CATALYTIC HYDROGEN RECOMBINATION FOR NUCLEAR CONTAINMENTS

G.W. Koroll, D.W.P. Lau, W.A. Dewit and W.R.C. Graham

ABSTRACT

Catalytic recombiners appear to be a credible option for hydrogen mitigation in nuclear containments. The passive operation, versatility and ease of back fitting are appealing for existing stations and new designs. Recently, a generation of wet-proofed catalyst materials have been developed at AECL which are highly specific to H_2-O_2, are active at ambient temperatures and are being evaluated for containment applications.

Two types of catalytic recombiners were evaluated for hydrogen removal in containments based on the AECL catalyst. The first is a catalytic combustor for application in existing air streams such as provided by fans or ventilation systems. The second is an autocatalytic recombiner which uses the enthalpy of reaction to produce natural convective flow over the catalyst elements.

Intermediate-scale results obtained in 6 m^3 and 10 m^3 spherical and cylindrical vessels are given to demonstrate self-starting limits, operating limits, removal capacity, scaling parameters, flow resistance, mixing behaviour in the vicinity of an operating recombiner and sensitivity to poisoning, fouling and radiation.

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1.0 INTRODUCTION

Hydrogen gas generated in a reactor accident poses a threat to structures and essential equipment if allowed to accumulate to flammable concentrations and become ignited. Means of removing hydrogen at non-flammable concentrations would contribute to improved margins of safety.

Catalytic oxidation is a means of reacting hydrogen with oxygen at below flammable concentrations that shows promise for containment applications [1-6]. Historically, catalyst materials most suited to hydrogen were prone to deactivation by ambient water vapour. Recently, a generation of modern catalyst materials has been developed at AECL which are highly specific to H_2-O_2 and which are active at ambient temperatures, wet or dry. The AECL catalyst is the product of a program of advanced catalyst engineering directed at catalytic processes for heavy water production, an important aspect of CANDU technology. The catalysts created for that program show extraordinary wet-proofing and robustness, which are also desirable properties for hydrogen removal in post-accident containment applications.

This paper reports results of an evaluation of two types of catalytic recombiners for hydrogen removal in containment based on the AECL catalyst. The first is a catalytic combustor for application in existing air streams, such as provided by fans or ventilation systems. The second is an autocatalytic recombiner which uses the enthalpy of reaction to produce natural convective flow over the catalyst elements and requires no other power or operator action.

Because the CANDU employs a subatmospheric containment with active pressure suppression systems consisting of sprays and air cooling units, performance under cool, wet conditions was emphasized in the development and test program.

2.0 AECL WET-PROOFED CATALYSTS

Engineering of wet-proofed catalysts for the H_2-O_2 reaction has been underway at AECL for over 20 years, as part of a continuing program of research into methods of producing heavy water using catalytic isotope exchange processes. Briefly, in the liquid-phase catalytic exchange (LPCE) process, hydrogen gas and liquid water flow counter currently through a catalyst bed. Two steps occur in the LPCE process; platinum-catalyzed transfer of deuterium from hydrogen gas to water vapour, and physical exchange of deuterated water between vapour and liquid phases. For optimum process performance, the catalyst must be near the mass transfer surface. However, the pores in conventional catalysts are quickly filled by liquid water, hindering diffusion of the gaseous components to the catalytically active metal sites, so wetproofing was required to prevent contact between the liquid and the catalyst surface. Further, the transfer of deuterium from hydrogen gas to liquid water is thermodynamically favoured at low temperatures, so wetproofed catalysts were developed specifically with low-temperature, humid performance in mind.

The first wetproofed catalysts consisted of conventional catalyst pellets protected with a gas-permeable PTFE (Teflon) coating [7], and were susceptible to slow deactivation by water vapour. The second generation of LPCE catalysts used a mixed bed of hydrophilic elements (to provide wettable surface area for mass transfer between liquid water and water vapour) and PTFE-coated platinized carbon. The current generation of isotope exchange catalyst uses a structured (ordered bed) packing and is not deactivated by water vapour [8]. The ordered bed is made of alternating hydrophilic and hydrophobic (catalyst) layers arranged to maximize catalyst activity and minimize pressure drop.

In the 1980s, AECL identified many other applications where catalyst resistance to water vapour is desirable. One of the first to be developed was hydrogen recombination. Wetproofed recombiners can operate in cool humid conditions and have a significant advantage over conventional recombiners, which must be heated to prevent catalyst deactivation. Trickle-bed recombiners, which use liquid water to remove the heat of recombination from the catalyst, were developed for recombining near-stoichiometric mixtures of hydrogen and oxygen [9,10]. Gas-phase wetproofed recombiners were also developed for many diverse applications, such as tritium sampling [11] and removal of radiolytic hydrogen in canisters of wet radioactive material [12].

Some of the identified recombiner applications expose the catalyst to radiation fields. Since PTFE wetproofing agent is somewhat susceptible to damage by radiation, AECL has developed non-PTFE wetproofing technology for applications where the catalysts must continue operating after exposure to high radiation fields. High radiation resistant wetproofed catalysts have been extensively tested and used for hydrogen control in canisters of wet radioactive wastes [12].

The catalyst used in the autocatalytic recombiners described in this work is a proprietary AECL formulation developed specifically for hydrogen recombination in post-accident containments [2,3]. The catalytic material is coated on a steel screen with a porous hydrophobic binder. The catalyst has a high catalytic activity for hydrogen oxidation, is not deactivated by water vapour or steam and is specially formulated for operation over a very wide range of temperatures. It has operated at high temperatures (up to 1000 K) without loss of activity, and is unaffected by high radiation exposures. Additionally, it has shown excellent resistance to poisoning by anticipated containment gases.

The catalyst can be formed into modules made of alternating layers of flat and corrugated sheets, giving an open structure with a very low pressure drop, making it ideal for forced convection recombiner application. The modules can be of any desired shape and can readily be scaled up or down in size. The corrugation size can be adjusted to give the module an optimum openness. Alternatively, catalyst sheets can be arranged in a holder with regular spacing to give an extremely open structure suited to the natural convection mode of operation. The catalyst module design is tailored to fit the application.

3.0 RESULTS

Two types of catalytic recombiners were evaluated for potential application in post-accident containments: 1) a forced convection recombiner (catalytic combustor) for use with fans or as a hydrogen scrubber in ventilation systems and, 2) a natural convection (passive, autocatalytic) recombiner which uses the enthalpy of reaction to produce natural convective flow over the catalyst elements.

The purpose of the investigation was to obtain complete performance and scaling parameters with test model recombiners over the range of foreseeable containment conditions so that designers could begin the engineering of recombiners into existing containments.

