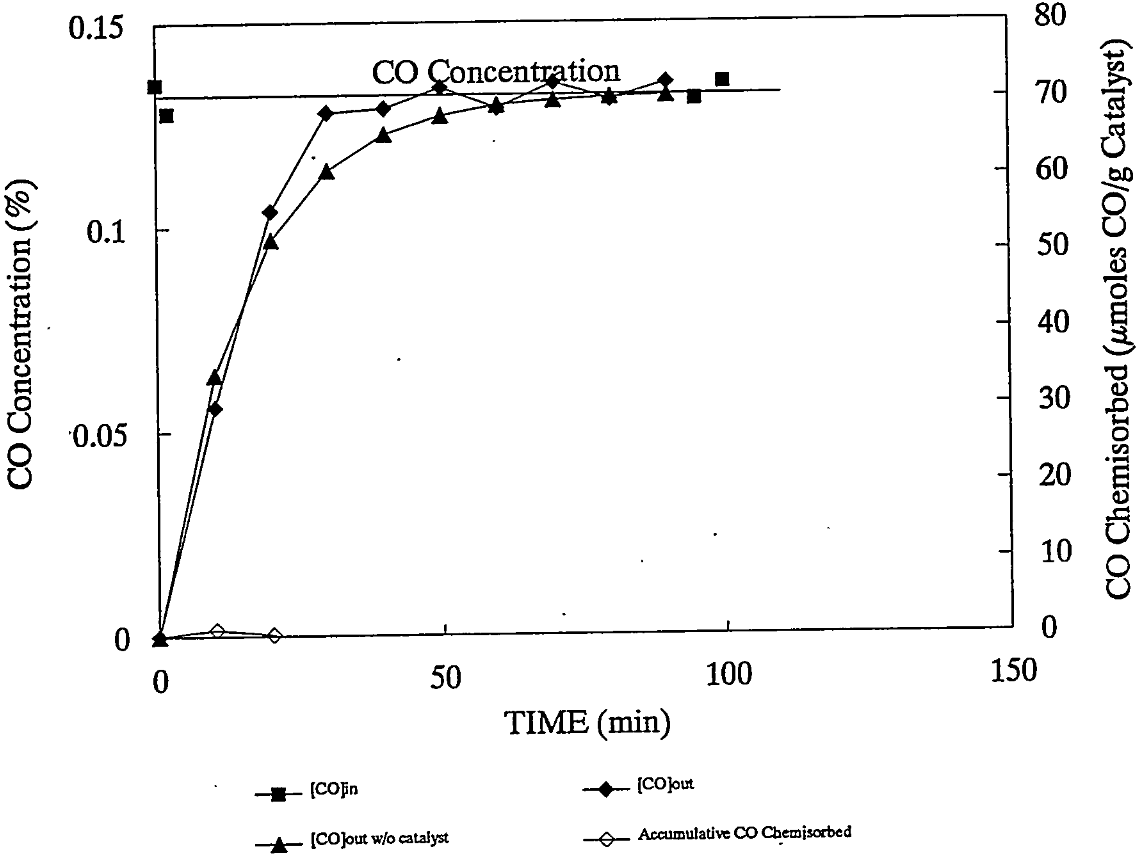
Sorption Capacity = 1.8 ± 0.4 μmoles CO/g Catalyst



20 g Catalyst (10 g Englehard Deoxo Type 18467, 10 g AECL Hydrophobic Type 85−42)
Reactor Volume 7571 mL, 1 atm, 15°C
500 sccm 0.135% CO in Nitrogen
Regeneration Method: ~~Virgin Catalyst~~ NITROGEN FLUSH MDB
12 L/min for 17 min
204 L of air, Total
10.2 L air/g catalyst

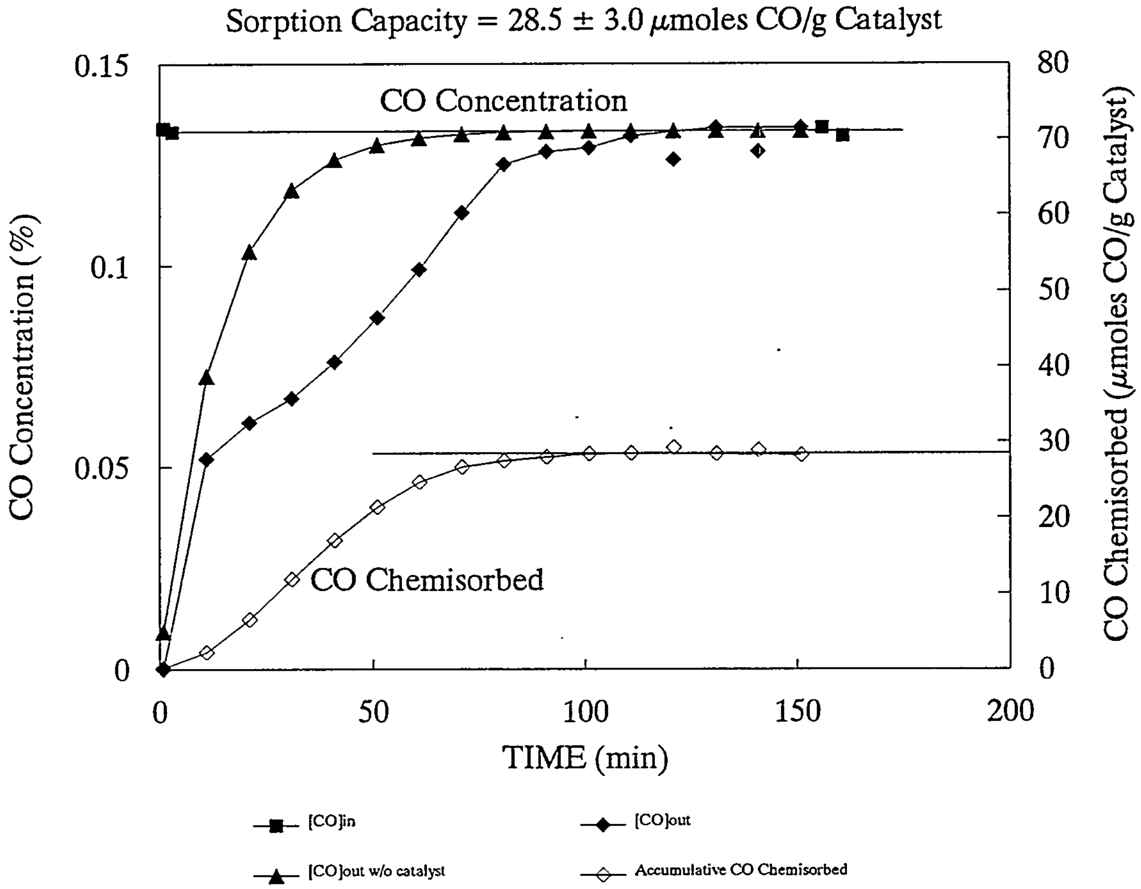
Figure B-6. Sorption Capacity Test - Run 76.

Sorption Capacity = 0.8 ± 0.1 μmoles CO/g Catalyst



20 g Catalyst (10 g Englehard Deoxo Type 18467, 10 g AECL Hydrophobic Type 85−42)
Reactor Volume 7571 mL, 1 atm, 14°C
500 sccm 0.132% CO in Nitrogen
Regeneration Method: Nitrogen Flush
30 L/min @ 10 psi for 20 min
600 L of air, Total
30.0 L air/g catalyst

Figure B-7. Sorption Capacity Test - Run 77.

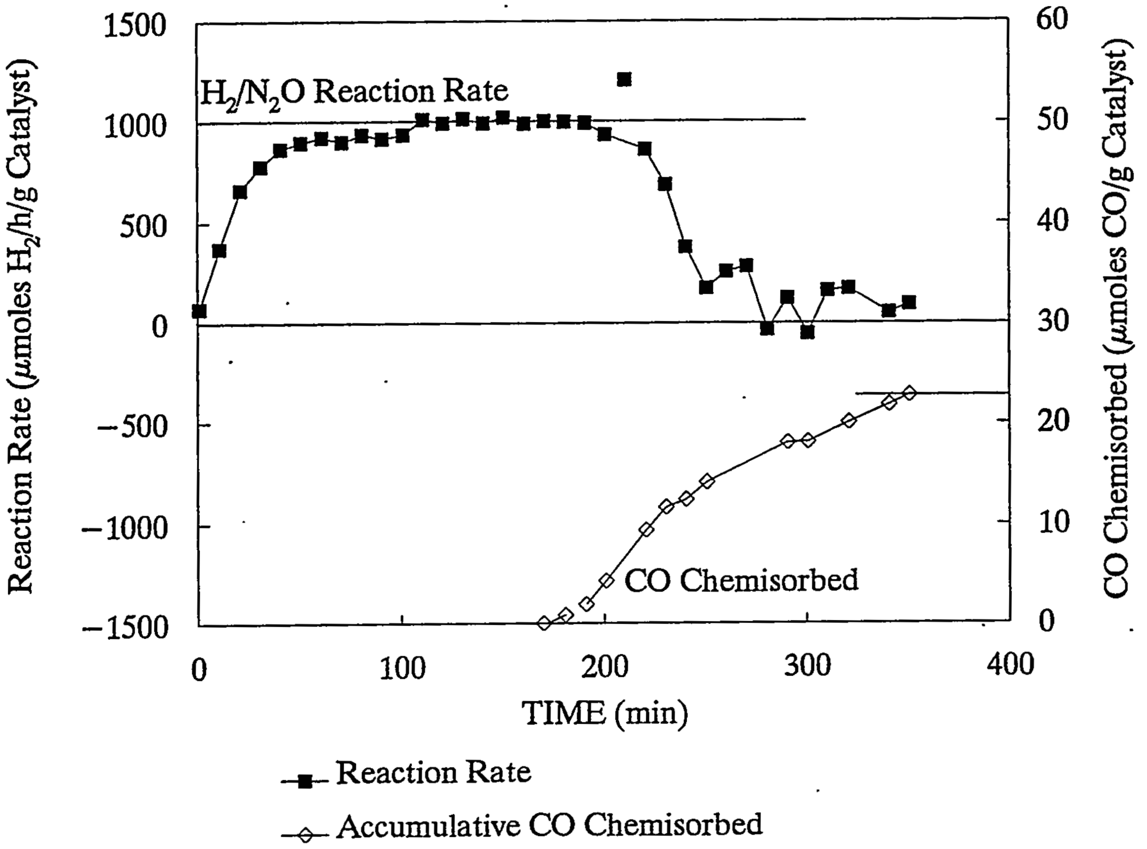


20 g Catalyst (10 g Englehard Deoxo Type 18467, 10 g AECL Hydrophobic Type 85−42)
Reactor Volume 7571 mL, 1 atm, 17°C
500 sccm 0.133% CO in Nitrogen
Regeneration Method: Air Flush
30 L/min @ 10 psi for 15 min
450 L of air, Total
22.5 L air/g catalyst

Note: The air was not purged from the reactor before this run, therefore the SC is artificaly high and is not used for the average SC.

