Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Butler, J. P.(1980) 'Hydrogen Isotope Separation by Catalyzed Exchange Between Hydrogen and Liquid Water', Separation Science and Technology, 15: 3, 371 — 396

To link to this Article: DOI: 10.1080/01496398008068488

URL: http://dx.doi.org/10.1080/01496398008068488

SEPARATION SCIENCE AND TECHNOLOGY, 15(3), pp. 371-396, 1980

HYDROGEN ISOTOPE SEPARATION BY CATALYZED EXCHANGE BETWEEN HYDROGEN AND LIQUID WATER

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ABSTRACT

The discovery, at Chalk River Nuclear Laboratories, of a simple method of wetproofing platinum catalysts so that they retain their activity in liquid water stimulated a concentrated research program for the development of catalysts for the hydrogen-water isotopic exchange reaction. This paper reviews 10 years of study which have resulted in the development of highly active platinum catalysts which remain effective in water for periods greater than a year.

The most efficient way to use these catalysts for the separation of hydrogen isotopes is in a trickle bed reactor which effects a continuous separation. The catalyst is packed in a column with hydrogen and water flowing countercurrently through the bed. The overall isotope transfer rate measured for the exchange reaction is influenced by various parameters, such as hydrogen and water flow rates, temperature, hydrogen pressure, and platinum metal loading. The effect of these parameters as well as the improved performance obtained by diluting the hydrophobic catalyst with inert hydrophilic packing are discussed.

The hydrophobic catalysts can be effectively used in a variety of applications of particular interest in the nuclear industry. A Combined Electrolysis Catalytic Exchange - Heavy Water Process (CECE-HWP) is being developed at Chalk River with the ultimate aim of producing parasitic heavy water from electrolytic hydrogen streams. Other more immediate applications include the final enrichment of heavy water and the extraction of tritium from light and heavy water. Pilot plant studies on these latter processes are currently in progress.

INTRODUCTION

The separation of the isotopes of hydrogen--deuterium from protium, tritium from protium, and tritium from deuterium-- is of great importance to the nuclear industry. Research in this field has been primarily concerned with deuterium-protium separation because of the large quantities of heavy water required for nuclear power reactors fueled with natural uranium and moderated with heavy water. This has been the situation in Canada; the CANada Deuterium Uranium (CANDU) reactor requires 0.85 Mg of D_2O per electrical MW of installed capacity. Although almost all heavy water production today is based on the chemical exchange reaction between water and hydrogen sulfide, the Girdler-Sulfide or GS process, there are a number of other methods of producing heavy water as reviewed recently by Rae (1). In Canada, we have had a continuing program to develop alternative and hopefully better methods for deuterium separation.

As the nuclear industry has developed, however, tritium separation has also become very important. Tritium is formed by neutron capture in deuterium and by the fission of uranium. In heavy water reactors the concentration of tritium in the D_2O gradually increases and eventually the tritium must be removed to reduce the man-rem exposure at nuclear power stations. The aqueous wastes from fuel reprocessing plants and all water cooled reactors also contain appreciable quantities of tritium as HTO. The recovery of tritium from these sources will become necessary to minimize tritium release to the environment, so tritium separation plants will become increasingly common. Fusion reactors, of course, will require tritium separation on a larger scale.

The advantages of separating the isotopes of hydrogen by a process based on the isotopic exchange between hydrogen and water have been recognized for many years (2). However, for an isotope separation process to be efficient, a multistage countercurrent cascade is required, and this necessitates the water being present as liquid. Although effective catalysts have been known for exchange between hydrogen and water vapour, they are characterized by extremely low exchange rates in the presence of liquid water. Stevens' (3) concept of a wetproofed noble metal catalyst, and our subsequent development (4) at Chalk River Nuclear Laboratories (CRNL) of a very efficient hydrophobic platinum catalyst that retains its activity in liquid water, has made the hydrogen-water exchange process a reality. Over the past ten years, we have developed efficient and stable catalysts and have devised processes for specific applications involving the separation of the various isotopes of hydrogen.

HISTORY

Hydrogen-water exchange has long seemed an attractive process for the production of heavy water. The exchange reaction was extensively investigated during the days of the Manhattan Project (5) and was the basis of Canada's first industrial heavy water plant (6) that operated at Trail, B.C., from 1943 until 1956. The process used deuterium exchange between water and an enriched hydrogen stream provided by electrolysis. Deuterium was transferred from hydrogen to water vapour by a catalyst at about 70°C and from water vapour to liquid water in bubble cap trays. The two steps were physically separated in the column because the catalyst was deactivated by liquid water. Because of the complexity and size of the exchange towers, the process proved to be uneconomic, although a somewhat similar plant is still operating in Norway (6).

Later, Becker and co-workers (7) developed a slurry catalyst of platinum on finely divided charcoal. This catalyst was effective in water at very high pressures (about 20 MPa) where the concentration of dissolved hydrogen is appreciable. However, the process also proved uneconomical because of the high platinum inventory and unacceptable losses of the finely divided catalyst.

The development of hydrophobic catalysts at CRNL eliminates many of the disadvantages of these processes. By allowing catalysis to take place in the presence of liquid water, the exchange columns become simple and are reduced in size about 20 fold from those required at Trail. More recently, the Japanese have begun an intensive program to develop their own hydrophobic catalysts (8,9).

MATERIALS AND METHODS

The Separation Reaction

The overall hydrogen-water isotopic exchange reaction involves the transfer of an isotope of hydrogen from hydrogen gas to liquid water, and, for the deuterium-protium separation, is written as:

$$HD + H_2O_{liq} \rightleftarrows HDO_{liq} + H_2. \qquad (1)$$

The separation factor, α, for this exchange reaction is defined in terms of the deuterium to protium atom ratios in the two phases at equilibrium:

$$\alpha = (D/H)_{liq} / (D/H)_{gas}.$$

At low deuterium concentrations, α is equal to the equilibrium constant for the exchange reaction. Separation factors for the various isotopes of hydrogen are given in Table 1 for three temperatures. The values for deuterium-protium were taken from our own direct measurements (10), and those for the other separations

TABLE 1

Hydrogen-Liquid Water Separation Factors

Temperature (°C)	D from H	T from H	T from D
25	3.806	7.00	1.658
45	3.389	5.91	1.584
60	3.140	5.29	1.538

were evaluated from the theoretical data of Bron, et al. (11). The high deuterium-protium separation factor, about twice the value of that for the H_2S-H_2O exchange used in the GS process, makes the H_2-H_2O exchange inherently attractive for heavy water production. Higher recoveries from smaller plants are theoretically possible.