3.1 Forced Convection Recombiner (Catalytic Combustor)

The forced convection recombiner is intended for installation in combination with engineered air delivery systems, such as already may exist in the form of ventilation/cooling systems or systems specially designed for the purpose.

A test model catalytic combustor was evaluated in terms of conversion efficiency, operating temperature and resistance to flow. The test variables were hydrogen concentration (0-4%), initial temperature (15-35°C), moisture content (dry,saturated) and flow velocity (0.1-10.0 m/s). As well, effects of potential fouling agents such as iodine, organic vapours and carbon monoxide were examined. A description of the test apparatus and preliminary findings were reported previously [2].

Briefly, the test apparatus comprises an 8-cm-diameter instrumented stainless steel pipe into which the cylindrical catalyst element is installed (see Figure 1). Air and hydrogen are delivered in the desired proportions through electronic mass flowmeters. Steam from a separate steam source is blended with the air stream. Prior to introducing the hydrogen, the moist air stream flows over the catalyst elements continuously for 30 minutes. Pressure, temperature and composition of the gas stream is measured upstream and downstream of the catalyst element.

Figures 2 and 3 shows the conversion efficiency and pressure drop at different hydrogen concentrations with flow velocities from 0.1 m/s to 10 m/s, corresponding to residence times as low as 10 milliseconds over a 10 cm length catalyst element. Figure 2 illustrates two key aspects of forced convection recombiner performance. The first is a `kinetic limit' for self-start at low hydrogen concentrations which becomes evident at high flow velocities. With small increases in hydrogen concentration, there is additional heat release which greatly increases the catalyst activity. At about 1% to 1.5% H_2, the recombiner is at its full efficiency. The second aspect is the increased recombination efficiency at high inlet velocities. This is attributable to enhanced mass transfer to the catalyst surface due to turbulence in the high velocity flows. Figures 4 and 5 show the effect of initial temperature and humidity on the kinetic self-start limit under forced convection. Self-start and high efficiency of hydrogen removal appears assured at between 1% and 2% under the most severe conditions (cold, wet and high inlet velocities).

3.2 Natural Convection (Passive, Autocatalytic) Recombiner

The enthalpy of reaction at the catalyst surface provides a driving force for buoyancy-induced flow over suitably arranged catalyst elements, without mechanical assistance or outside power. The action is self-starting in response to the presence of hydrogen with available oxygen and continues until the hydrogen (or oxygen) in the enclosure has been completely consumed. This natural convection mode of operation was investigated in detail using a test model recombiner in the 6.6 m^3 (see Figure 6) and 10.7 m^3 vessels of the Containment Test Facility (CTF) at AECL. Self-starting limits, operating limits, removal capacity, scaling parameters and mixing behaviour in the vicinity of an operating recombiner were demonstrated along with resistance to poisoning, fouling and radiation.

A special device was fitted to the test module to remotely open and close the module so that the experimenter was able to isolate the catalyst from its surroundings so that initial test conditions could be precisely established without the recombiner operating.

<u>Self-start Limits</u>

Figure 7 shows a typical self-start test result with a 1 L catalyst module located in the 6.6 m^2 CTF sphere containing 1% H_2 in air at 25°C under saturated conditions. Hydrogen was introduced at t = 250 s and the recombiner was opened at t = 720 s. Start-up was spontaneous. At lower hydrogen concentrations, approaching detection limit, self-starting is still observed, as evidenced by a temperature increase in the recombiner, but at very low hydrogen concentrations, there are proportionately lower operating temperatures and only a small driving force for flow through the recombiner. Self-starting is also observed in oxygen-depleted atmospheres at less than 1% oxygen.

<u>Capacity and Scaling Parameters</u>

The capacity of a natural convection recombiner depends strongly on the hydrogen concentration. Increased hydrogen concentrations contribute to higher operating temperatures which increases the kinetic rate of the catalyst and the driving force for flow over the catalyst elements so a greater volume of gas is processed. Capacity also depends on the particular physical arrangement of catalyst material and the aerodynamics of the enclosure. The most useful scaling parameter, given a particular arrangement of internals, is the inlet cross-section area of the recombiner module. Figure 8 shows the capacity of the recombiner module in terms of inlet area at different hydrogen concentrations. (Tests with and without mixing fans showed the contents are well-mixed by the recombiner action). The capacity increases from 1 kg/h for the reference 1 m^2 cross section in 1% H_2 to more than 20 kg/h in 8% H_2. At the flammability limit, 4% H_2, the capacity is about 5 kg/h per m^2 inlet. The shape of the curve (i.e., the dependence of capacity on hydrogen concentration) in Figure 8 can be tailored to particular requirements by modifying the catalyst formulation and arrangement or the housing design. This particular catalyst configuration was designed to achieve low self-start limits and optimum capacity at low hydrogen concentrations, using the minimum amount of catalyst material.

Tests in mixtures up to 2 atmospheres show the capacity of the recombiner increases linearly with increased initial pressure. This trend is expected to continue at higher initial pressures. The fuel density increases with increased initial pressure, but the operating temperature, (and hence the convection velocity) does not significantly change. From forced convection tests it was evident that the capacity was limited by mass transfer not by kinetics limited and conversion efficiency was diminished at 10 times typical convection velocities.

Mixing

The air flow through an operating recombiner is ten to one hundred times the volume of the module per minute (depending on the operating temperature) and will significantly affect air movement in containment. Knowledge of the flow and mixing behaviour in the vicinity of an operating recombiner is thus necessary for containment thermalhydraulic calculations, generally, and specifically to determine optimum placement of recombiner units.

Mixing behaviour was investigated with stratified gas layers above the test model recombiner in the 1.5 m x 5.7 m high CTF cylinder. A special procedure, described in a separate paper [13], was developed to create very stable concentration gradients of hydrogen in air, verified by sampling at eleven different elevations of the cylindrical vessel. Figure 9 shows, schematically, how the test model recombiner was placed near the bottom of the cylinder containing in a low concentration of hydrogen with a high concentration of hydrogen several meters above. The vessel volume was $\sim 10^4$ times the volume of the module. Figure 10 shows that within minutes of opening the recombiner module, gases in the vessel become homogenized.

Combustion Survivability

The recombiner was intentionally exposed to repeated deflagrations of gas mixtures containing 10% hydrogen in air, and ignited by an electrical spark. Subsequent performance of the recombiner was unaffected.

Radiation Resistance

The catalyst used in these tests was exposed to an accumulated dose of 5×10^7 Gy with γ-radiation from a cobalt source. Following the radiation exposure, there was no observable change in performance.