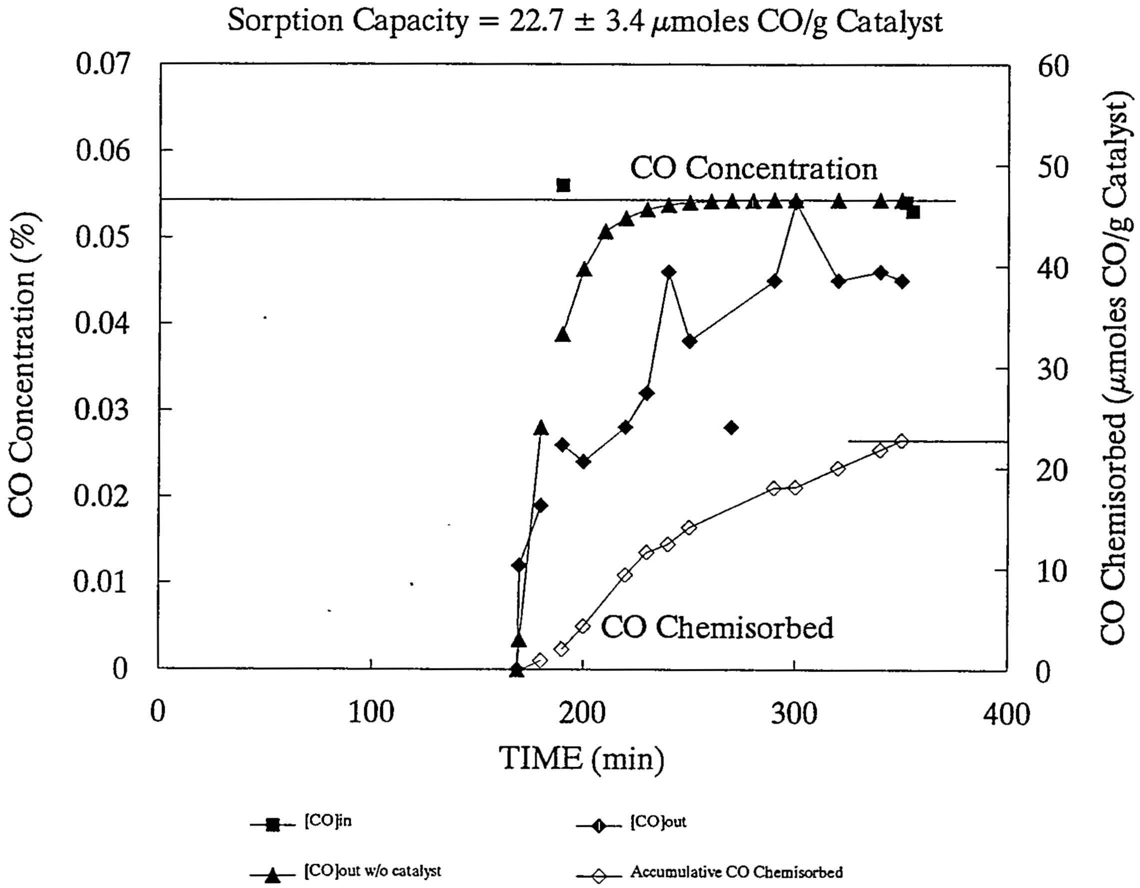
Figure B-8. Reaction Rate Decline - Run 78.

Reaction Rate = 1005.4 ± 10.2 μmole H_2/h/g Catalyst



20 g Catalyst (10 g Englehard Deoxo Type 18467, 10 g AECL Hydrophobic Type 85−42)
Reactor Volume 7571 mL, 1 atm, 17°C
500 sccm 1.774% H_2 in Nitrogen
500 sccm 1.924 H_2 and 0.054% CO in Nitrogen
Regeneration Method: Air Flush
30 L/min @ 10 psi for 15 min
450 L of air, Total
22.5 L air/g catalyst

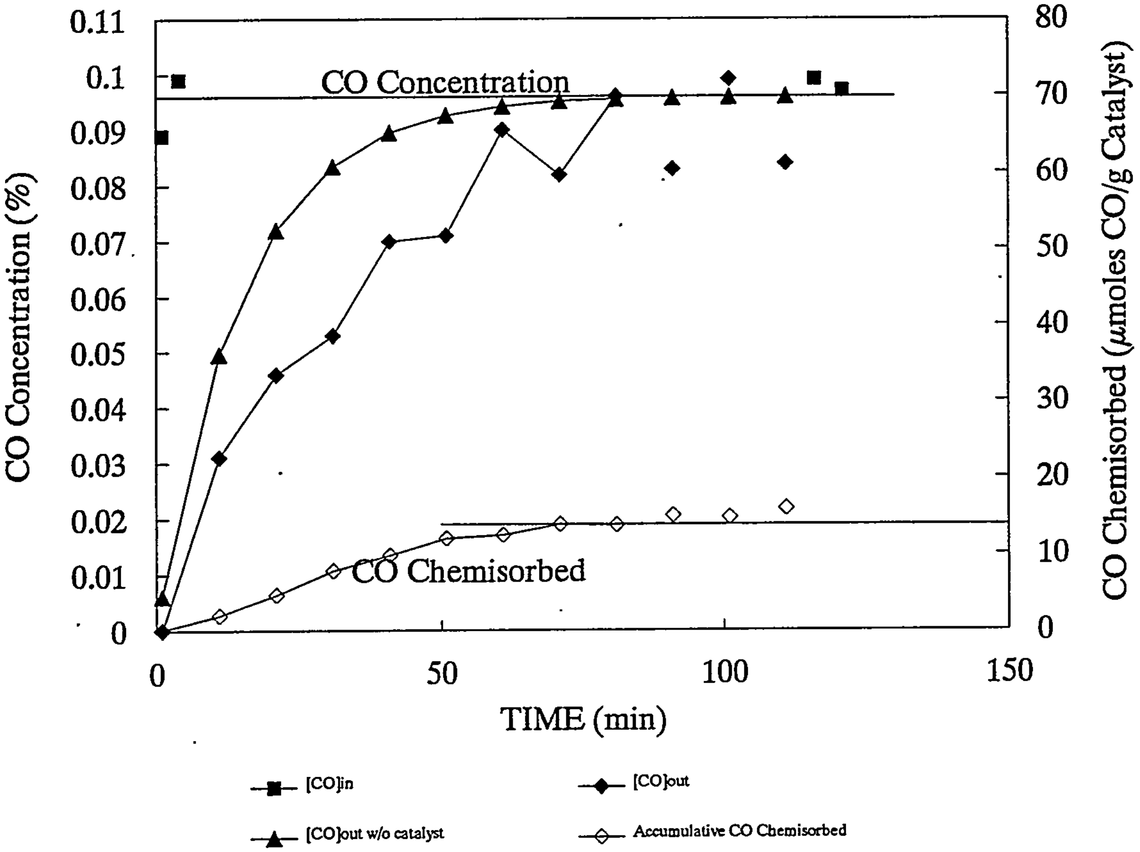
Figure B-9. Sorption Capacity Test - Run 78.



20 g Catalyst (10 g Englehard Deoxo Type 18467, 10 g AECL Hydrophobic Type 85-42)
Reactor Volume 7571 mL, 1 atm, 17°C
500 sccm 1.924 H_2 and 0.054% CO in Nitrogen
Regeneration Method: Air Flush
30 L/min @ 10 psi for 15 min
450 L of air, Total
22.5 L air/g catalyst

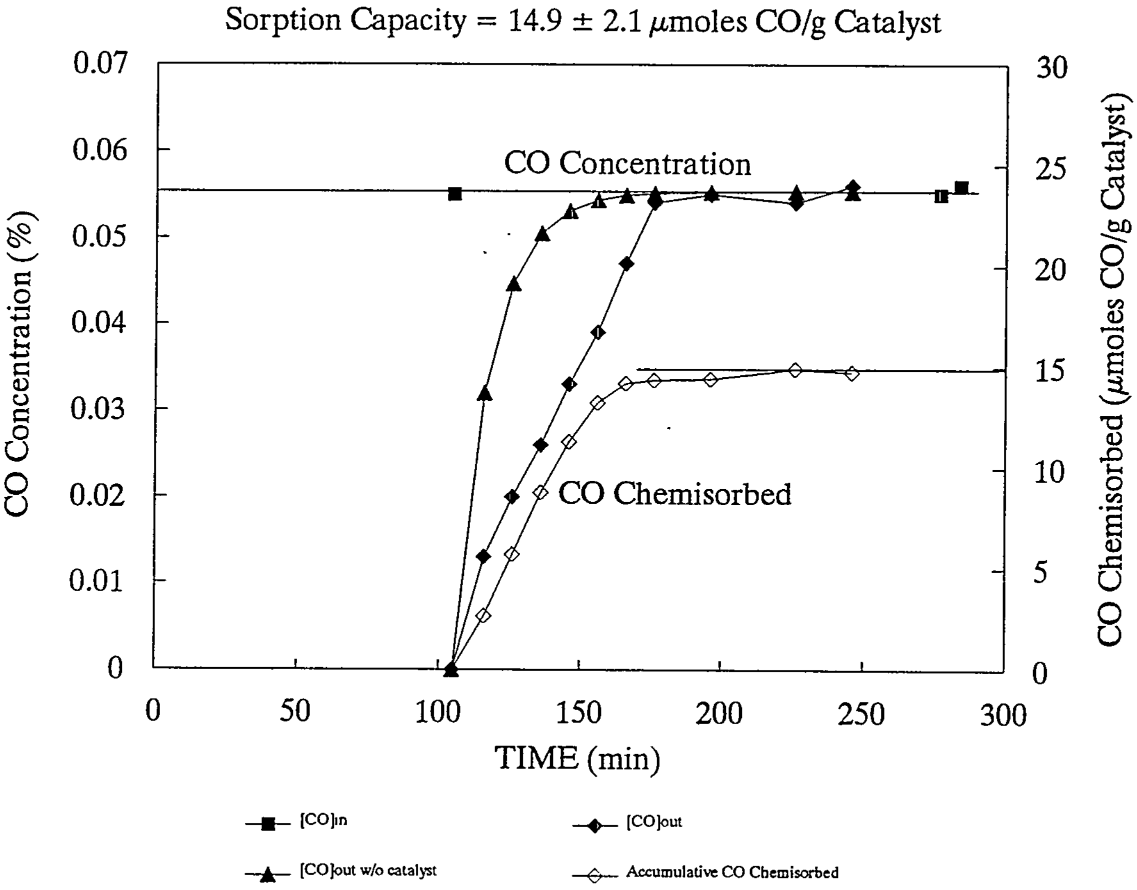
Figure B-10. Sorption Capacity Test - Run 80.