From the earliest stages in the program, we recognized that the overall transfer of deuterium between streams of hydrogen and liquid water over wetproofed catalysts takes place in two consecutive transfer steps. The first reaction involves the catalytic transfer of deuterium from the enriched hydrogen stream to water vapour, and the second corresponds to the transfer from water vapour to liquid as shown in Eqs. (2) and (3):

$$HD + H_2O_{(vap)} \rightleftarrows HDO_{(vap)} + H_2, \qquad (2)$$

$$HDO_{(vap)} + H_2O_{(liq)} \rightleftarrows HDO_{(liq)} + H_2O_{(vap)}. \qquad (3)$$

The catalytic reaction (2) occurs on active catalyst sites while the vapour-liquid transfer reaction (3) occurs on any surface. This latter transfer step is really a condensation-evaporation reaction. Because these reactions occur consecutively, high overall transfer rates for deuterium can only be achieved by maximizing the rates of both transfer reactions. The individual transfer rates have been measured simultaneously in a trickle bed reactor (12), but for simplicity only the overall rate is discussed in this paper.

The Catalyst

Stevens' (3) ingenious idea of wetproofing a noble metal catalyst, enabling it to remain active in liquid water, was a real breakthrough for processes based on the hydrogen-water exchange reaction. For the first time, both transfer steps could proceed rapidly in the same volume in a packed column. This first catalyst was not very active, and its activity decayed in water in a matter of days, but it presented challenging possibilities. A program was initiated in late 1969 at CRNL for the development of more stable and active catalysts as well as a full investigation of the hydrogen-water exchange reaction.

The first catalysts were prepared from commercial vapour-phase catalysts, platinum on γ-alumina, by applying a thin coat of silicone to prevent wetting of the platinum crystallites (2). Subsequently, catalysts were made by depositing platinum on porous polytetrafluoroethylene (13) in an attempt to provide an improved hydrophobic environment for the platinum. A more successful approach has been to deposit platinum on high surface area carbon and to bond the platinized carbon to a variety of column packings or carriers using Teflon as the bonding and wetproofing agent (4). These latter catalysts have proven to be very stable and effective for the hydrogen-water exchange reaction.

To illustrate the wetproofing action of the Teflon, Fig. 1 shows photographs of Pt-C-Teflon catalyst on 6.1-mm rough ceramic spheres, immersed in water and in alcohol. The sample in water shows a silvery sheen on the surface of the spheres resulting from air trapped between the surface of the catalyst and the water. This

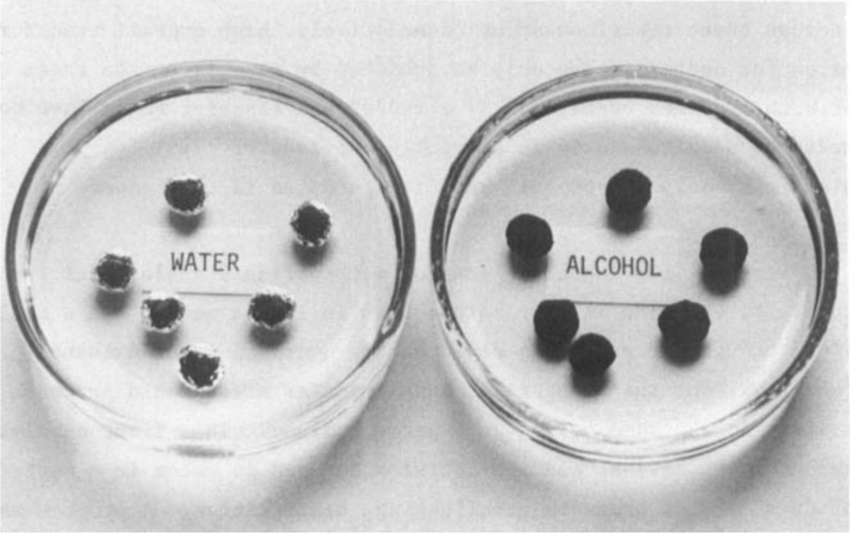

FIGURE 1. Hydrophobic Pt-C-Teflon catalysts in water (left) and alcohol (right).

simple illustration shows that the hydrophobic Teflon layer prevents the wetting of the catalyst surface in water. In contrast, the sample in alcohol appears jet black, and no air sack is observed because the lower surface tension of the alcohol allows complete wetting of the catalyst.

Catalyst Activity

The activity of these wetproofed catalysts for hydrogen-water isotopic exchange is measured in a single pass, trickle bed reactor described in previous publications (12, 14). Water is passed downward through the packed catalyst bed and hydrogen gas, saturated with water vapour, flows countercurrently upward. From the known deuterium (or tritium) concentrations of the water entering the top of the column, and the concentration in the inlet and outlet hydrogen gas, the activity of the catalyst can be measured. The activity is expressed as the overall gas-phase volume transfer rate, K_ya, given in the units $m^3(H_2 \text{ at STP})\cdot s^{-1}\cdot m^{-3}$ (catalyst bed), and is evaluated from the equation:

$$K_ya = \frac{F}{h} \cdot NTU, \qquad (4)$$

where

F = superficial hydrogen flow rate, $m\cdot s^{-1}$ at STP;

h = height of catalyst bed, m;

NTU = number of transfer units in the bed.

The number of transfer units (15) is related to the change in the deuterium concentration in the hydrogen over the length of the column, and for low deuterium concentrations is calculated from the equation

$$NTU = \frac{y_b - y_t}{(y_b - y_b^*) - (y_t - y_t^*)} \cdot \ln \left[\frac{y_b - y_b^*}{y_t - y_t^*}\right], \qquad (5)$$

where

y = the atom fraction of deuterium in the hydrogen gas.

The subscripts t and b refer to the top and bottom of the exchange column, and the superscript (*) denotes the deuterium concentration in the hydrogen in equilibrium with the water. The value of y* is calculated from the exact relation

$$y^* = \frac{x}{\alpha - x(\alpha - 1)} , \qquad (6)$$

where

x = the atom fraction of deuterium in the water.