Chemical Vapours

The catalyst was exposed to methyl iodide vapours (10^{-7} M), molecular iodine (10^{-6} M) and carbon monoxide (2% by volume) under prototypical post-accident conditions. The capacity of the recombiner (at 2% hydrogen concentrations) was unaffected. Since the recombiner is intended to process, in time, very large volumes of containment air, it has the potential to accumulate or concentrate poisons and other fouling agents. Therefore, the ratio of the test module volume to the enclosure volume was selected to be approximately that which would exist in a nuclear containment fitted with recombiners (~1:5000).

Cumulative Effects and Ageing

The catalyst elements used in these tests were manufactured in 1989 and have been used and handled in an industrial atmosphere without protection or special storage since that time. The tests described above, self-start limits, high temperature limits, radiation tests, combustion tests and exposure to chemical poisons were carried out on the same material over a three year period. The performance of the test model at the end of the test program was indistinguishable from results obtained at the start of the project.

4.0 SUMMARY

Catalytic recombiners appear to be a credible option for hydrogen mitigation in nuclear containments. The passive operation, versatility and ease of back fitting are appealing for existing stations and new designs. The AECL wet-proofed catalyst has shown superior self-start properties under challenging conditions (cold, condensing atmosphere) and resistance to anticipated poisoning agents. The material is physically robust and unaffected by temperatures up to 1000 K. The capacity in forced convection and natural convection modes has been demonstrated. In forced convection mode self-start is passive and the capacity depends on the capacity (and availability) of the air delivery system. The hydrogen removal capacity in the natural convection mode is sufficient (>100 kg/h feasible) to make a useful contribution to safety margins for hydrogen. As well, convective flow produced by the recombiner was shown to effectively contribute to mixing in stratified mixtures.

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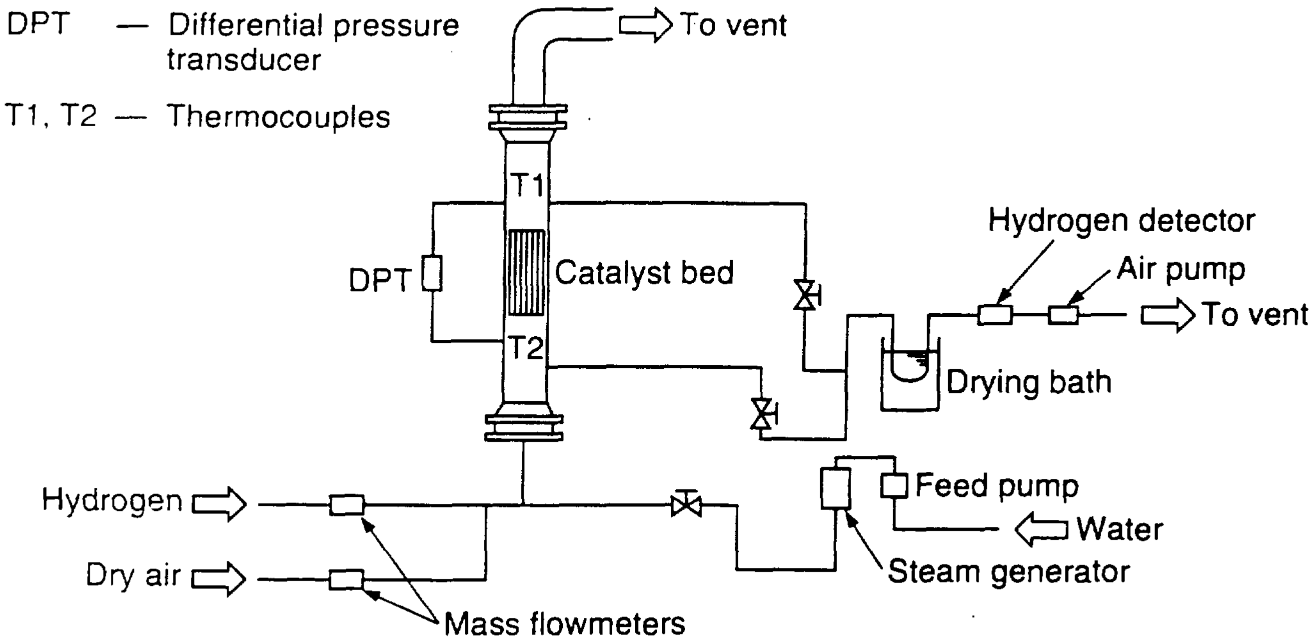

FIGURE 1: Schematic of an Apparatus for Testing the Performance of Cylindrical Catalyst Elements in H_2-Air-Steam Under Forced Convection