Sorption Capacity = 13.8 ± 1.4 μmoles CO/g Catalyst



20 g Catalyst (10 g Englehard Deoxo Type 18467, 10 g AECL Hydrophobic Type 85–42)
Reactor Volume 7571 mL, 1 atm, 17°C
500 sccm 0.096% CO in Nitrogen
Regeneration Method: Air Flush
17 L/min for 10 min
170 L of air, Total
8.5 L air/g catalyst

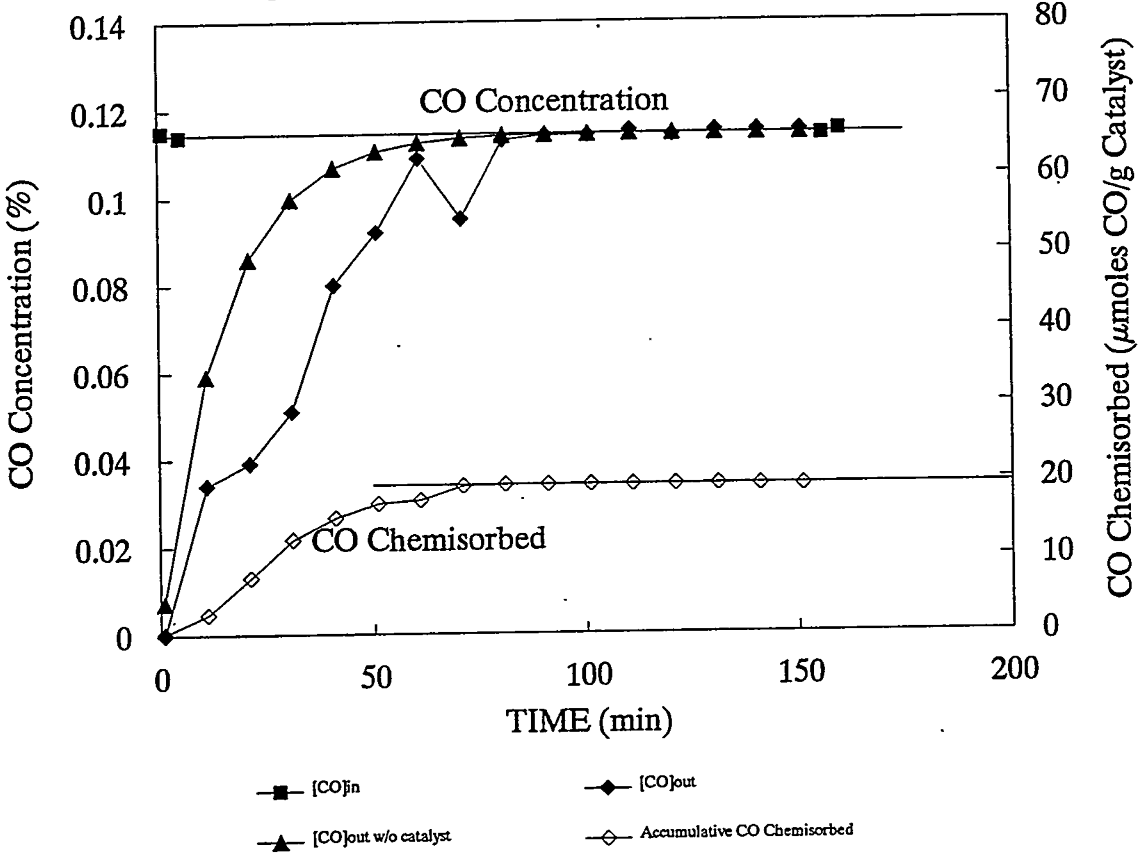
Figure B-11. Sorption Capacity Test - Run 82.



20 g Catalyst (10 g Englehard Deoxo Type 18467, 10 g AECL Hydrophobic Type 85–42)
Reactor Volume 7571 mL, 1 atm, 17°C
595 sccm 0.701 H_2 and 0.055% CO in Nitrogen
Regeneration Method: Air Flush
30 L/min @ 10 psi for 15 min
450 L of air, Total
22.5 L air/g catalyst

Figure B-12. Sorption Capacity Test - Run 83.

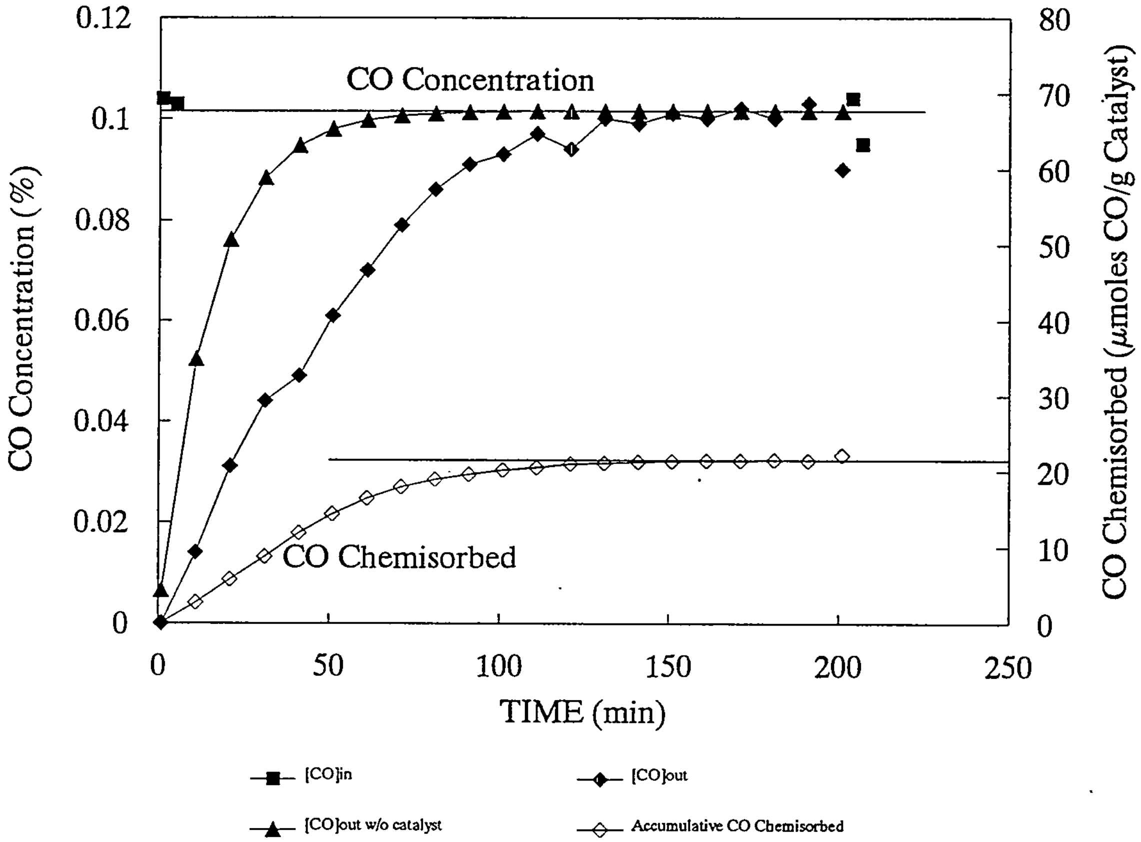
Sorption Capacity = 19.5 ± 2.2 μmoles CO/g Catalyst



20 g Catalyst (10 g Englehard Deoxo Type 18467, 10 g AECL Hydrophobic Type 85–42)
Reactor Volume 7571 mL, 1 atm, 16°C
500 sccm 0.115% CO in Nitrogen
Regeneration Method: Air Flush
30 L/min @ 10 psi for 28 min
840 L of air, Total
42.0 L air/g catalyst

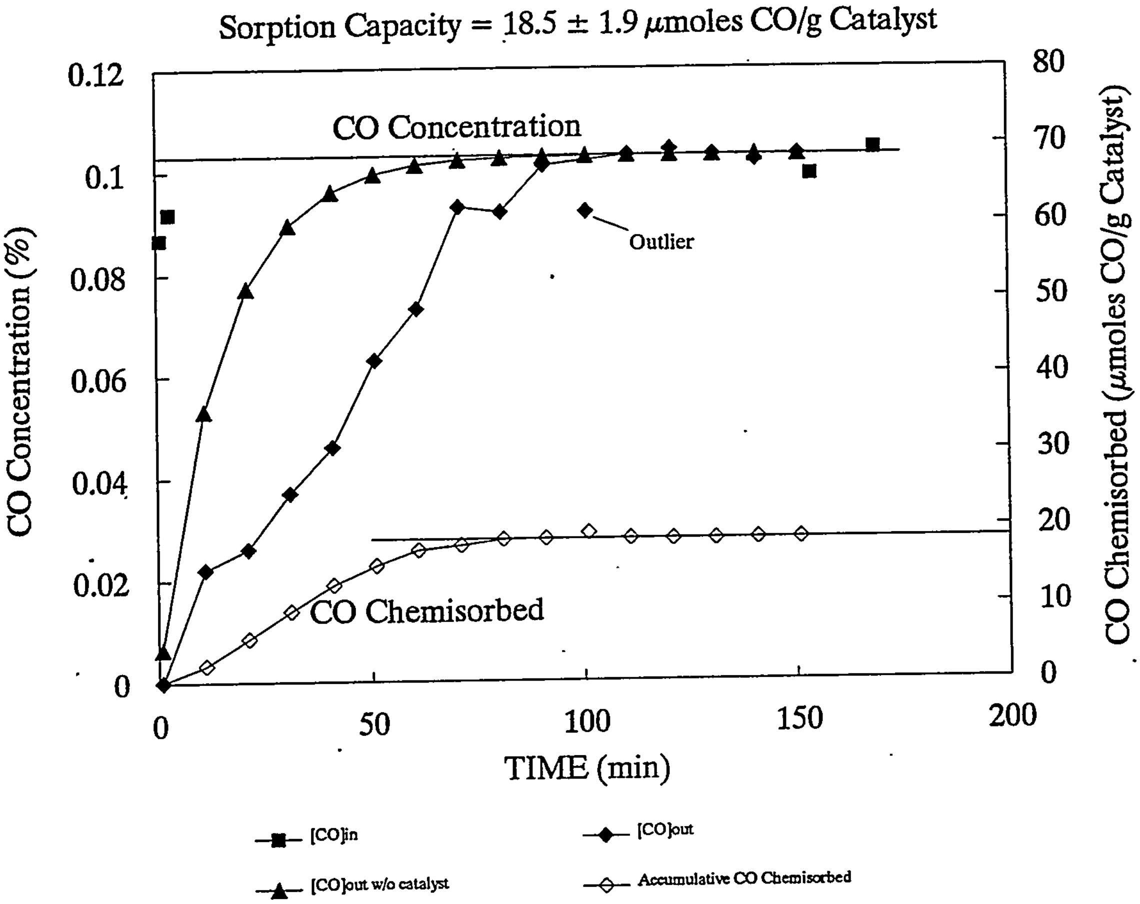
Figure B-13. Sorption Capacity Test - Run 85.