The relationship for the NTU is an approximation, in that it assumes a mass balance between the liquid and hydrogen streams, and neglects the flow of water vapour in the gas stream. However, at low humidities the error is small, and for short laboratory columns (about 0.3 m) operating at 25°C the error is <1%.

RESULTS AND DISCUSSION

Catalyst Activity

The performance of our catalysts has greatly improved over the years and Table 2 summarizes some achievements. The activity, K_ya,

TABLE 2

Improvement in Catalyst Performance

Catalyst	K_ya $m^3(STP)\cdot s^{-1}m^{-3}$	Rel. Specific Activity
1. Pt-Charcoal, Taylor	0.017	2.0
2. 0.5% Pt-Al_2O_3 Untreated	0.005	1.0
3. 0.5% Pt-Al_2O_3 Silicone treated	0.22	42
4. 0.4% Pt-Porous Teflon	0.20	58
5. 0.4% Pt-C-Teflon	0.58	133
6. 0.1% Pt-C-Teflon	1.05	1920
7. 0.39% Pt-C-Teflon Ordered bed	2.40	2580

for each catalyst is given for standard column operating conditions of 25°C, 1 atm pressure, and a superficial hydrogen flow rate of $1.0\ m\cdot s^{-1}$ at STP. The silicone treated catalyst No. 3 represents Stevens' original discovery. Although the activity is 42 times that of the untreated catalyst, it was still quite low. Platinum on porous Teflon resulted in a more stable catalyst but showed no improvement in activity. Depositing platinum on high surface area carbon and bonding this to a carrier with Teflon (catalyst No. 5) resulted in about a threefold improvement in activity. By mixing the catalyst with hydrophilic packing (discussed in detail later) and increasing the platinum dispersion (catalyst No. 6), the activity was increased by a further factor of 2. This was achieved using only 1/4 the platinum concentration, and the improvement per unit of platinum is 1900 relative to the untreated 0.5% $Pt\text{-}Al_2O_3$. Finally, more active catalysts are prepared by packing a hydrophobic catalyst and hydrophilic material in a column in a specific ordered bed arrangement. The resulting catalyst No. 7 has a specific activity about 2600 times that of the untreated catalyst and 1300 times greater than the catalyst patented by Taylor (16) for this exchange reaction in 1954. Although further improvements in catalyst activity are anticipated, a catalyst with a K_ya about 0.5 is sufficiently active for many of the small scale applications currently being considered for the hydrogen-water exchange reaction.

Mixed Catalyst Beds

With very hydrophobic catalysts, water flow through the column became a problem. To improve water distribution in the bed, the catalyst was mixed with hydrophilic packing, and the effect on the activity is shown in Fig. 2. Catalyst columns containing 50% catalyst and 50% hydrophilic packing had about the same activity as columns containing 100% catalyst. The mixed beds not only had better water distribution but also produced the same activity with only half the amount of catalyst as the 100% beds (17). The use of a mixed catalyst bed represents a considerable cost saving in any commercial application.

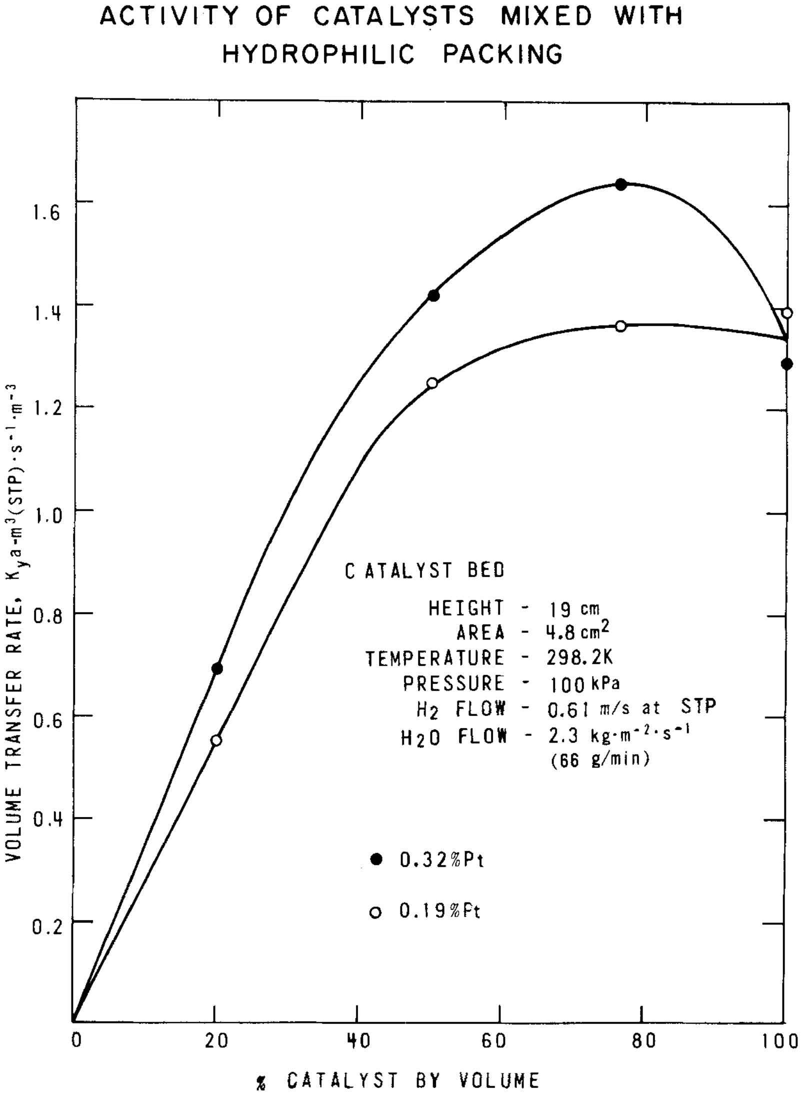

FIGURE 2. The activity, $K_y a$, of Pt-C-Teflon catalysts on 6.1-mm ceramic spheres as a function of dilution with hydrophilic ceramic spheres of the same size.