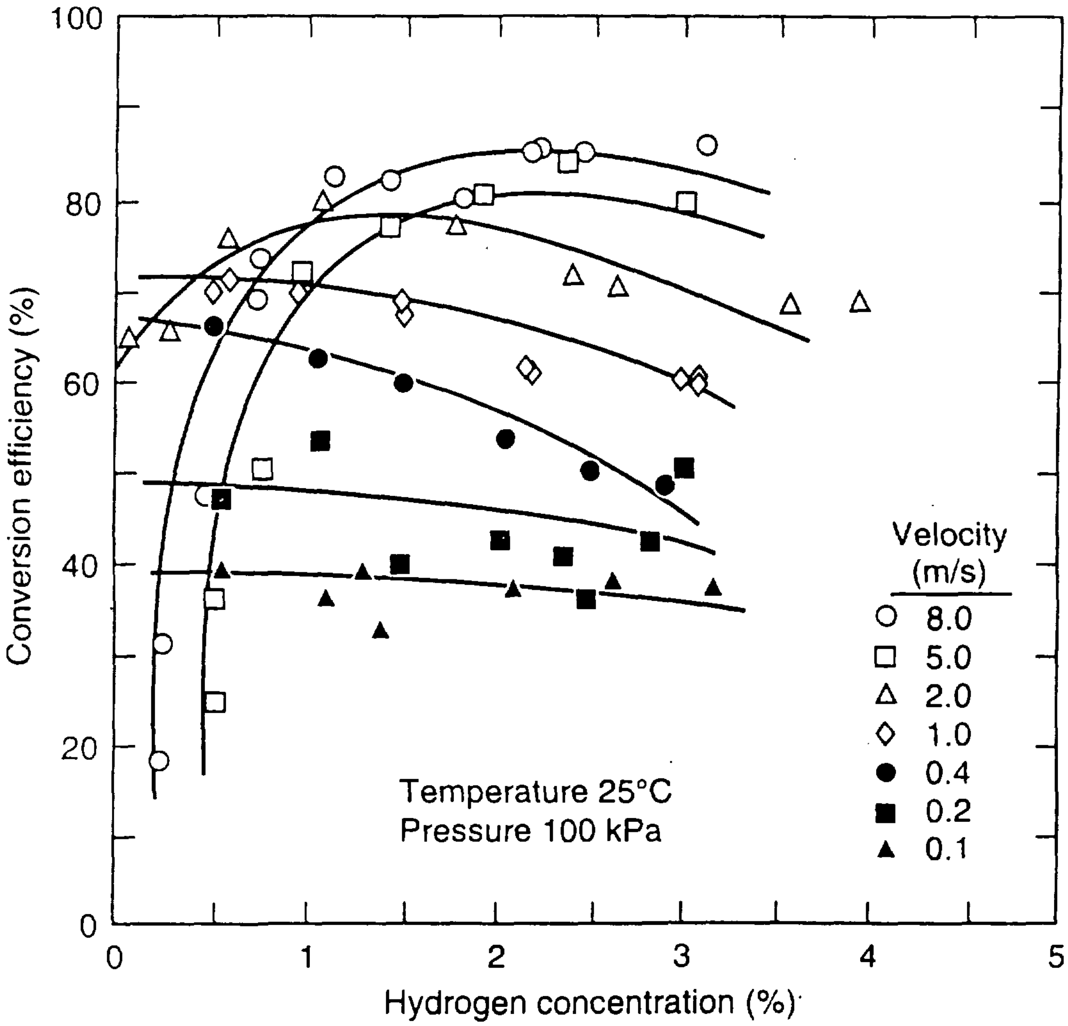

FIGURE 2: Hydrogen Recombination Efficiency of a 100 mm-Deep Catalyst Element Under Forced Convection

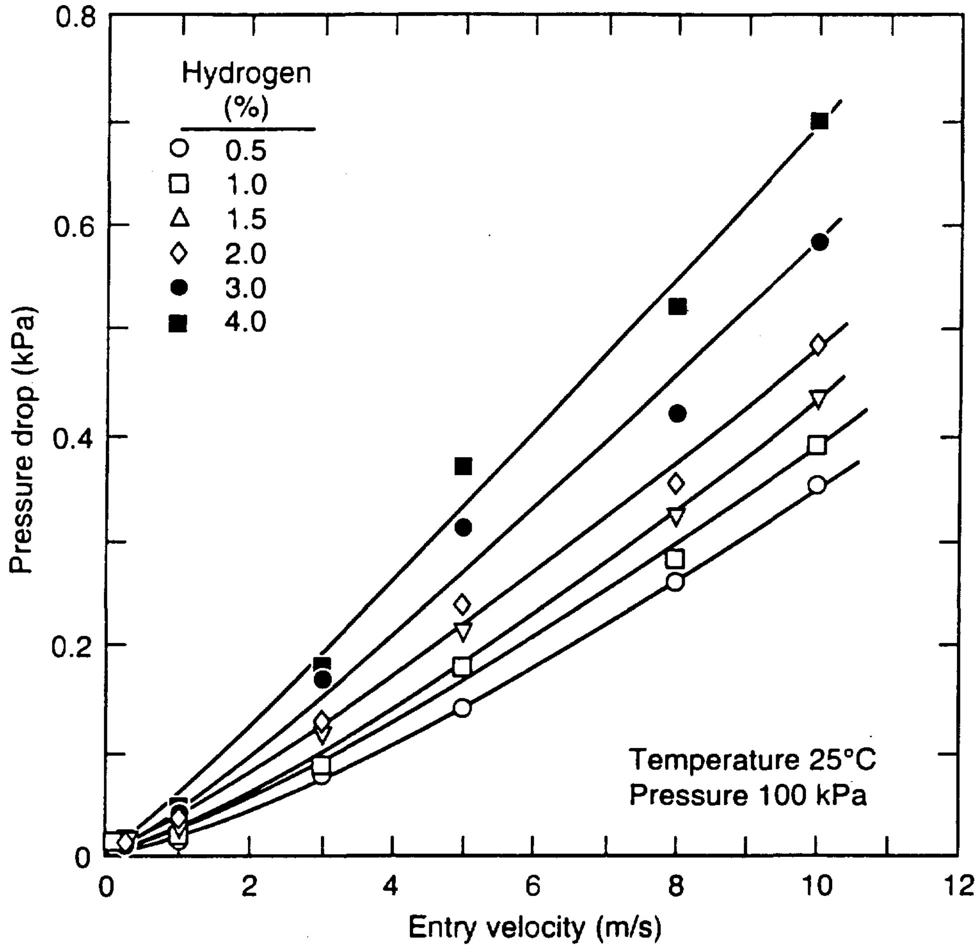

FIGURE 3: Pressure Drop with Forced Convection Across a Catalyst Element with 80% Efficiency for Hydrogen Removal