Sorption Capacity = 21.5 ± 2.3 μmoles CO/g Catalyst



30 g Catalyst (15 g Englehard Deoxo Type 18467, 15 g AECL Hydrophobic Type 85–42)
Reactor Volume 7571 mL, 1 atm, 15°C
500 sccm 0.102% CO in Nitrogen
Regeneration Method: Air Flush
30 L/min @ 10 psi for 15 min
450 L of air, Total
15.0 L air/g catalyst

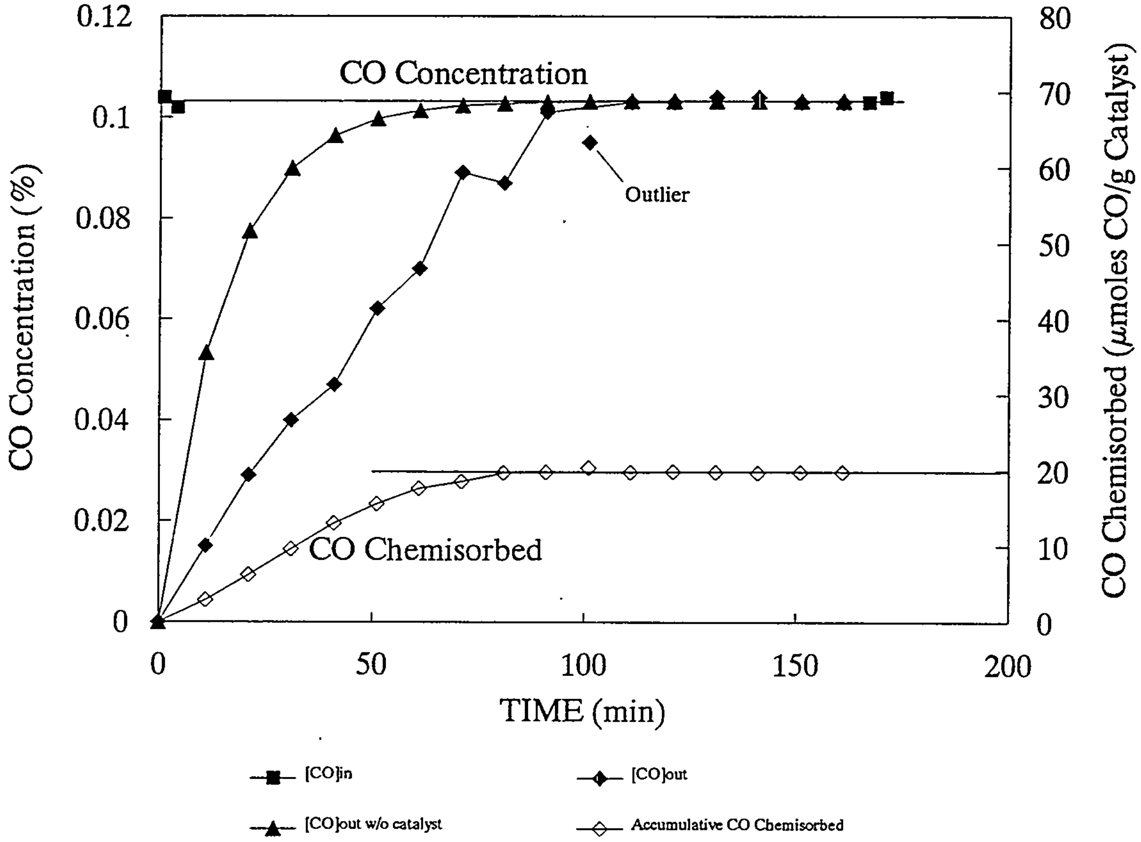
Figure B-14. Sorption Capacity Test - Run 86.



30 g Catalyst (15 g Englehard Deoxo Type 18467, 15 g AECL Hydrophobic Type 85-42)
Reactor Volume 7571 mL, 1 atm, 15°C
500 sccm 0.103% CO in Nitrogen
Regeneration Method: Air Flush
37.7 L/min @ 10 psi for 20 min
754 L of air, Total
25.1 L air/g catalyst

Figure B-15. Sorption Capacity Test - Run 87.

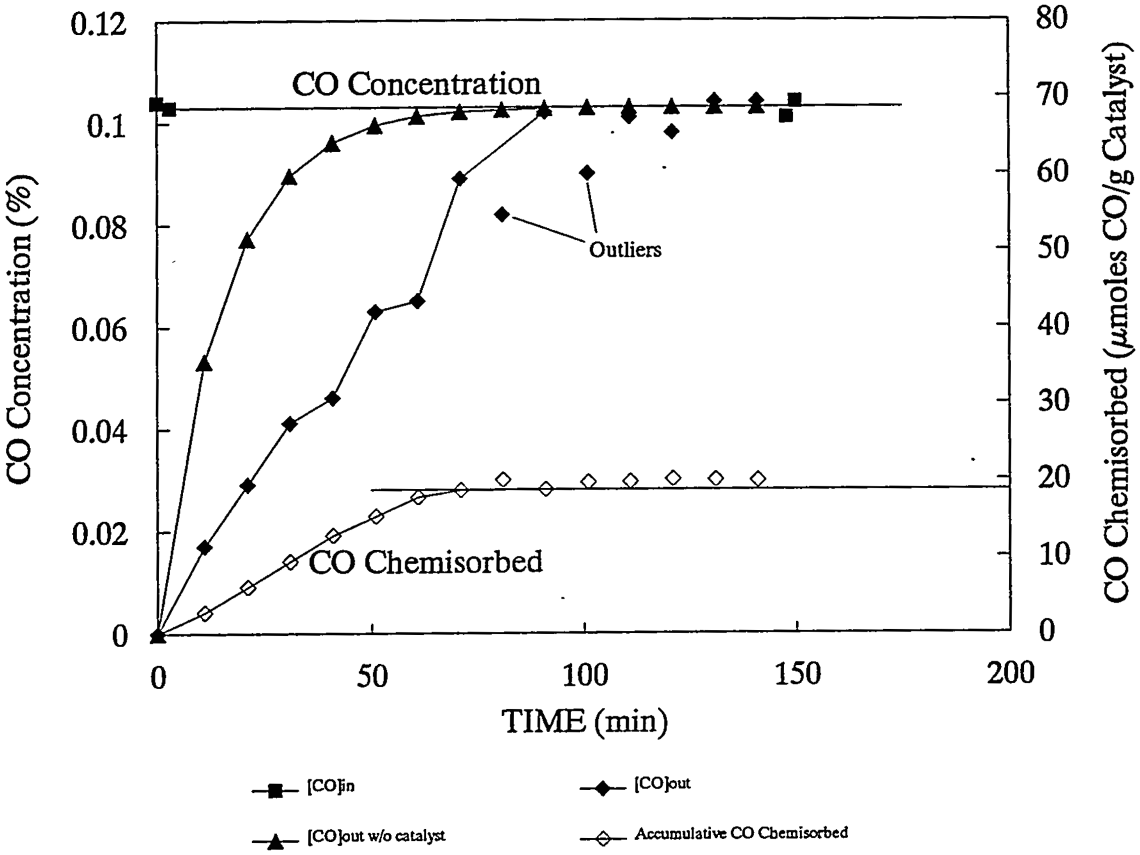
Sorption Capacity = 19.8 ± 2.1 μmoles CO/g Catalyst



30 g Catalyst (15 g Englehard Deoxo Type 18467, 15 g AECL Hydrophobic Type 85−42)
Reactor Volume 7571 mL, 1 atm, 17°C
500 sccm 0.103% CO in Nitrogen
Regeneration Method: Air Flush
0.5 L/min for 900 min
450 L of air, Total
15.0 L air/g catalyst

Figure B-16. Sorption Capacity Test - Run 88.

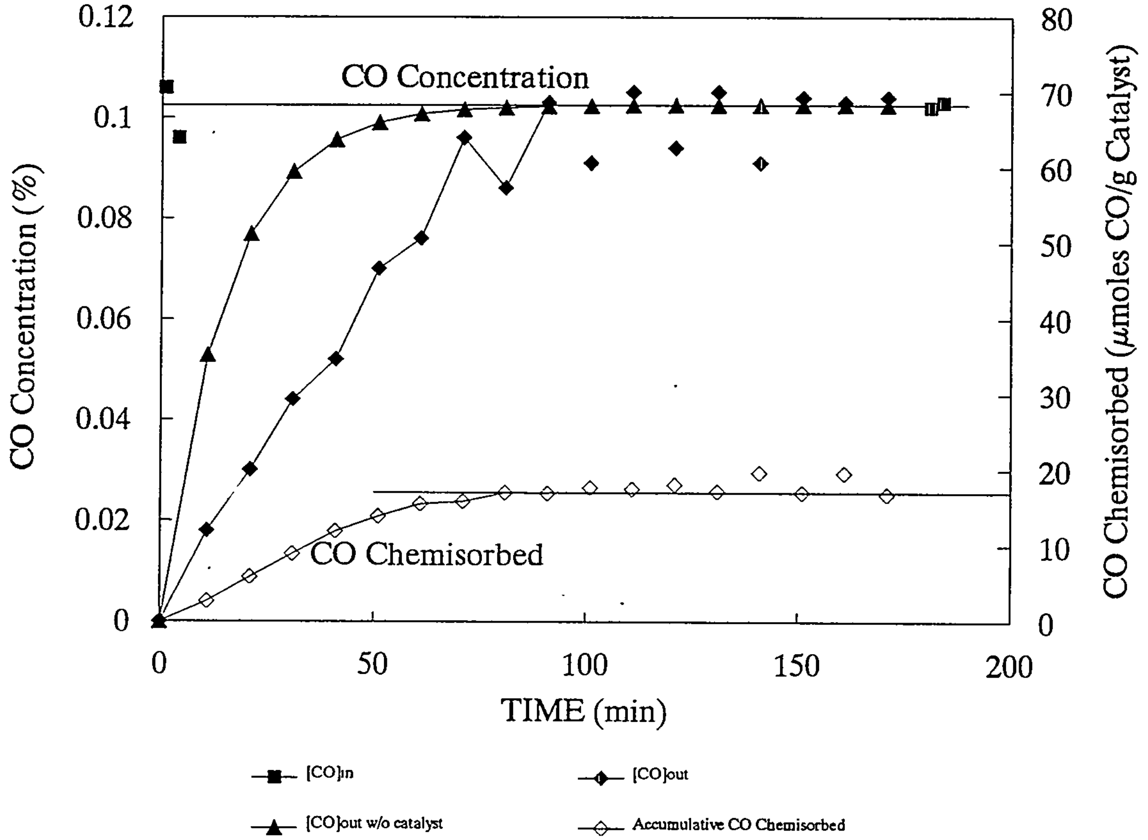
Sorption Capacity = 18.7 ± 1.9 μmoles CO/g Catalyst



30 g Catalyst (15 g Englehard Deoxo Type 18467, 15 g AECL Hydrophobic Type 85–42)
Reactor Volume 7571 mL, 1 atm, 16°C
500 sccm 0.103% CO in Nitrogen
Regeneration Method: Air Flush
0.58 L/min for 418 min
241 L of air, Total
8.0 L air/g catalyst

Figure B-17. Sorption Capacity Test - Run 89.