The explanation for this effect is obvious on considering the two reaction steps involved in the overall transfer of deuterium; the catalytic transfer of deuterium from hydrogen to water vapour, and the vapour-liquid transfer from water vapour to liquid water. The latter rate is increased by the addition of hydrophilic packing, which increases the liquid surface area, and for active catalysts the vapour-liquid transfer was limiting the overall exchange. An extension of this principal has led to the superior performance of the ordered catalyst beds (17).

Column Operation Parameters

Some twenty different parameters affecting catalyst activity have been investigated, but this paper will be limited to parameters affecting column operation. All studies have been done using mixed beds containing 50% by volume catalyst and 50% hydrophilic packing.

The effect of temperature and hydrogen flow rate are shown in Fig. 3 for a 0.37% Pt-C-Teflon catalyst on 6.1 mm ceramic spheres. For this type of catalyst, K_ya increases approximately as the 0.3 power of the hydrogen flow rate in the range 0.05 to 1.4 $m \cdot s^{-1}$. The isotopic exchange reaction here is very fast; for example, at 25°C and a hydrogen flow rate of 1.0 $m \cdot s^{-1}$(STP), $K_ya = 1.2$, and this is equivalent to an equilibration half-time of 0.18 sec. The half-time is calculated using the actual hydrogen flow rate which is 3.1 times the superficial flow rate for this particular catalyst bed assembly (the volume fraction of gas in the operating column is 0.32). The solid points in Fig. 3 were obtained using enriched hydrogen (D/H = 250 ppm), where the deuterium is transferred from the hydrogen gas to the liquid water; the open points were obtained using enriched water (D/H = 1130 ppm), where deuterium is transferred from the liquid water to the hydrogen gas. From the data, no difference can be detected in the rate of deuterium transfer for the net reaction occurring in either direction. The effect of temperature on the activity of the catalyst is also illustrated in Fig. 3. For an increase in temperature from 25 to 60°C, K_ya

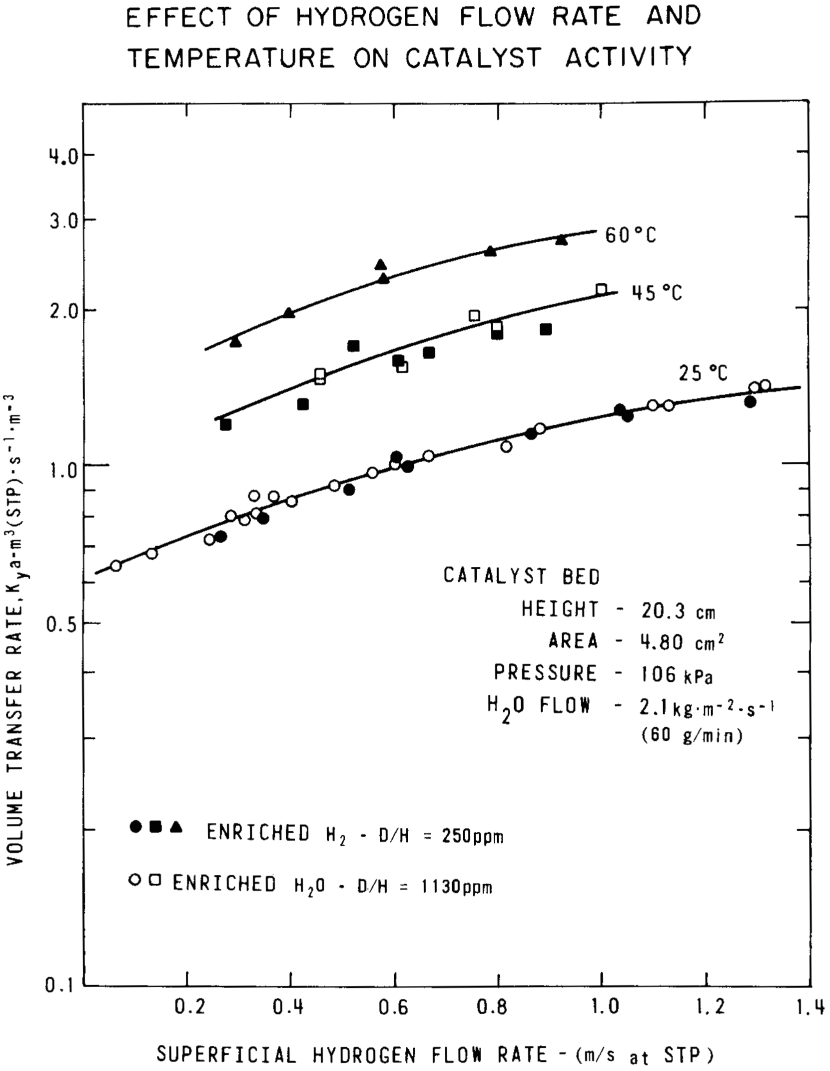

FIGURE 3. Effect of hydrogen gas flow rate and temperature on the activity, K_ya, of a 0.37% Pt-C-Teflon catalyst on 6.1-mm ceramic spheres.

increases by a factor of 2.4. From more extensive measurements, the temperature coefficient of K_ya in the range 15 to 60°C is equivalent to an Arrhenius activation energy of 26 ± 4 kJ·mol^{-1} or 6.2 ± 1.0 kcal·mol^{-1}.

The activity of the catalyst changes only slightly with liquid flow, and Fig. 4 shows the variation in activity of a 0.25% Pt-C-Teflon catalyst over a large range of liquid flow rates and a constant hydrogen flow of 0.56 m·s^{-1}(STP). K_ya increases as the 0.08 power