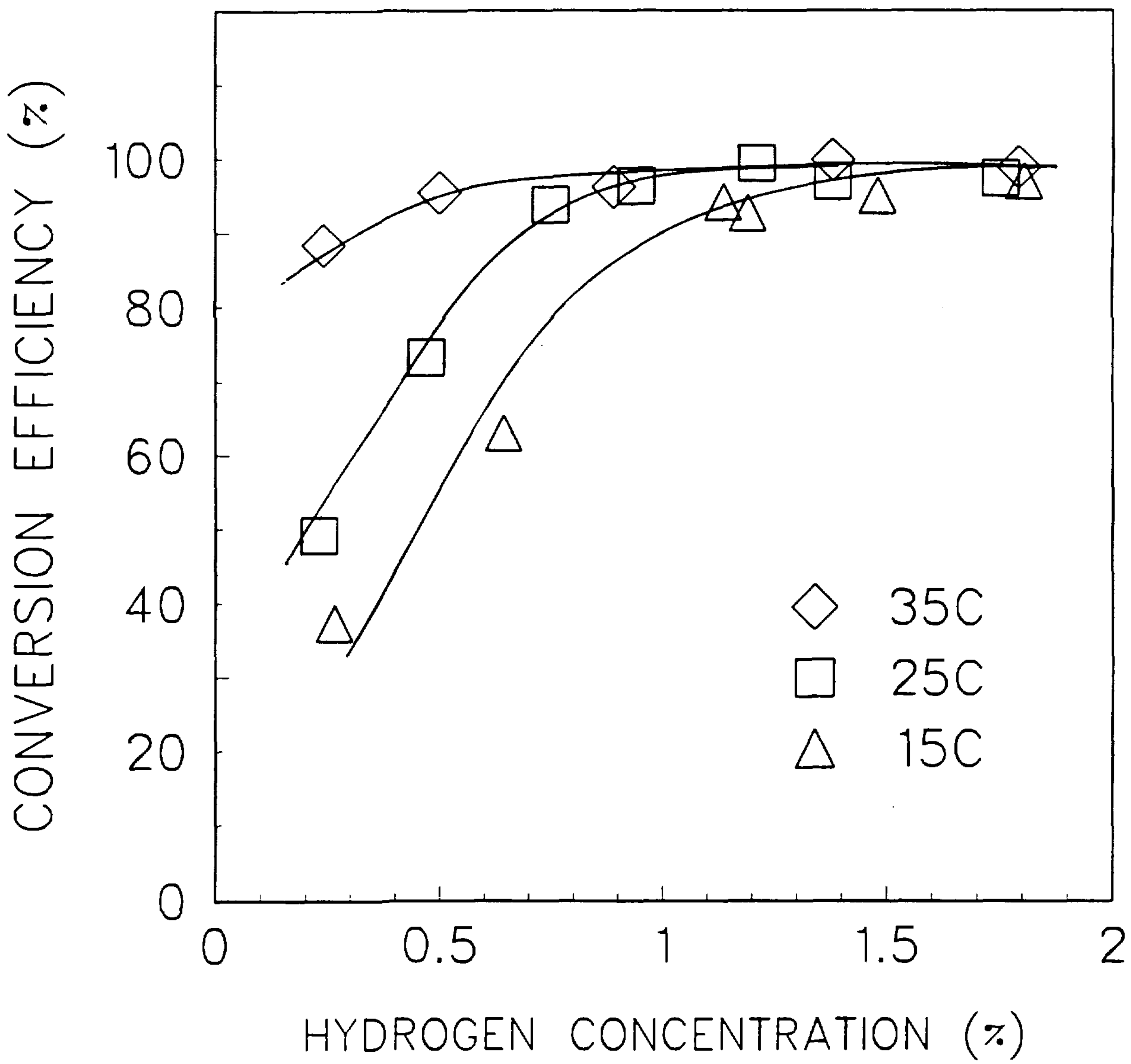

FIGURE 4: Effect of Inlet Gas Temperature on Conversion Efficiency Under Forced Convection (200 mm-deep element, 3 m/s flow velocity)

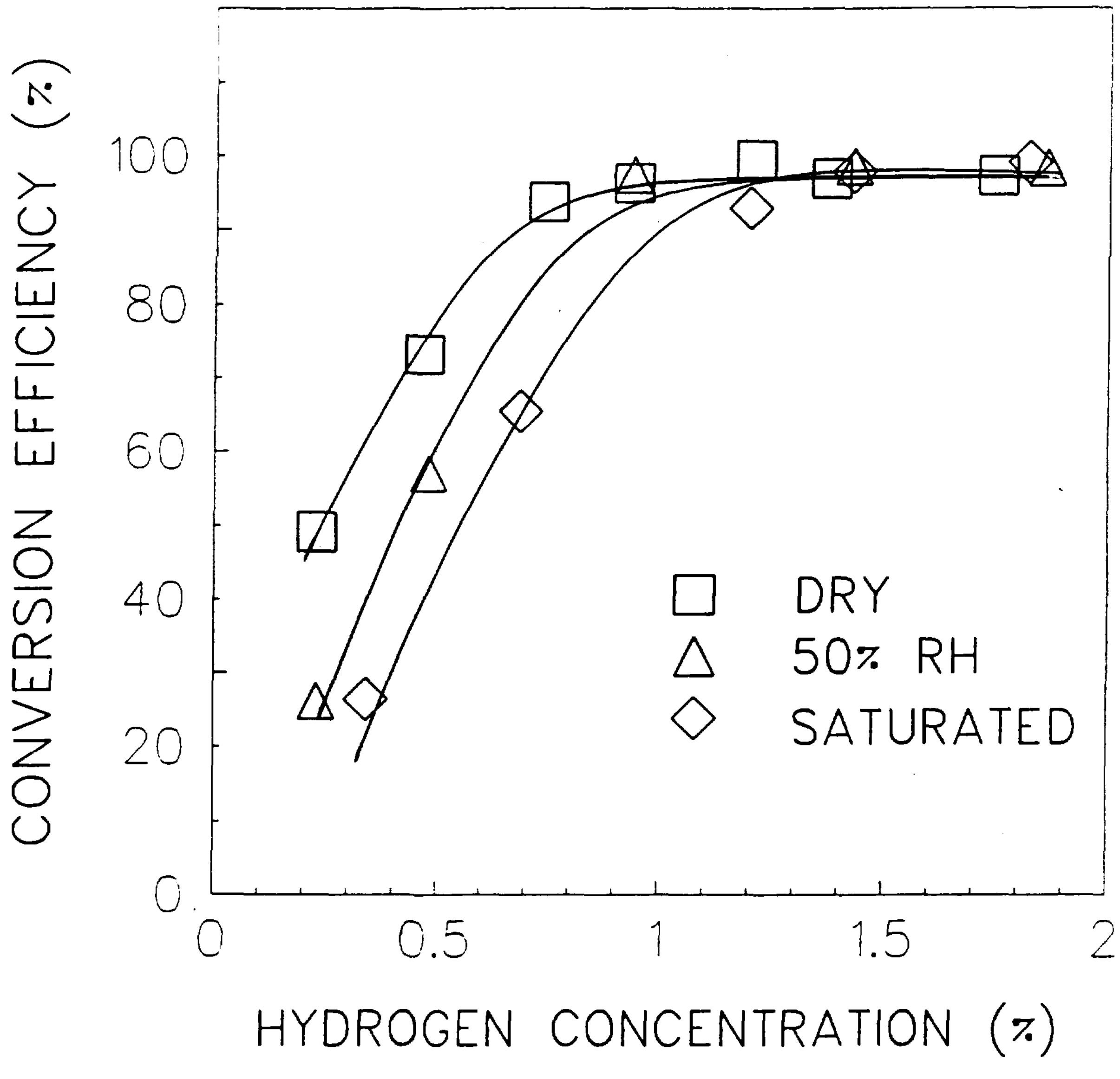

FIGURE 5: Effect of Humidity on Self-Start Under Forced Convection (200 mm-deep element with a 3 m/s flow velocity)