Sorption Capacity = 17.0 ± 1.8 μmoles CO/g Catalyst



30 g Catalyst (15 g Englehard Deoxo Type 18467, 15 g AECL Hydrophobic Type 85−42)
Reactor Volume 7571 mL, 1 atm, 16°C
500 sccm 0.103% CO in Nitrogen
Regeneration Method: Air Flush
0.5 L/min for 60 min
30 L of air, Total
1.0 L air/g catalyst

Table B-1. Run Data for the Sorption Capacity Test.

Run #	Notes	Catalyst Mass g	Sample #	Regeneration Method Gas	P psia	Q L/min	t min	Total L	L gas / g Catlyst	% CO	Sorption Capacity µmoles CO / g Catalyst
65	a	10		N2							
66	a	10		N2							
67	a, v	10	93–175 to 93–195	None						0.122	
68	a	10	93–196 to 93–209	N2						0.123	
69	v	20	93–210 to 93–238	None		–	–	–	None	0.090	18.5 ± 2.0
70	a		93–239 to 93–255	N2							±
71	a		93–256 to 93–275	N2							±
72		20	93–276 to 93–298	N2		0.5	20	10	0.5	0.117	1.8 ± 0.7
73		20	93–299 to 93–313	N2		0.5	984	492	24.6	0.123	3.7 ± 0.7
74	v	20	93–314 to 93–344	None		–	–	–	None	0.121	17.9 ± 1.9
75		20	93–345 to 93–363	N2		12	17	204	10.2	0.135	1.8 ± 0.4
76		20	93–364 to 93–377	N2		30	20	600	30.0	0.132	0.8 ± 0.1
77	b	20	93–378 to 93–397	Air	10	30	15	450	22.5	0.133	28.5 ± 3.0
78	c, d	20	93–398 to 93–441	Air	12	31	10	310	15.5	0.052	
79	a	20	93–442 to 93–450	Air		60	5	300	15.0	0.110	
80		20	93–451 to 93–465	Air		17	10	170	8.5	0.096	13.8 ± 1.4
81	a		93–466 to 93–491	Air		0.5	390	195			
82	d	20	93–492 to 93–518	Air		30	18	540	27.0	0.056	14.9 ± 2.1
83		20	93–519 to 93–537	Air	10	30	28	840	42.0	0.123	19.5 ± 2.2
84		20	93–538 to 93–556	Air	7	30	10	300	15.0	0.105	16.2 ± 1.7
85	v	30	93–557 to 93–580	None					None	0.100	21.5 ± 2.3
86		30	93–581 to 93–599	Air		0.5	900	450	15.0	0.101	18.5 ± 1.9
87		30	93–600 to 93–619	Air		37.7	20	754	25.1	0.103	19.8 ± 2.1
88		30	93–620 to 93–637	Air		0.577	418	241	8.0	0.101	18.7 ± 1.9
89		30	93–638 to 93–658	Air		0.500	60	30	1.0	0.102	17.0 ± 1.8

a Runs aborted or data lost.

b The reactor was not purged with N_2 before the Run 77. Therefore, the SC is high due to O_2 left in the reactor.

c Run 78 had poor loading data.

d This run was used to measure the declining reaction rate.

v Virgin catalyst used in this run. All other runs use regenerated catalyst.

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APPENDIX C

EXPERIMENTAL DESIGN CALCULATIONS

APPENDIX C: EXPERIMENTAL DESIGN CALCULATIONS

MINIMUM AND MAXIMUM SPECIFIC FLOWRATES

Because the reaction rate of the H_2/N_2O reaction was unknown, the test apparatus was designed to handle a wide range of specific flowrates (SF). The SF operability range of the apparatus was chosen so that the crucial reaction rate region could be investigated. Reaction rates outside the operability region were not considered important. If the reaction rate was too high to be measured accurately in this test, the catalyst would have no problem in performing in the grout vault leachate sump. And, if the reaction rate was too low, it would not be practical to use the catalyst in the leachate sump.

The catalyst bed was designed to hold between 50 and 1650 g of catalyst. Also, the apparatus was designed to meter between 50 and 750 mL/min of gas into the reactor. The minimum and maximum SFs that the test apparatus can be operated at can be calculated by the equations:

$$SF_{\min} = 60\frac{PQ_{\min}}{RTW_{\max}}\left(\frac{X_{H,in}}{100}\right) \qquad \text{(Eqn C-1)}$$

$$SF_{\max} = 60\frac{PQ_{\max}}{RTW_{\min}}\left(\frac{X_{H,in}}{100}\right) \qquad \text{(Eqn C-2)}$$

Where:

Q_{min} = 50 mL/min [8]

Q_{max} = 750 mL/min [8]

P = 1 atm [8]

R = $8.206*10^{-5}\ \frac{\text{mL}\cdot\text{atm}}{\mu\text{mole}\cdot\text{K}}$

T = 298 K [8]

W_{min} = 50 g

W_{max} = 1650 g

$X_{H,in}$ = 1.00 mole%

$$SF_{\min} = \frac{60\frac{\min}{h}\left(50\frac{mL}{\min}\right)(1\ atm)}{\left(8.206*10^{-5}\frac{mL\cdot atm}{\mu mole\cdot K}\right)(298\,K)\,(1650\,g)}\left(\frac{1.0\%}{100\%}\right) = 0.74\ \frac{\mu mol}{h\cdot g\ catalyst}$$

$$SF_{\max} = \frac{60\frac{\min}{h}\left(750\frac{mL}{\min}\right)(1\ atm)}{\left(8.206*10^{-5}\frac{mL\cdot atm}{\mu mole\cdot K}\right)(298\,K)\,(50\,g)}\left(\frac{1.0\%}{100\%}\right) = 370\ \frac{\mu mol}{h\cdot g\ catalyst}$$

---

[8] Flowrate readings were displayed by the flowmeters in sccm and were referenced to 25°C and 1 atm.

MNIMUM AND MAXIMUM DETECTABLE REACTION RATES

The maximum observable conversion is 100 percent which is the complete oxidation of the H_2. Assuming that the minimum decrease in the H_2 concentration (due to H_2 oxidation) that can accurately be observed is 5%, the minimum detectable conversion for the test is 5 percent.

The definition of the conversion (X) is the reaction rate (r_H) divided by the SF. This can be rearranged to calculate r_H. The equations for the minimum and maximum detectable r_H are:

$$r_{H,\min} = \frac{X_{\min}}{100\%} SF_{\min} \qquad \text{(Eqn C-3)}$$

$$r_{H,\max} = \frac{X_{\max}}{100\%} SF_{\max} \qquad \text{(Eqn C-4)}$$

X_{min} = 5%
X_{max} = 100%
SF_{min} = 0.74 µmol/h/g
SFmax = 370 µmol/h/g

$$r_{H,\min} = \frac{(5\%)}{100\%}\left(0.74\frac{\mu mol}{h\cdot g\ catalyst}\right) = 0.037\ \frac{\mu mol}{h\cdot g\ catalyst}$$

$$r_{H,\max} = \frac{(100\%)}{100\%}\left(370\frac{\mu mol}{h\cdot g\ catalyst}\right) = 370\frac{\mu mol}{h\cdot g\ catalyst}$$

MINIMUM AND MAXIMUM CATALYST MASSES

The bounding case for H_2 generation in the grout vault is 1.3 mol/h (Roblyer 1993). Also, the bulk density of the catalyst is approximately 1 g/mL. The mass of catalyst that would be needed to catalyze the H_2 being regenerated as base on the minimum and maximum reaction rates can be found with the equations:

$$W_{\min} = \frac{Q_H}{r_{H,\max}} \qquad \text{(Eqn C-5)}$$

$$W_{\max} = \frac{Q_H}{r_{H,\min}} \qquad \text{(Eqn C-6)}$$

Q_H = $1.3*10^6$ μmoles H_2/h
$r_{H,min}$ = 0.037 μmol/h/g catalyst
$r_{H,max}$ = 370 μmol/h/g catalyst

$$W_{\min} = \frac{1.3*10^6 \frac{\mu mol\ H_2}{h}}{370 \ \frac{\mu mole\ H_2}{h \cdot g\ catalyst}}$$

$$\boldsymbol{W_{\min} = 3{,}500\ g\ of\ catalyst = 3.5\ L\ of\ catalyst}$$

$$W_{\max} = \frac{1.3*10^6 \frac{\mu mol\ H2}{h}}{0.037 \ \frac{\mu mole\ H_2}{h \cdot g\ catalyst}}$$

$$\boldsymbol{W_{\min} = 3.5*10^7\ g\ catalyst = 35{,}000\ L\ of\ catalyst}$$

This shows that the experimental device was designed to operate in a range of reation rates applicable to the assumed sump conditions.

APPENDIX D

EQUATION DERIVATIONS AND SAMPLE CALCULATIONS

APPENDIX D: DERIVATION OF EQUATIONS

PERCENT AIR CONTAMINATION

Inlet and outlet gas samples of the runs were taken and analyzed for several gas species. Contamination of the samples with air was expected to some extent. Possible causes of this contamination are an incomplete evacuation of the line when the sample container was connected to the analytic equipment, or an air intrusion in the valves or piping. The extent of air contamination was determined by calculating the Percent Air Contamination (Φ) which is the volume percent of the analyzed sample which is air rather than pure sample. From this the true sample compositions were determined and large mistakes were detected.