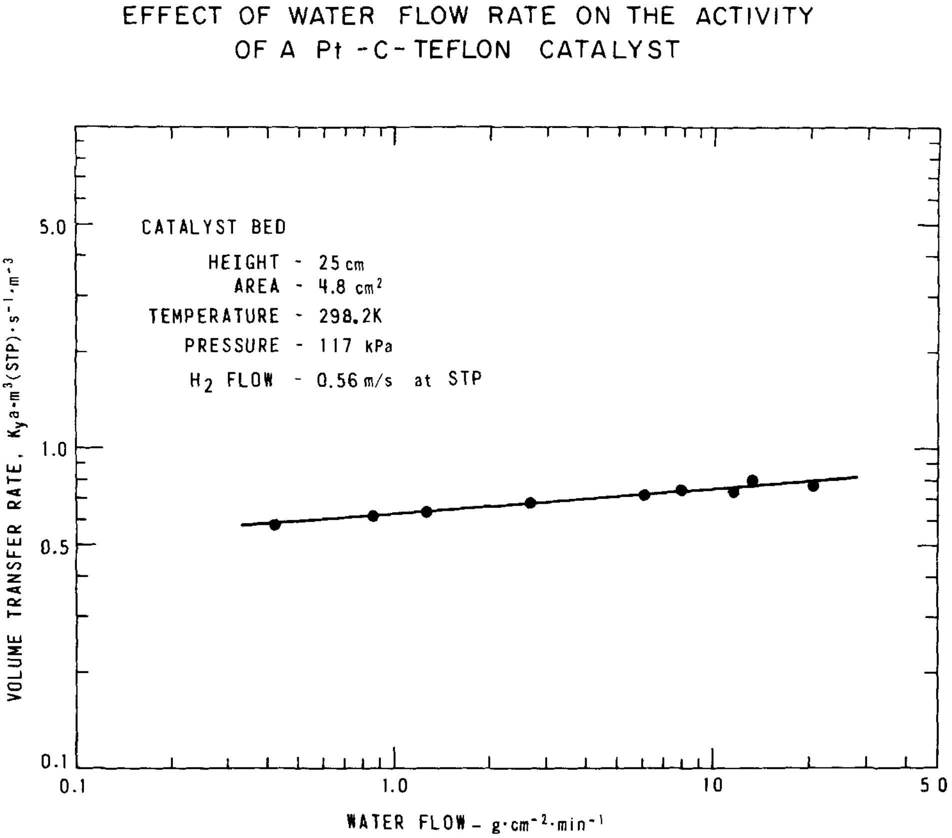

FIGURE 4. Dependence of the activity, K_ya, on liquid flow rate for a 0.25% Pt-C-Teflon catalyst on 6.1-mm ceramic spheres.

of the liquid flow rate. This minor dependence on liquid flow results from increased turbulence in the bed at higher flows and is typical of mass transfer reactions in packed columns.

The effect of system pressure on catalyst activity was first reported by Enright and Chuang (18), and some of their results at different temperatures are summarized in Fig. 5. The activity of the catalyst decreases with increasing pressure, and its power dependence on pressure varied in the range -0.3 to -0.6. The

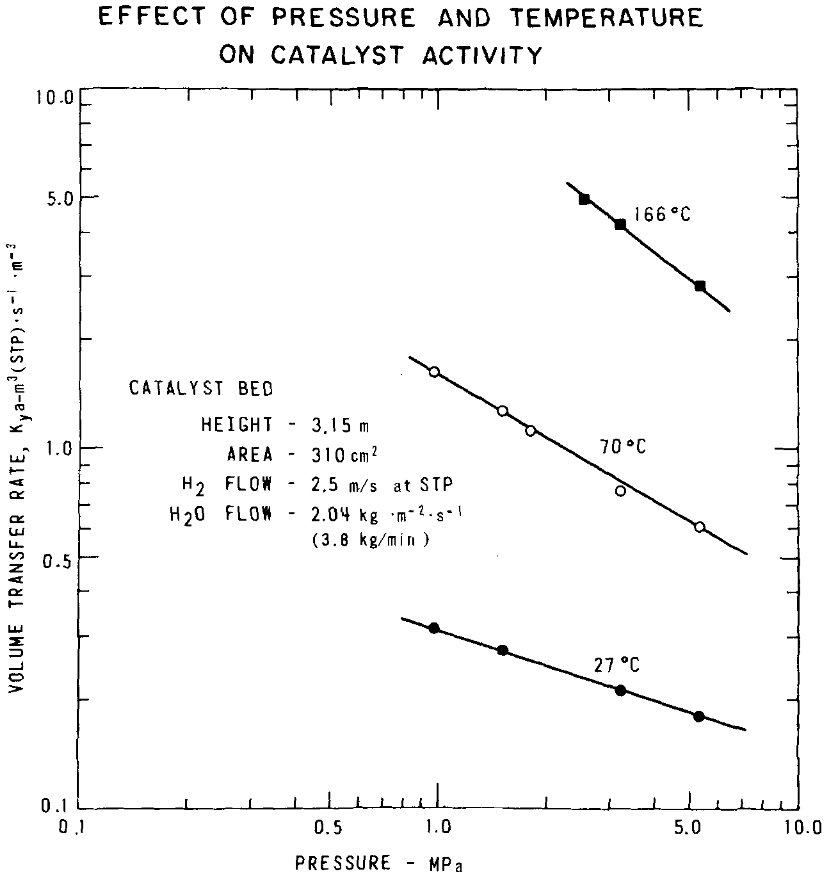

FIGURE 5. Effect of system pressure and temperature on the catalyst activity, K_ya.

higher power dependence is observed at the higher temperatures, where the catalyst activity is greater. More extensive laboratory studies on the effect of pressure in the range 0.1 to 1.7 MPa and temperatures from 25 to 60°C have shown that K_ya decreases as the 0.40 ± 0.05 power of the pressure (19). The power dependence of the pressure and flow parameters are such that, if the linear gas flow at pressure and the liquid to hydrogen molar flow ratio, L/G, are maintained constant for different pressures, then the activity decreases only slightly with pressure. Operating at a constant linear flow at pressure is equivalent to keeping the gas contact time with the catalyst constant. Thus, to minimize the decrease of activity with pressure, it is necessary to maintain a nearly constant linear flow at pressure.

The power dependences of the activity on pressure and gas and liquid flow rates just given are only applicable to mixed catalyst beds for which K_ya is about unity at 25°C, 0.1 MPa and a hydrogen flow rate of $1.0\ m{\cdot}s^{-1}$ at STP. For these catalysts the catalytic rate (reaction 2) and vapour-liquid transfer rate (reaction 3) are approximately equal. When the relative magnitudes of these individual rates differ, the power dependences will vary somewhat from the values reported here.