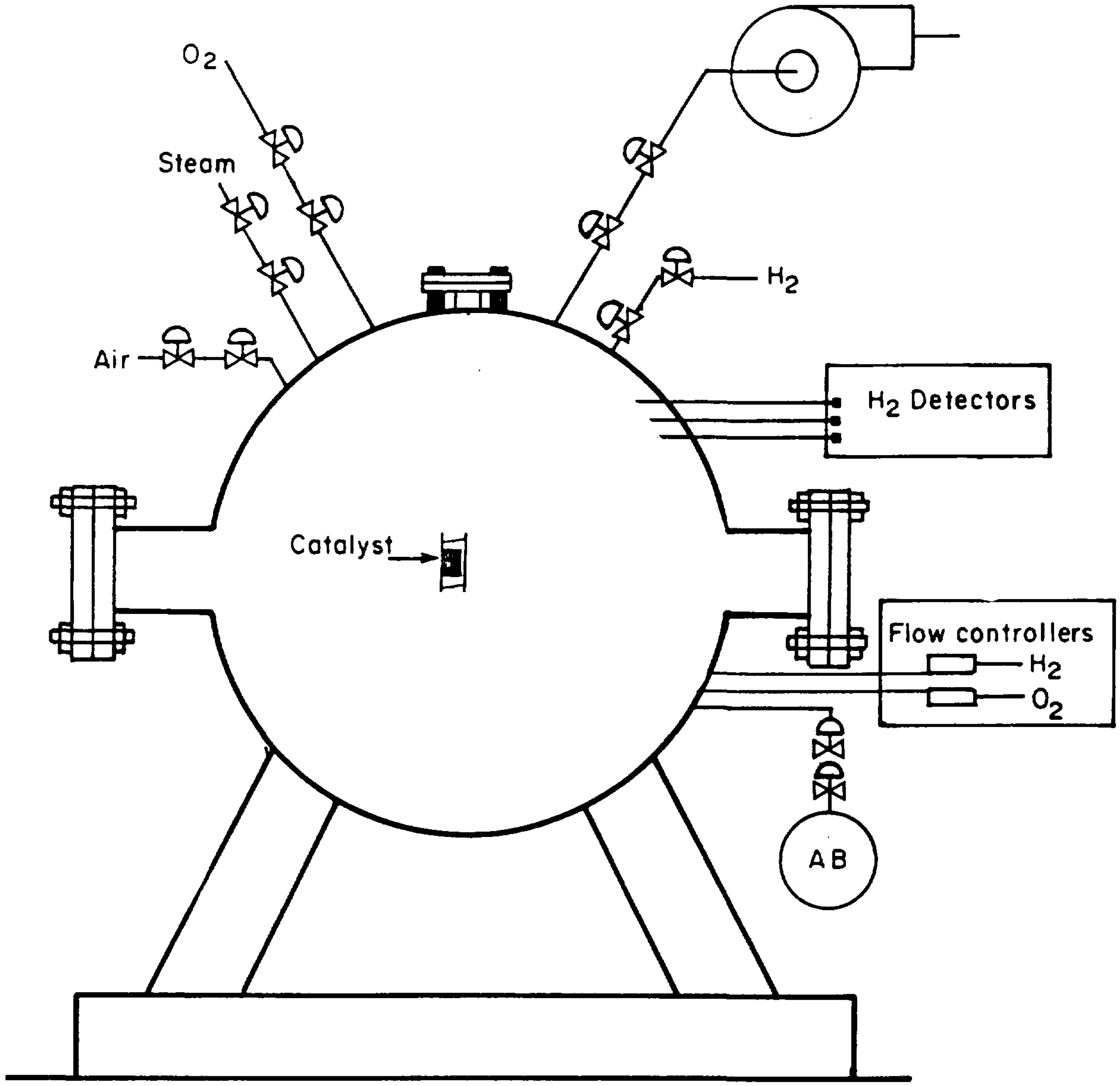

FIGURE 6: The 6.6 m^3 Containment Test Facility (CTF), Configured for Hydrogen Recombiner Tests