ARGON METHOD:

Because there is no argon (Ar) in any of the feed gases, any Ar in the sample comes from the air contaminating the sample. This fact is used to calculate Φ for samples analyzed by Pacific Northwest Laboratories using a mass spectrometer.

$$\phi = \frac{X_{Ar}}{Y_{Ar}} * 100\% \qquad \text{(Eqn D-1)}$$

The squared relative standard deviation (RSD) for Φ, which is the ratio of two independent and uncorrelated variables, is approximately:

$$RSD^2(\phi) \doteq RSD^2(X_{Ar}) + RSD^2(Y_{Ar}) \qquad \text{(Eqn D-2)}$$

The RSD^2 of each variable is equal to the squared quantity of the standard deviation (Δ) of that variable divided by that variable. The equation then becomes:

$$\left(\frac{\Delta\phi}{\phi}\right)^2 \doteq \left(\frac{\Delta X_{Ar}}{Q_{Ar}}\right)^2 + \left(\frac{\Delta Y_{Ar}}{Y_{Ar}}\right)^2 \qquad \text{(Eqn D-3)}$$

The standard deviation of the reaction rate can then described by the equation:

$$\Delta\phi = \phi\left[\left(\frac{\Delta X_{Ar}}{X_{Ar}}\right)^2 + \left(\frac{\Delta Y_{Ar}}{Y_{Ar}}\right)^2\right]^{\frac{1}{2}} \qquad \text{(Eqn D-4)}$$

where:

Φ = Percent air contamination (%)
X_{Ar} = Mole percent of Ar in sample (%)
Y_{Ar} = Mole percent of Ar in air (%).

Sample Calculation: Sample 93-019, Run 7.

X_{Ar} = 0.014% ± 0.001%
Y_{Ar} = 0.934% ± 0.001%

$$\phi = \frac{0.014\%}{0.934\%} * 100\% = 1.5\%$$

$$\Delta\phi = (1.5\%) * \left[\left(\frac{0.001\%}{0.014\%}\right)^2 + \left(\frac{0.001\%}{0.934\%}\right)^2\right]^{\frac{1}{2}} = 0.11\%$$

$$\phi = 1.5 \pm 0.11\ \%$$

OXYGEN METHOD:

In most of the runs, no O_2 was used. In these runs, an O_2 analysis can be used to determine the Φ as an alternative to the Ar method. The equation for this is:

$$\phi = \frac{X_{O_2}}{Y_{O_2}} * 100\% \qquad \text{(Eqn D-5)}$$

$$\Delta\phi = \phi\left[\left(\frac{\Delta X_{O_2}}{X_{O_2}}\right)^2 + \left(\frac{\Delta Y_{O_2}}{Y_{O_2}}\right)^2\right]^{\frac{1}{2}} \qquad \text{(Eqn D-6)}$$

where:

Φ_{O_2} = Percent air contamination (%)
X_{O_2} = Mole percent of O_2 in sample (%)
Y_{O_2} = Mole percent of O_2 in air (%).

Sample Calculation: Sample 93-019, Run 7.

X_{O_2} = 0.250% ± 0.003%
Y_{O_2} = 20.946% ± 0.002%

$$\phi_{O_2} = \frac{0.250\%}{20.946\%} * 100\% = 1.2\%$$

$$\Delta\phi = (1.2\%) * \left[\left(\frac{0.003\%}{0.250\%}\right)^2 + \left(\frac{0.002\%}{20.946}\right)^2\right]^{\frac{1}{2}} = 0.014\%$$

$$\phi = 1.2 \pm 0.014\ \%$$

RESIDENCE TIME

The residence time (τ_r) is the time required for one reactor volume of fluid to flow out of the reactor. It is also the average time a molecule of gas will spend in the reactor. It was calculated with the equation (Levenspiel 1972):

$$\tau_r = \frac{V}{Q} \qquad \text{(Eqn D-7)}$$

$$\#\tau_r = \frac{t}{\tau_r} \qquad \text{(Eqn D-8)}$$

where:

τ_r = Residence time (min)
V = Volume of reactor (mL)
Q = Volumetric flowrate (mL/min)
t = Run time.

Sample Calculation: Run 7.

V = 7571 mL
Q_{tot} = 275 mL/min
time = 348 min

$$\tau_r = \frac{7571\ mL}{275\ mL/\text{min}} = 27.5\ \text{min}/\mathit{residence\ time}$$

$$\#\tau_r = \frac{348\ \text{min}}{27.5\ \text{min}/\mathit{residence\ time}} = 13\ \mathit{residence\ times}$$

SPECIFIC FLOWRATE

The specific flowrate (SF) is the rate at which H_2 was supplied to the reactor per gram of catalyst in the reactor. The SF is calculated from the inlet flowrate (Q) and the inlet H_2 concentration ($X_{H,in}$). The Ideal Gas Law was then used to convert the units to match those of the reaction rate. The equation used to calculate the SF was:

$$SF = 60\frac{PQ}{RTW}\left(\frac{X_{H,in}}{100}\right) \qquad \text{(Eqn D-9)}$$

where:

SF = Specific flowrate (μmol/h/g)
Q = Total volumetric flow rate (sccm)
P = Pressure (atm)
R = Ideal gas constant ($8.206 \times 10^{-5}\ \frac{\text{mL}\cdot\text{atm}}{\mu\text{mole}\cdot\text{K}}$)
T = Temperature (K)
W = Mass of catalyst (g)
X_H = Mole percent of H_2 in gas (mole %).

Sample Calculation: Run #7, sample 93-020.

Q = 275 sccm
P = 1 atm [9]
$R = 8.206 * 10^{-5} \frac{mL \cdot atm}{\mu mole \cdot K}$
T = 298 K [9]
W = 240 g
$X_{H,in}$ = 0.932 mole %

$$SF = \frac{60 \frac{min}{h} \ (1\,atm) \left(275 \frac{mL}{min}\right)}{\left(8.206 * 10^{-5} \frac{mL \cdot atm}{\mu mole \cdot K}\right) (298\,K)\ (240\,g)} \left(\frac{0.932\%}{100\%}\right) = 26.2 \ \frac{\mu moles\ H_2\ reacted}{h \cdot g\ Catalyst}$$

REACTION RATE

The reaction rate is based on a unit mass of catalyst and is defined in Levenspiel (1972) as:

$$r_H = \frac{1}{W}\frac{dn_H}{dt} = \frac{1}{W}\frac{n_H}{t} \qquad \text{(Eqn D-10)}$$

where:

r_H = Reaction rate of H_2 (μmol/h/g)
W = Mass of catalyst (g)
n_H = Moles of H_2 reacted (μmol)
t = Time (h).

The ideal gas law, PV=nRT, can be expressed as

$$n = \frac{P}{RT} V \ . \qquad \text{(Eqn D-11)}$$

The temperature and pressure in this equation are the flowrate's reference temperature and pressure not the test conditions. The flowmeters read the mass flowrate and display a volumetric flowrate referenced to 25°C (77°F) and 1 atm. The reference temperature and pressure are used in these equations to convert the volumetric flowrate back into a mass flowrate.

When Eqn D-11 is substituted into Eqn D-10, the equation for r_H becomes:

$$r_H = \frac{1}{W}\frac{P}{RT}\frac{V_H}{t} \ , \qquad \text{(Eqn D-12)}$$

where:

P = Flowrate reference pressure (1 atm)
R = Ideal gas constant $\left(\frac{mL \cdot atm}{\mu mole \cdot K}\right)$
T = Flowrate reference temperature (298 K)
V_H = Volume of gas in the reactor (mL).

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[9] The flowmeter reads mass flowrates and displays a volumetric flowrate referenced to 25°C and 1 atm. The temperature and pressure used in this equation are the flowmeters reference conditions, not the test conditions.

In turn, V_H can be expressed as:

$$V_H = 60\,t\,Q\left[\frac{X_{H,in} - X_{H,out}}{100}\right] . \qquad \text{(Eqn D-13)}$$

The unit of minutes in the flowrate is changed to hours by the conversion 60 min/h. When Eqn D-13 is substituted into Eqn D-12, r_H becomes:

$$r_H = 60\frac{PQ}{RTW}\left(\frac{X_{H,in} - X_{H,out}}{100}\right) , \qquad \text{(Eqn D-14)}$$

where:

r_H = Reaction rate (μmol/h/g)
Q = Total volumetric flow rate (sccm)
P = Flowrate reference pressure (1 atm)
T = Flowrate reference temperature (298 K)
R = Ideal gas constant $\left(\frac{\text{mL}\cdot\text{atm}}{\mu\text{mole}\cdot\text{K}}\right)$
W = Mass of catalyst (g)
X_H = Mole percent of H_2 in gas, in or out (mole %).

The squared relative standard deviation (RSD) for the reaction rate, which is the product and ratio of independent and uncorrelated variables, is approximately:

$$RSD^2(r_H) \doteq RSD^2(Q) + RSD^2(W) + RSD^2(X_{in} - X_{out}) \qquad \text{(Eqn D-15)}$$

The RSD^2 of each variable is equal to the squared quantity of the standard deviation (Δ) of that variable divided by that variable. The equation then becomes:

$$\left[\frac{\Delta r_H}{r_H}\right]^2 \doteq \left[\frac{\Delta Q}{Q}\right]^2 + \left[\frac{\Delta W}{W}\right]^2 + \left[\frac{\left[\Delta(X_{in} - X_{out})\right]^2}{(X_{in} - X_{out})^2}\right] \qquad \text{(Eqn D-16)}$$

Assuming that X_{in} and X_{out} are independent of each other, the equation becomes:

$$\left[\frac{\Delta r_H}{r_H}\right]^2 \doteq \left[\frac{\Delta Q}{Q}\right]^2 + \left[\frac{\Delta W}{W}\right]^2 + \left[\frac{\Delta X_{in}^2 + \Delta X_{out}^2}{(X_{in} - X_{out})^2}\right] \qquad \text{(Eqn D-17)}$$

The standard deviation of the reaction rate is then described by the equation:

$$\Delta r_H \doteq r_H\left[\left[\frac{\Delta Q}{Q}\right]^2 + \left[\frac{\Delta W}{W}\right]^2 + \left[\frac{\Delta X_{in}^2 + \Delta X_{out}^2}{(X_{in} - X_{out})^2}\right]\right]^{1/2} \qquad \text{(Eqn D-18)}$$

Sample Calculation: Run #7, samples 93-019 (out) and 93-020 (in).