Platinum Metal Area

The effect of platinum metal surface area on the activity of the catalyst is shown in Fig. 6, where K_ya is plotted against the platinum metal surface area, measured by hydrogen chemisorption, and expressed as m^2 per cm^3 of packed bed. Although K_ya increases with metal area, the increase is not directly proportional to the area. For metal areas below $0.06\ m^2{\cdot}cm^{-3}$, K_ya increases as the 0.75 power of the metal surface area and at higher metal areas the rate of increase is less. The curve appears to be approaching a maximum value. These results indicate that the vapour-liquid transfer rate, which is unaffected by increasing the platinum metal area, is seriously limiting the overall exchange reaction at the higher metal loadings.

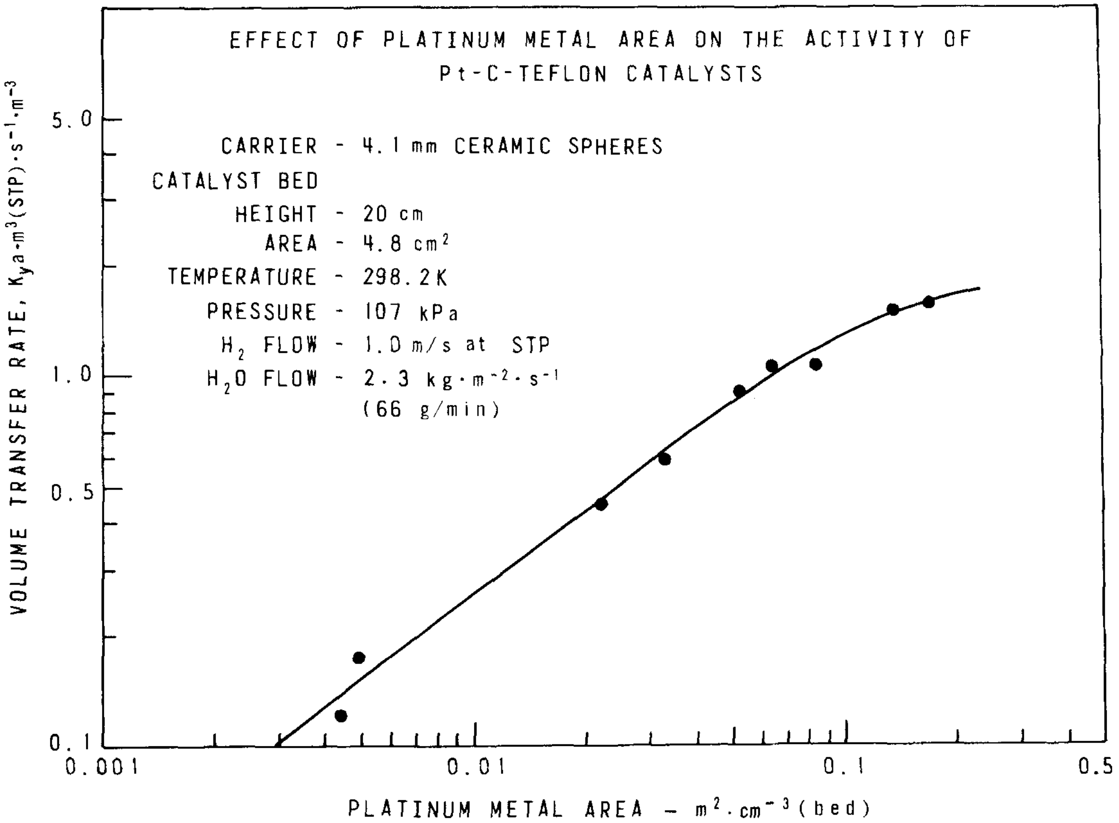

FIGURE 6. Dependence of the activity, K_ya, on the platinum metal area of Pt-C-Teflon catalysts.

Catalyst Stability

For the catalyst to be used commercially, it must be stable and have a long lifetime. Catalyst performance in columns has been studied for extensive periods, and one single charge of catalyst has been tested for 550 days. Figure 7 shows the results of such a lifetime study for two hydrogen flow rates, a high flow of 1.0 $m \cdot s^{-1}$ and a low flow of 0.20 $m \cdot s^{-1}$. After the initial run-in period the catalyst was stable and for some extended periods of time, up to 70 days, no measurable change in activity was observed. Over 170 days of continuous operation the activity decreased by only 13%, which is equivalent to a catalyst half-life longer than two years.

All our data on catalyst lifetime now suggest that there is no intrinsic decay of catalyst activity due to waterlogging or some other problem basic to the catalyst. All changes in activity seem

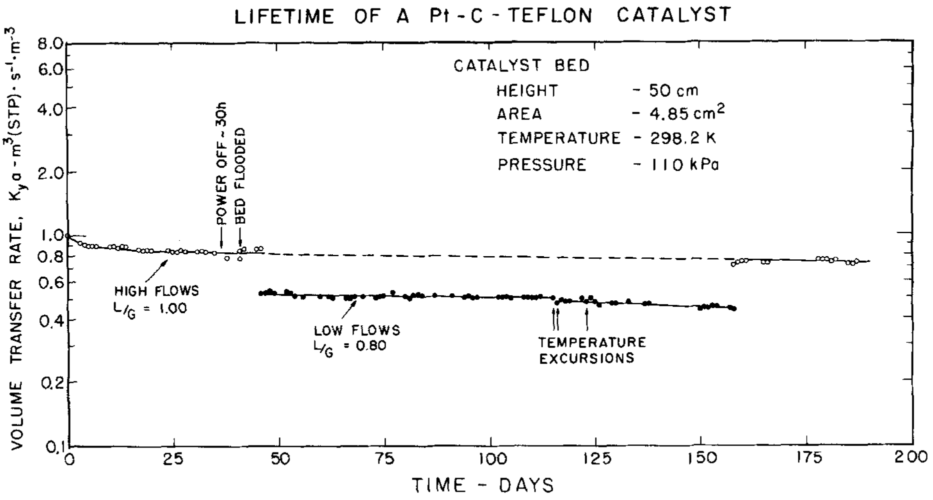

FIGURE 7. Lifetime of a 0.2% Pt-C-Teflon catalyst at high and low liquid and gas flow rates,

○ H_2 flow 1.0 $m \cdot s^{-1}$(STP), H_2O flow 0.80 $kg \cdot m^{-2} \cdot s^{-1}$

● H_2 flow 0.20 $m \cdot s^{-1}$(STP), H_2O flow 0.13 $kg \cdot m^{-2} \cdot s^{-1}$.

to result from operational upsets or contaminants in the feed supplies.