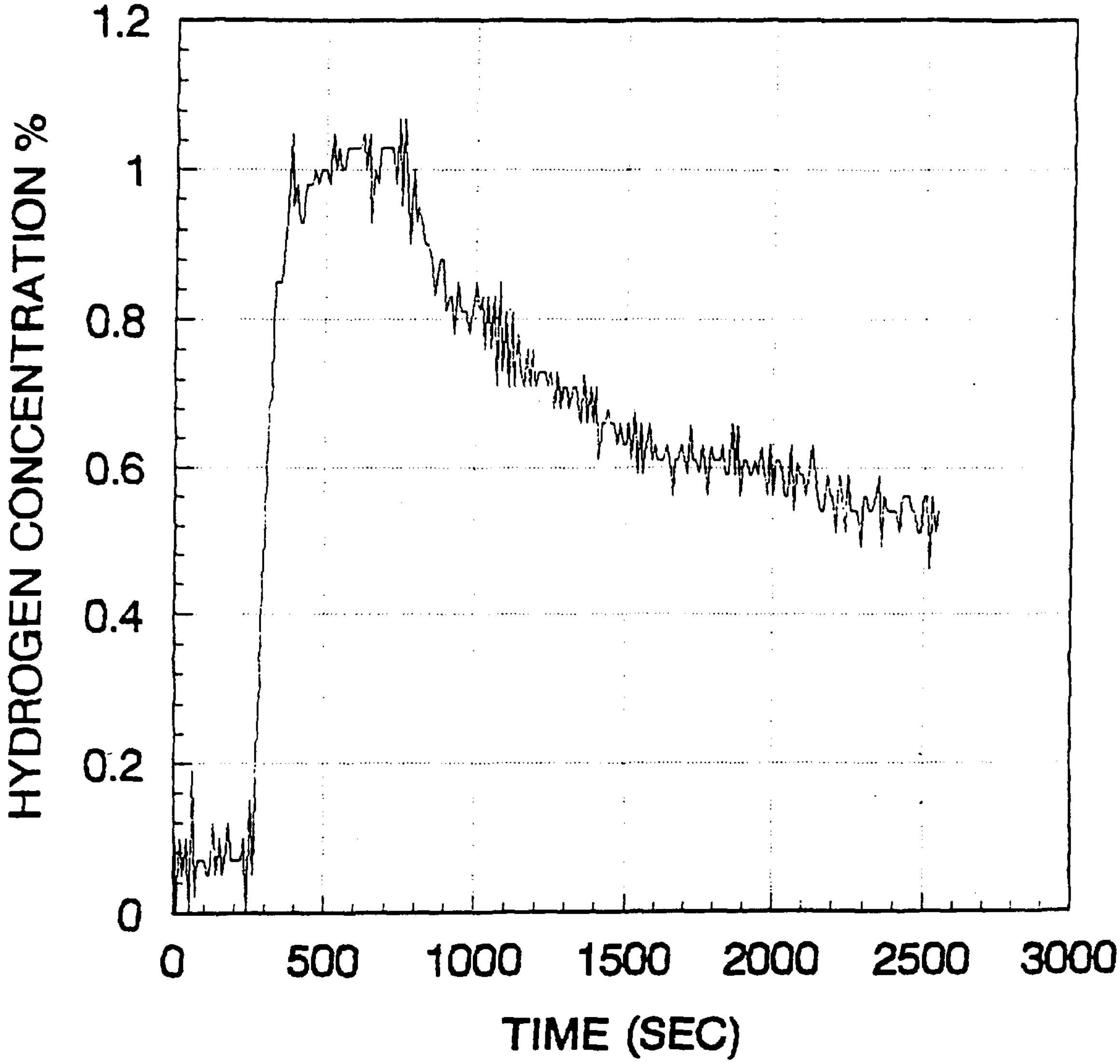

FIGURE 7: Example of Passive Self-Start of Catalytic Recombiner in 1% H_2 at 25°C, 100% R.H. Recombiner opened at 750 s.

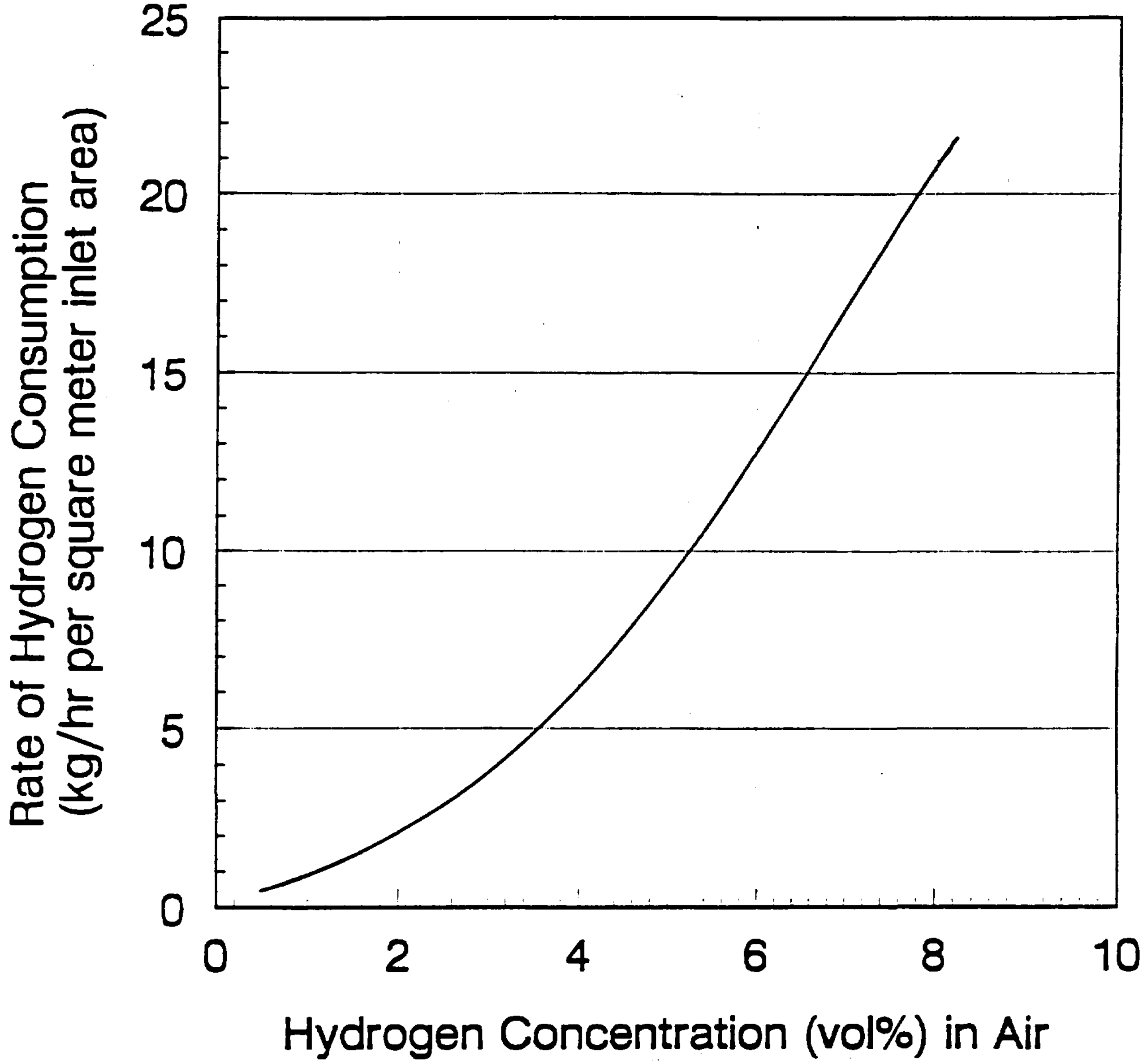

FIGURE 8: Typical Capacity of AECL Catalytic Recombiner Operating in Natural Convection (passive) Mode. Inlet conditions 100 kPa (abs), 25°C, 100% R.H.