Q = 275 ± 10 sccm
P = 1 atm[10]
$R = 8.206 \times 10^{-5}\ \frac{\text{mL}\cdot\text{atm}}{\mu\text{mole}\cdot\text{K}}$
T = 298 K
W = 240 ± 0.1 g
$X_{H,in}$ = 0.932 ± 0.009 mole %
$X_{H,out}$ = 0.016 ± 0.002 mole %

$$r_H = \frac{60\,\frac{\text{min}}{h}\,(1\,atm)\left(275\,\frac{mL}{\text{min}}\right)}{\left(8.206*10^{-5}\,\frac{mL\cdot atm}{\mu mole\cdot K}\right)(298\,K)\,(240\,g)} * \left(\frac{0.932\% - 0.016\%}{100\%}\right) = 25.8\ \frac{\mu moles\,H_2\,reacted}{h\cdot g\ Catalyst}$$

$$\Delta r_H \doteq 25.8\left[\left(\frac{10}{275}\right)^2 + \left(\frac{0.1}{240}\right)^2 + \left(\frac{0.009^2 + 0.002^2}{(0.932 - 0.016)^2}\right)^2\right]^{\frac{1}{2}} \doteq 0.94\ \frac{\mu moles\ H_2}{h\cdot g\ catalyst}$$

$$r_H = 25.8 \pm 0.94\ \frac{\mu moles\ H_2\ reacted}{h\cdot g\ catalyst}$$

CONVERSION

The conversion during a run is the ratio between the reaction rate and specific flowrate of H_2 which allows the reaction rates to be compared to each other with consideration of the different specific flowrates. The equation used for the conversion was:

$$\chi = \frac{r_H}{SF} * 100\% \qquad \text{(Eqn D-19)}$$

where:

χ = Conversion (%)
r_H = Reaction rate (µmol/h/g)
SF = Specific flowrate (µmol/h/g).

---

[10] The flowmeters read the mass flowrate and then displayed a volumetric flowrate referenced to 25°C (77°F) and 1 atm. Temperature and pressure are the flowrate's reference temperature and pressure and are used in these equations to convert the volumetric flowrate back into a mass flowrate. There is no error associated the reference temperature and pressure.

The conversion (χ) is typically defined as the fraction of available H_2 that was reacted. By substituting the equations for r_H and SF (Eqns D-14 and D-9) into Eqn D-19 and canceling terms, the equation for the conversion can be shown in its more common form (Levenspiel):

$$\chi = \frac{X_{H,in} - X_{H,out}}{X_{H,in}} * 100\% \; . \qquad \text{(Eqn D-20)}$$

Equation D-17 was used in the calculations.

Sample Calculation: Run #7.

r_H = 25.75 μmol/h/g

SF = 26.20 μmol/h/g.

$$\chi = \frac{25.75}{26.20} * 100\% = 98.3\%$$

CORRECTED COMPOSITION

The oxygen compositions for runs using FM 1 were corrected for the air contamination by lowering the measured composition by the average O_2 composition deviation at that Φ. The average deviation was calculated by dividing the average X_O by the average Φ and multiplying by the Φ (Ar method) for that sample. The average X_O and Φ were determined by averaging all the non-FM1 values for X_O and Φ. The equation for the corrected composition was:

$$X_O' = X_O - \frac{X_{O,ave}}{\Phi_{ave}}(\Phi) \qquad \text{(Eqn D-21)}$$

where:

X_O' = Mole percent component i in sample corrected for air contamination
X_O = Mole percent component i in sample as analyzed
$X_{O,ave}$ = Average mole percent component i in sample as analyzed
Φ = Percent air contamination
Φ_{ave} = Average percent air contamination

Sample Calculation: Run #7.

X_O = 0.525% O_2
$X_{O,ave}$ = 0.26914% O_2
Φ = 3.105%
Φ_{ave} = 2.07078%

$$X_O' = 0.525\% - \frac{0.26914\%}{2.07078\%}(3.105\%) = 0.121\% \; O_2$$

SORPTION CAPACITY

The CO sorption capacity of the catalyst (SC) is the total amount of CO that chemisorbs to the catalyst. To calculate this, the manner in which the reactor works needs to be understood.

The reactor in the experimental apparatus closely approximates a mixed flow reactor where the inlet gas is mixed with the bulk of the gas in the reactor. Therefore, the outlet gas concentration ($X_{CO,out}$) is the same as the concentration of the gas in the reactor. Starting with zero percent CO in the reactor, the $X_{CO,out}$ increases with time until arriving at the inlet concentration ($X_{CO,in}$). The difference between the $X_{CO,out}$ and $X_{CO,in}$ is the amount of CO the reactor retains in the gas phase. Assuming the gas remains at a constant density (constant pressure and temperature), and CO is retained only in the gas phase of the reactor, and the reactor acts as a perfectly mixed stirred tank reactor, $X_{CO,out}$ should follow a first order equation for a mixed flow reactor. This can be derived as:

$$\mathit{Accumulation} = \mathit{In} - \mathit{Out}$$

$$V\frac{dX}{dt} = X_{CO,in}Q - X^{est}_{CO,out}Q$$

$$\int_0^{X_{CO,in}} \frac{1}{X_{CO,in} - X^{est}_{CO,out}}\,dX = \frac{Q}{V}\int_0^t dt$$

$$-Ln\left|X_{CO,in} - X^{est}_{CO,out}\right| = \frac{Q}{V}t$$

$$\tau_r = \frac{V}{Q}$$

$$-Ln\left[\frac{X_{CO,in} - X^{est}_{CO,out}}{X_{CO,in}}\right] = \frac{t}{\tau_r}$$

$$1 - \frac{X^{est}_{CO,out}}{X_{CO,in}} = e^{-\frac{t}{\tau_r}}$$

$$X^{est}_{CO,out} = X_{CO,in}\left(1 - e^{-\frac{t}{\tau_r}}\right) \qquad \text{(Eqn D-22)}$$

where:

V = Volume of the reactor (mL)
t = Time from the start of the inlet flow (min)
$X^{est}_{CO,out}$ = CO concentration in the offgas assuming no CO chemisorption (%)
$X_{CO,in}$ = CO concentration in the feed gas (%)
Q = Total volumetric flowrate into and out of the reactor (mL/min)
W = Mass of catalyst (g)
τ_r = Residence time of the gas in the reactor (min).

Assuming that both t and τ_r are constants the squared residual standard deviation of $X^{est}_{CO,out}$ equals that of the $X_{CO,in}$. The standard deviation for the estimated outlet CO concentration is then:

$$\Delta X^{est}_{CO,out} = X^{est}_{CO,out} \frac{\Delta X_{CO,in}}{X_{CO,in}} \quad \text{(Eqn D-23)}$$

The SC is the total amount of CO that one gram of catalyst will chemisorb. SC is calculated by finding the difference between the estimated CO concentration ($X^{est}_{CO,out}$) and the actual CO concentration of the outlet stream ($X^{act}_{CO,out}$). The outlet CO concentration is measured at intervals of I. The summation of the estimated and actual CO concentrations over all the intervals is then multiplied by the Q. When the Ideal Gas Law is applied, the equation for SC becomes:

$$SC = \frac{PQ}{RTW} \frac{\sum_i \left[I_i \left(X^{est}_{CO,out_i} - X^{act}_{CO,out_i}\right)\right]}{100} \quad \text{(Eqn D-24)}$$

The temperature (T) and pressure (P) used in this equation are the flowrate's reference to standard. These variables are used to convert the units from volume to moles and do not have an error associated with them. Their error is in the flowrate.

Assuming no error in T and P and assuming the sampling interval (I) is constant throughout each run, the squared residual standard deviation of the SC is approximately:

$$\begin{aligned} RSD^2(SC) &\doteq RSD^2(Q) + RSD^2(I) + RSD^2(W) \\ &+ RSD^2\left[\sum_i \left(X^{est}_{CO,out,i} - X^{act}_{CO,out,i}\right)\right] \end{aligned} \quad \text{(Eqn D-25)}$$

Assuming that X is uncorrelated between sampling intervals:

$$RSD^2\left[\sum \left(X^{est}_{CO,out,i} - X^{act}_{CO,out,i}\right)\right] = \frac{var\left[\sum_i \left(X^{est}_{CO,out,i} - X^{act}_{CO,out,i}\right)\right]}{mean\left[\sum_i \left(X^{est}_{CO,out,i} - X^{act}_{CO,out,i}\right)\right]} \quad \text{(Eqn D-26)}$$

and assuming that X^{est} and X^{act} are uncorrelated:

$$\frac{var\left[\sum_i \left(X^{est}_{CO,out,i} - X^{act}_{CO,out,i}\right)\right]}{mean\left[\sum_i \left(X^{est}_{CO,out,i} - X^{act}_{CO,out,i}\right)\right]} = \frac{\sum_i \left[\left(\Delta X^{est}_{CO,out,i}\right)^2 + \left(\Delta X^{act}_{CO,out,i}\right)^2\right]}{\left[\sum_i \left(X^{est}_{CO,out,i} - X^{act}_{CO,out,i}\right)\right]^2} \quad \text{(Eqn D-27)}$$

the equation for the standard deviation of the sorption capacity (ΔSC) is:

$$\Delta SC = SC\left[\left[\frac{\Delta Q}{Q}\right]^2 + \left[\frac{\Delta I}{I}\right]^2 + \left[\frac{\Delta W}{W}\right]^2 + \frac{\sum_i\left[\left(\Delta X^{est}_{CO,out,i}\right)^2 + \left(\Delta X^{act}_{CO,out,i}\right)^2\right]}{\left[\sum_i\left(X^{est}_{CO,out,i} - X^{act}_{CO,out,i}\right)\right]^2}\right]^{\frac{1}{2}} \qquad \text{(Eqn D-28)}$$

Sample Calculation: Run # 84

$X^{act}_{CO,in}$ = 0.106 ± 0.001%
t = 1 minute
τ_r = 14.0 min

$$X^{est,1}_{CO,out} = (0.106\%)\left(1 - e^{-\frac{1\,min}{14\,min}}\right) = 0.007\%$$

P = 1 atm
Q = 540 ± 50 mL/min
R = $8.206*10^{-5}\ \frac{mL\cdot atm}{\mu mole\cdot K}$
T = 298 K
W = 20 ± 0.1 g catalyst
I = 10 ± 0.2 min

Table D-1. Run 84 Data for Sorption Capacity Calculation.

t	$X^{est}_{CO,out}$	$X^{act}_{CO,out}$	$I*(X^{est}_{CO,out} - X^{act}_{CO,out})$	$(\Delta X^{est}_{CO,out})^2$	$(\Delta X^{act}_{CO,out})^2$	$X^{est}_{CO,out} - X^{act}_{CO,out}$
1	0.007	0.000	0.0073	0	0	0.00723
11	0.057	0.020	0.3709	$1.000*10^{-6}$	$8.225*10^{-6}$	0.03709
21	0.082	0.040	0.4152	$1.000*10^{-6}$	$4.193*10^{-6}$	0.04152
31	0.093	0.054	0.3949	$1.000*10^{-6}$	$3.026*10^{-6}$	0.03949
41	0.099	0.071	0.2836	$1.000*10^{-6}$	$1.977*10^{-6}$	0.02836
51	0.102	0.088	0.1424	$1.000*10^{-6}$	$1.363*10^{-6}$	0.01424
61	0.104	0.098	0.0564	$1.000*10^{-6}$	$1.129*10^{-6}$	0.00565
71	0.104	0.103	0.0134	$1.000*10^{-6}$	$1.036*10^{-6}$	0.00134
81	0.105	0.104	0.0068	$1.000*10^{-6}$	$1.023*10^{-6}$	0.00068
91	0.105	0.104	0.0084	0	0	0.00084
Summation			1.6984	$8.000*10^{-6}$	$2.1764*10^{-5}$	0.1764

$$SC = \frac{(1\ atm)\left(540\frac{mL}{\min}\right)}{\left(8.206*10^{-5}\frac{mL\cdot atm}{\mu moles\cdot K}\right)(298\,K)\ (20\ g\ cat)}\ \frac{(1.6984\ \%CO\cdot \min)}{100\%} = 18.8\ \frac{\mu moles\ CO}{g\ catalyst}$$

$$\Delta SC = 18.8 * \left[\left[\frac{50}{540}\right]^2 + \left[\frac{0.2}{10}\right]^2 + \left[\frac{0.1}{20}\right]^2 + \frac{\left(8.000*10^{-6}\right)+\left(2.1764*10^{-5}\right)}{(0.1764\ )^2}\right]^{\frac{1}{2}} = 1.9\ \frac{\mu\text{moles CO}}{\text{g catalyst}}$$

$$\boldsymbol{SC = 18.8 \pm 1.9\ \frac{\mu moles\ CO}{g\ catalyst}}$$

APPENDIX E

PERFORMANCE TEST PROCEDURES

APPENDIX E: PERFORMANCE TEST PROCEDURES

PERFORMANCE TEST RUN PROCEDURE

This procedure was used to operate the HRC test apparatus and conduct the HRC performance test runs.