The catalyst can be rapidly poisoned by contaminants which are strongly adsorbed on platinum, such as carbon monoxide. However, it can be easily regenerated, in situ, by heating in air. We have never encountered a catalyst that could not be regenerated to at least 85% of its original activity. Extensive studies indicate that, with periodic regeneration, the catalyst should remain active for many years if the purity of the hydrogen and water feeds are carefully controlled.

The Combined Electrolysis Catalytic Exchange (CECE) Process

The original purpose of this research was to develop an alternative to the GS process for the production of heavy water. Although active and stable catalysts have been prepared, our standard catalysts are not yet sufficiently active to make a bithermal hydrogen-water exchange plant economically competitive with the GS process. The volume of the exchange columns and the cost of the catalyst are, as yet, too great. Additionally, little work has been done on the development of a catalyst suitable for hot tower operation. However, very efficient hydrogen isotope separation can be accomplished by coupling a catalyst exchange column to the hydrogen stream from an electrolysis cell. This Combined Electrolysis Catalytic Exchange (CECE) process is reviewed in detail by Hammerli and coworkers in several papers (20, 21, 22), and it will be discussed briefly later. Because the separation factor, α, for the hydrogen-water exchange is higher than that for the GS system, a much higher recovery of deuterium from natural water is possible, 70% for the CECE process compared to 19% for GS. The higher recovery means that lower water and gas flows are required in the plant and, with the very active catalysts that have been developed, the exchange columns will be quite small. Although most of the separative work is accomplished in the exchange columns, their volume would only be about 10% of the exchange volume in current GS plants, for the same production of heavy water.

Before discussing applications of the CECE process, it is worth mentioning that the production of heavy water by this process also involves the production of large quantities of hydrogen and oxygen. Both hydrogen and heavy water have considerable commercial value. If hydrogen becomes a significant source of portable energy, as is being suggested, then the CECE process should become a major source of heavy water in the future.

Applications of the CECE Process

Although large scale production of heavy water by the CECE process is not yet seriously being considered, a number of small scale applications important to the nuclear industry are currently feasible, and these are summarized below.

Deuterium Enrichment

1. Upgrading of D_2O. Heavy water at CANDU power stations that has become downgraded with light water to as low as 1% can be re-enriched to reactor grade, 99.8% D_2O, by the CECE process.
2. On-line moderator upgrading. The moderator of operating reactors could be continually upgraded by the CECE process to a higher deuterium concentration, say 99.9% D_2O. This would significantly improve neutron utilization in CANDU power reactors.
3. Final enrichment in GS plants. The GS process produces 10 to 20% D_2O which is currently enriched to reactor grade by water distillation. We estimate this can be done more economically by the CECE process.
4. Small D_2O plant. A small (20 to 100 Mg/a) D_2O plant would be feasible where a market exists for both the heavy water and the large amounts of electrolytic hydrogen produced.

Tritium Recovery

1. Tritium extraction from D_2O. Tritium builds up in the heavy water in CANDU reactors. The recovery of this tritium would reduce the radiation hazards for reactor operators (23) and may become environmentally desirable in the future.

2. Tritium recovery from light water. Tritium can be recovered from light water wastes from reactors and from plants operated by Department of Energy contractors in the U.S.A. Pilot plant studies of the CECE process for tritium recovery have been in progress at Mound Facility (24) for several years. Tritium recovery will also be required in nuclear fuel reprocessing plants since tritium is a product of the fission process.

A simplified flow diagram of the CECE process for tritium recovery from light water waste is shown in Fig. 8. Waste water containing tritium from a fuel reprocessing plant enters the mid-section of a hydrogen water exchange column. Electrolytic hydrogen containing tritium passes upward through the column and steadily loses tritium to the water flowing countercurrently downward. The water becomes enriched in tritium as it passes down the catalyst

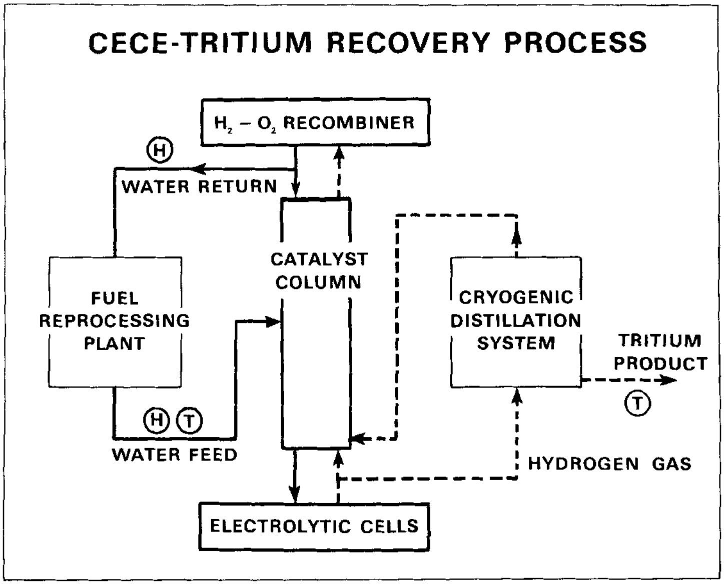

FIGURE 8. A simple schematic flowsheet of the CECE process for the recovery of tritium from waste aqueous streams from a nuclear fuel reprocessing plant.

bed to the electrolysis cell. The stripped hydrogen from the top of the exchange column is recombined with the oxygen and part of the resulting detritiated water is returned to the reprocessing plant while the remainder enters the top of the column as a reflux stream. Final separation of the tritium, as illustrated in Fig. 8, is accomplished by cryogenic distillation of hydrogen, which is the only practical method of concentrating tritium to 99% T_2. Essentially the same system can also be used for the detritiation of heavy water.

Mound Facility (24) personnel are testing the CECE process for tritium removal from light water, using two 7.5 m columns packed with catalyst from CRNL. Because of the very high tritium-protium separation factor, 7.0, they have achieved tritium concentration changes in the hydrogen of greater than 2×10^3 over 7.5 m of column length. The activity of the catalyst under their operating conditions is in good agreement with measurements made in our laboratory. The system has been operated intermittently for over 20 months with no appreciable deterioration in catalyst performance (25).