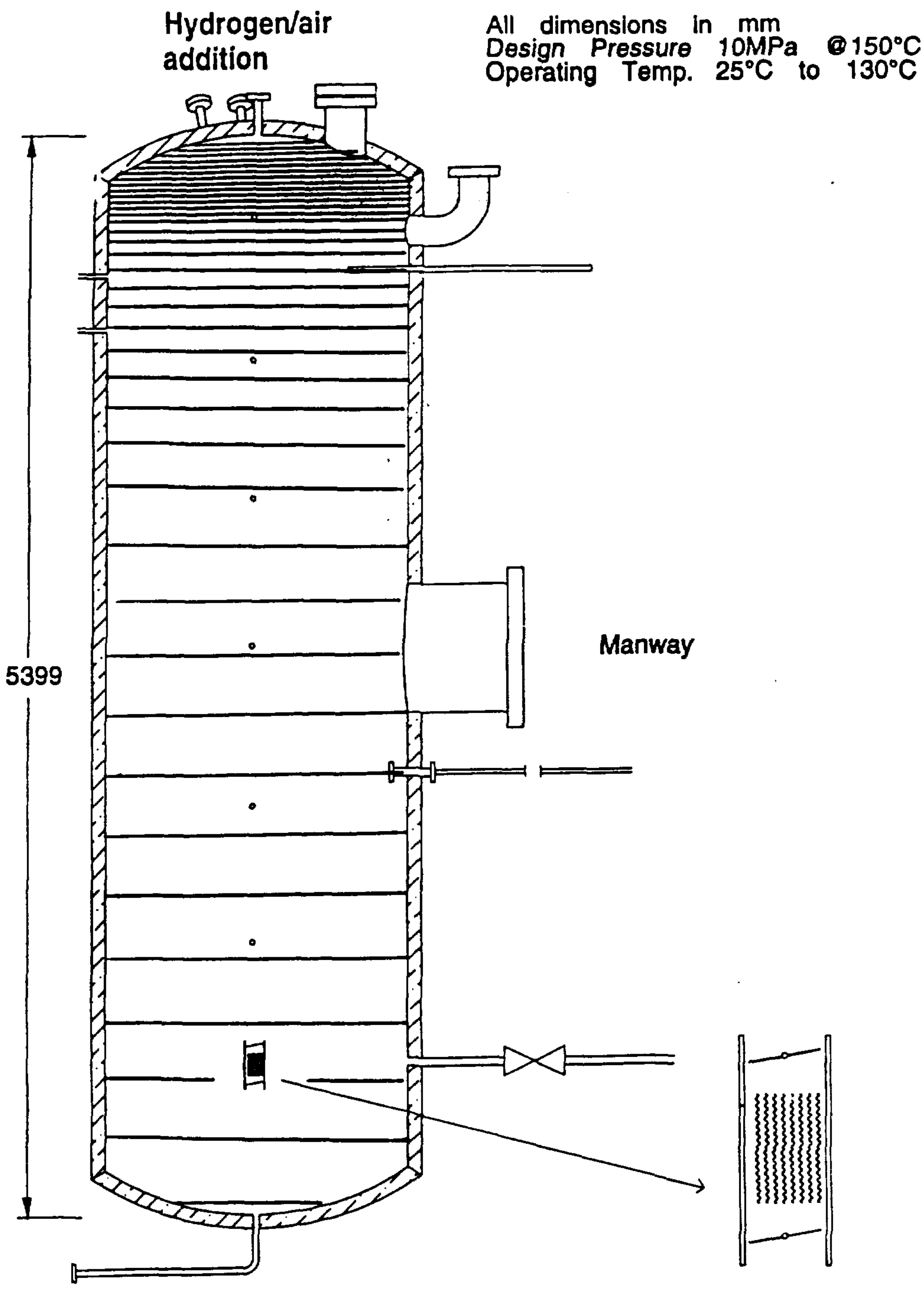

FIGURE 9: The 10.7 m^3 CTF Cylinder Configured for Testing Catalytic Recombiner Performance in Stratified Mixtures

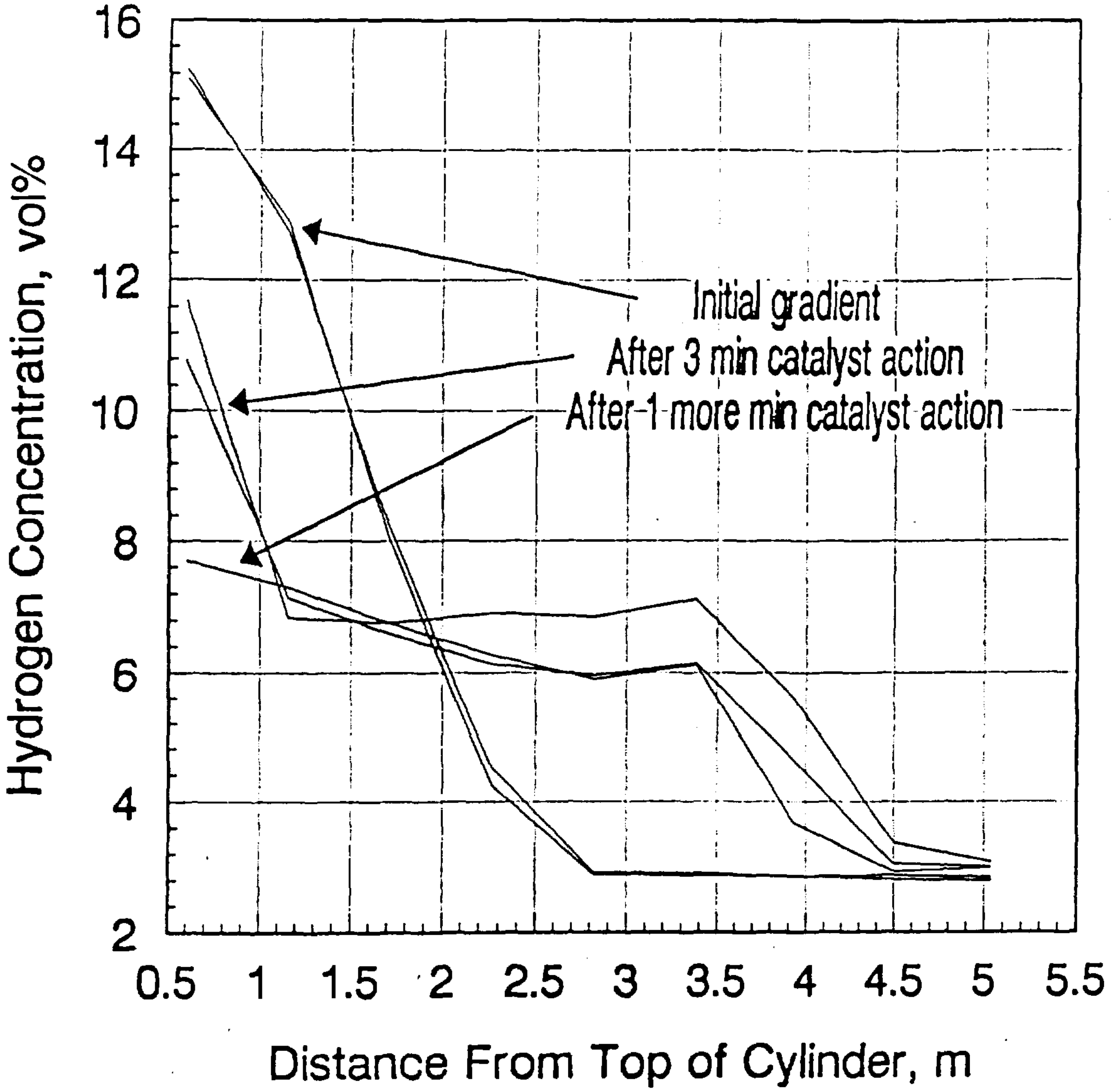

FIGURE 10: Typical Mixing Behaviour in Stratified Mixtures with Catalytic Recombiner Arranged Approximately 1 m from the Bottom as Shown in Figure 9