1. If needed: Turn on the chiller attached to the heat exchanger.
2. Reinstall the reactor head and reconnect all tubing.
3. Check for leaks in the reactor (refer to the pressure testing section).
4. Pressurize the regulators on all the cylinders to be used to 20 psi.
5. Check the cylinders for enough gas to complete the test.
6. Open FC-5 and V-1 to purge from the flow controllers to the reactor.
7. Open V-9 to purge the reactor vapor space and the offgas tubing.
8. Wait 10 minutes, approximately 10 residence times.
9. Close V-1 and V-9.
10. If needed: Check the water level in the humidifier and fill as necessary.
11. Depressurize the reactor. Wait for P-3 to decrease.
12. Set the mass flow controllers to the predetermined test flowrates, starting with N_2.
13. Start temperature strip chart.
14. Record in the logbook the following:
    Date and time
    Run #
    Apparatus #
    Feed mixture # (FM #)
    Mass flowrates from FC-1 through FC-5.
15. If needed: Check the inlet gas temperature (T-2). Adjust the chiller temperature if T-2 is above ambient.
16. Record in Logbook the following:
    Volumetric flowrates from F-1 and F-2,
    Temperatures from T-1 and T-2
    Pressures from P-1, P-2, and P-3.
17. Wait for 5 to 10 residence times or let the system run until equilibrium is suspected.
18. Take the first H_2 measurement. (Refer to the Online Hydrogen Analysis Procedure.)
19. Let the system run for 15 to 30 minutes.

20. Take another H_2 measurement. (Refer to the Online Hydrogen Analysis Procedure.)

HOLD: If the online hydrogen analysis indicates equilibrium has been reached, proceed to step 20; otherwise, go back to step 18.

21. Take the first outlet gas sample. (Refer to the Sampling Procedure).
22. Wait for 15 to 30 minutes, allowing the system to run.
23. Take another H_2 measurement. (Refer to the Online Hydrogen Analysis Procedure.)

HOLD: If the online hydrogen analysis indicates equilibrium has been reached, proceed to step 24; otherwise, go back to step 18.

24. Take the second outlet gas sample. (Refer to the Sampling Procedure).
25. Take the inlet gas sample. (Refer to the Sampling Procedure).
26. Turn off the mass flow controllers, FC-1 through FC-4.
27. Purge the system with N_2.
28. Turn off FC-5.
29. Turn off PR-1 through PR-6 if another run will not be performed immediately.

<u>Optional</u>:

30. Remove the reactor head.
31. Inspect the catalyst bed. Remove any excess water in the bottom of the reactor.

PERFORMANCE TEST PRESSURE TESTING

The following was the method used to check for leaks in the test apparatus. It was used each time the reactor head was reinstalled or tubing was reconfigured.

1. Close the offgas valve.
2. Pressurize purge gas cylinder to 90 psi.
3. Open V-1 (or V-9).
4. Wait for reactor pressure to reach 90 psi.
5. Close V-1 (or V-9).

6. If pressure on P-1, P-2, and P-3 decreases, tighten the fittings and reactor head clamp.
7. When pressure as read on P-3 is maintained for 15 minutes, open the offgas valve and continue.

PERFORMANCE TEST ONLINE HYDROGEN ANALYSIS PROCEDURE

The procedure followed for performing online hydrogen analysis using the Whittaker hydrogen analyzer was as follows.

1. Open V-16.
2. Turn V-14 (or V-5) to redirect the gas flow towards HA-1.
3. Wait 5 to 10 minutes, letting the inlet/outlet gas into the analyzer.
4. Record the measurement in the logbook along with the date and time.
5. Put V-14 (or V-5) back to the original position.
6. Open V-15 to flush out the HA-1 sample chamber.

NOTE: Do not open V-15 all the way. The increase in pressure will drive the H_2 into the analyzer's membrane.

7. Close V-16 after running the approximately 10 minutes.

PERFORMANCE TEST SAMPLING PROCEDURE

The procedure followed for taking inlet and outlet gas samples was as follows.

1. Install the GSC to the sampling ports.
2. Open the GSC valves.
3. Open the sampling valves (V-7 & V-8 or V-11 & V-12).
4. Close V-6 or V-10 to divert the gas flow.
5. Open V-6 or V-10 to re-divert the gas flow.
6. Close the sampling valves (V-7 & V-8 or V-11 & V-12).
7. Close the GSC valves.
8. Detach the GSC
9. Screw plugs into the sampling ports or install another GSC.
10. Label sample and record in logbook. Store sample for shipping to analysis.

APPENDIX F

CO SORPTION CAPACITY TEST PROCEDURES

APPENDIX F: CO SORPTION CAPACITY TEST PROCEDURES

SORPTION CAPACITY TEST RUN PROCEDURE

This procedure was used to operate the HRC test apparatus and conduct the CO sorption capacity test runs.

1. Reinstall the reactor head and reconnect all tubing.
2. Check for leaks in the reactor (refer to the Pressure Testing section).
3. Pressurize the regulators on all the cylinders to be used to 20 psi.
4. Check the cylinders for enough gas to complete the test.
5. Open V-9 and V-10 to purge the reactor vapor space and the offgas tubing.
6. Wait 10 minutes. Approximately 10 residence times.
7. Close V-9 and depressurize the reactor. Wait for P-3 to decrease. Close V-6 and V-10 to isolate the reactor.
8. Set the mass flow controllers to the predetermined test flowrates and Open V-7.
9. Take an inlet sample from V-7 using a Tedlar bag and analyze. If the gas composition is correct, proceed to the next step. If not, re-adjust the mass flow controllers and resample. (Refer to the Sampling Procedure).

Optional:

10. Check the inlet flowrate with a bag and stop watch. (Refer to the Flowrate Measurement Procedure).
11. Close V-7 and open V-6 to route the feed mixture into the reactor.
12. Start the stopwatch.
13. Record the following in the logbook
    Date and time
    Run #
    Feed mixture # (FM #)
14. Take an outlet sample every 10 or 15 minutes. (Refer to the Sampling Procedure).
15. Repeat Step 14 until the outlet concentration equals the inlet concentration.

Optional:

16. Take an inlet sample from V-7 using a Tedlar bag. Then run this sample on the gas chromatograph. (Refer to the Sampling Procedure).
17. Turn off the mass flow controllers.
18. Close V-6 and V-10 to isolate the reactor.
19. Proceed to the Regeneration Procedure.

REGENERATION PROCEDURE

This is the procedure used to regenerate the catalyst in the CO sorption capacity test. Either bottled N_2 or bottled air was used as the regeneration gas.

1. Open V-10
2. Open V-9 and allow the regeneration gas to flush the reactor.
3. Time the regeneration.
4. Record:
   mass of catalyst
   type of regeneration gas (N_2 or bottled air)
   regeneration gas flowrate
   regeneration pressure
   length of regeneration.
5. Calculate:
   total volume of regeneration gas
   volume of regeneration gas per mass of catalyst.

FLOWRATE MEASUREMENT PROCEDURE

This procedure was used to perform a bag and stopwatch check on the inlet feed mixture flowrate.

1. Take an inlet sample (approximately 2 minutes) and accurately time it. (Refer to the Sampling Procedure).
2. Using a scale, tare a bucket that is filled to the rim with water.
3. Completely submerge the inflated sample bag in the bucket of water. The displaced water will run over the side of the bucket.
4. Remove the sample bag.

5. Scrape all the water off of the scale and weigh the water bucket.
6. The difference between the initial and final bucket weights is the mass of water displaced.
7. Assume the water density is 1 g/mL and multiply this times the displaced water mass to find the volume of the sample. Then divided by the sampling time to find the flowrate.

PRESSURE TESTING

The following was the method used to check for leaks in the test apparatus. It was used each time the reactor head was reinstalled or tubing was reconfigured.

1. Close the offgas valve.
2. Pressurize purge gas cylinder to 90 psi.
3. Open V-1 (or V-9).
4. Wait for reactor pressure to reach 90 psi.
5. Close V-1 (or V-9).
6. If pressure on P-1, P-2, and P-3 decreases, tighten the fittings and reactor head clamp.
7. When pressure as read on P-3 is maintained for 15 minutes, open the offgas valve and continue.

SORPTION CAPACITY TEST SAMPLING PROCEDURE

The procedure followed for taking outlet (and inlet) gas samples was as follows.

1. Install the Tedlar bag onto V-11 (or V-7 for inlet samples).
2. Open the sampling valve V-11 (or V-7).
3. Open the Tedlar bag valve and close V-10 (or V-6) to divert the gas flow.
4. Fill bag for 2 minutes.
5. Open or V-10 (or V-6) to re-divert the gas flow.
6. Close the Tedlar bag valve.
7. Close the sampling valve V-11 (or V-7).
8. Detach the Tedlar bag.
9. Label the sample and record time and sample number in logbook.

10. Record the following information on the Sample Logsheet:
    - sample number
    - run number
    - logbook page number
    - apparatus number
    - run time (time from start of run)
    - flowrate
    - gas temperature in reactor
    - feed mixture (FM) number
    - Inlet/Outlet
    - notes
11. Connect the Tedlar bag fitting to the injector port of the Gas Chromatograph (GC) and start the GC.