With slight modifications, the system given in Fig. 8 can be used for upgrading heavy water, and in this application the cryogenic system is not required. The product stream is taken from the enriched water from the bottom of the catalyst column, and part of the water from the recombiner, which has a low deuterium concentration, is discarded as waste.

An engineering test facility using the CECE process for upgrading of heavy water is currently being operated at CRNL (26). Some problems have been encountered with contaminants, but these have been identified and alterations to the test facility are underway to eliminate the problem.

Liquid Phase Catalytic Exchange (LPCE)

An alternative method for tritium extraction from heavy water, using the hydrophobic catalyst, is the Liquid Phase Catalytic Exchange (LPCE) process, first suggested by Dombra (27) at CRNL.

This process uses a catalytic exchange column without an electrolysis cell and is shown schematically in Fig. 9. Heavy water from a reactor, containing protium and tritium, passes down a catalyst column and deuterium gas, depleted in tritium and protium, flows countercurrently upward. Protium and tritium are transferred to the gas stream which then goes to the cryogenic distillation system for separation and enrichment, while the stripped deuterium gas is returned to the catalyst column. The effluent water from the column, stripped of tritium and protium, is returned to the reactor.

This system is attractive because of its simplicity. The electrolysis cell and the H_2-O_2 recombiner of the CECE process are not required. It has the added advantage that tritium at high concentrations is only handled in the elemental form, which is much less hazardous to health than tritium as oxide. In the CECE process, tritium is concentrated in the liquid phase by a large

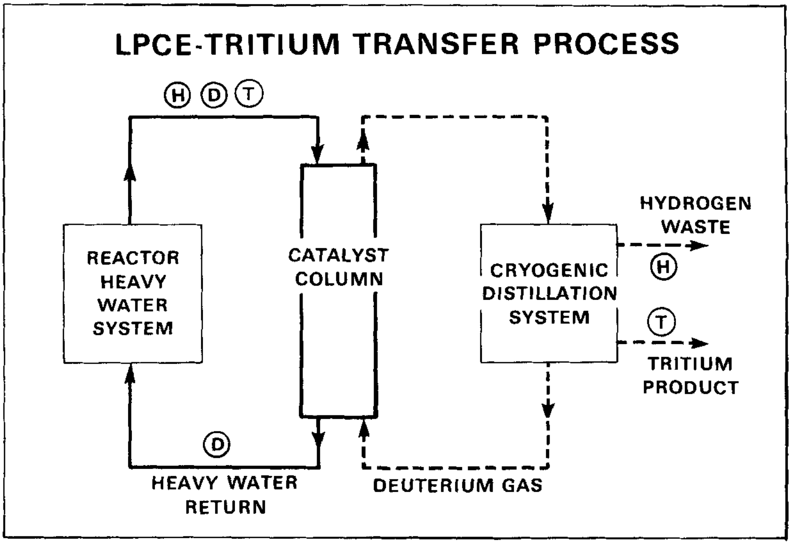

FIGURE 9. A simple schematic flowsheet of the LPCE process for the recovery of tritium from heavy water.

factor, about 100, thus posing a higher health hazard. A disadvantage of the LPCE system, of course, is that tritium is not concentrated in the catalyst column; thus the capacity of the cryogenic distillation unit must be about 100 times greater than in the CECE process.

The catalyst section of the LPCE process is being tested in an engineering facility at CRNL using a column 1.8 m in length (26). The system was operated successfully for five months with light water, separating deuterium from protium. Over this period of continuous operation the catalyst activity was essentially constant, within 15% of that predicted from laboratory studies. Modifications are in progress to study the performance of the system for the separation of tritium from heavy water.

The LPCE process has been chosen for CRNL's proposed demonstration plant for tritium recovery from heavy water. The simplicity of the process and the lower concentrations of tritium oxide were the major factors influencing the choice over the CECE process. The plant will process heavy water from research and prototype reactors owned by Atomic Energy of Canada Ltd. Under steady-state operating condition with a feed flow of 15.7 kg D_2O per hour containing 3.5 Ci of tritium/kg, the plant will recover 0.4 MCi (or 40 g) of tritium per year as 99% T_2. After processing, the concentration of tritium in the heavy water will be reduced to 0.35 Ci/kg. Our present schedule calls for the demonstration plant to be on stream by the end of 1982.

SUMMARY

Hydrogen isotope separation is important for the continuing success of the nuclear industry. Large quantities of D_2O are required for power reactors moderated with heavy water such as the CANDU reactors. The recovery of tritium from reactors and nuclear fuel reprocessing plants is becoming increasingly important to reduce occupational exposures and to minimize the release of radioactivity to the environment.

The development of active and stable hydrophobic catalysts has made the hydrogen-water exchange reaction a simple and effective method for the separation of hydrogen isotopes. This exchange reaction is used most efficiently in the Combined Electrolysis Catalytic Exchange (CECE) process, which couples a hydrogen-water catalytic exchange column to the hydrogen stream from an electrolysis cell. A number of applications of this process for deuterium enrichment and tritium recovery are being studied in engineering test facilities.

The Liquid Phase Catalytic Exchange (LPCE) process offers an alternative method for the detritiation of heavy water. The catalyst column transfers tritium from the liquid phase to deuterium gas which is then passed to a hydrogen cryogenic distillation unit. The simplicity of this system offers some advantages for the separation of tritium from D_2O.

These applications using hydrogen-water isotopic exchange are of immediate interest to the nuclear industry. However, if the predicted demand for hydrogen as the energy source of the future materializes, then the CECE process, which produces both heavy water and hydrogen, should play a significant role in the economy. It is conceivable that a large amount of heavy water may be produced by the CECE process in the future.

ACKNOWLEDGMENTS

The work reported in this paper was only possible with the cooperation of many of my associates at CRNL. In particular, I express my thanks for Drs. W. H. Stevens, M. Hemmerli, J. H. Rolston and K. T. Chuang who have been intimately involved in the experimental program. I also thank my assistants, J. den Hartog and F. W. Molson whose innovative techniques and careful measurements have contributed greatly to the development of active wetproofed catalysts.

Finally, we are most grateful to our colleagues at Mound Facility whose interest in the CECE process has been an encouragement to our development program.

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