Session 14

CARBON-14 AND TRITIUM

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$^{14}$CO$_2$ MONITORING WITH LONG PATH LENGTH INFRARED DIODE LASER ABSORPTION
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CARBON-14 IMMOBILIZATION VIA THE CO$_2$-Ba(OH)$_2$ HYDRATE GAS-SOLID REACTION
G.L. Haag

1,4-DIPHENYL BUTADIYNE AS A POTENTIAL TRITIUM GETTER
H.H. Miller, E.R. Bissell, R.T. Tsugawa, P.C. Souers

1033
Abstract

Long path length infrared tunable diode laser absorption spectroscopy is being developed as a technique for monitoring several low energy beta-decay radioisotopes associated with nuclear waste offgases. We will report a determination of sensitivity for $^{14}$CO$_2$ and an evaluation of potential interferences. Recent experiments have also demonstrated an applicability for measuring iodine isotopes such as H$^{129}$I. Development work will be reported demonstrating the feasibility of also monitoring tritium as TF or TCl.

1. Introduction

For the past three years, the Optical Diagnostics Section of the Chemistry Division at NRL, with support from DoE, has been developing optical methods of monitoring for nuclear waste offgases. These studies have been mainly directed toward measurements of offgases at the DoE Idaho Falls Waste Calcining Facility, and deal with monitoring in near real-time, release levels of $^{129}$I, $^{14}$C, and T.

Reprocessing plants represent a significant potential production source for $^{14}$C. For instance, a production is estimated in the range of 400-2200 Ci of $^{14}$C per year for a LWR fuel reprocessing plant treating 1500 metric tons of heavy metal annually with a range of 40-240 ppb of $^{14}$CO$_2$ in a reference flow of 500 scfm of gas.\(^\text{(1)}\)

Release rates from PWR and BWR stations have been measured to be in the region of 608 Ci/GW(e) year \(^\text{(2,3)}\) In the BWR stations this release is at levels up to several hundred picocuries/cm$^3$ of air.\(^\text{(4)}\) $^{14}$C release from the HTGR reprocessing facility has been evaluated by Snider and Kaye.\(^\text{(5)}\)

At this point no requirements have been issued relating to the monitoring and control of Carbon 14 effluents. A large body of literature\(^\text{(6,8)}\) and studies\(^\text{(9-10)}\) on the environmental impact of $^{14}$C are now available.

*Work supported by the Department of Energy, Nuclear Fuel Cycle Waste Management Division, and by the Naval Research Laboratory.
Current Carbon-14 Monitoring Methods

A carbon-14 radioactivity level of 100 pci/cm$^3$ corresponds to a $^{14}$CO$_2$ concentration of $2.3 \times 10^{-11}$ g/cm$^3$ or $3 \times 10^{11}$ molecules/cm$^3$. In air this level of activity corresponds to a concentration of 10 ppb. Therefore, any real time detection technique with practical sensitivity must have routine detection capability in the range of 1-10 ppb. At the present time no such instrumentation exists. The only instrumentation currently available with near real-time capability is conventional infrared spectroscopy. The practical detection limit for these instruments is $\sim$1 ppm. In addition, it is doubtful that this equipment can distinguish $^{14}$CO$_2$ from $^{12}$CO$_2$.

Several scrubbing techniques have been developed with greater sensitivity. The most sophisticated of these systems separates Carbon-14 gaseous compounds with a gas chromatograph and measures them by radio counting. This instrumentation is expensive and too complex for routine use. More typically CO$_2$ is removed from feed streams by scrubbing with bubblers in a dissolving solvent followed by radio counting. This technique is tedious to use, subject to contamination by other radioactive species and has not yet proven effective at below the ppm range.

The most reliable instrumentation for use at the sub-ppm range currently involves use of a fractionating column with nickel catalyst to convert carbon species to CH$_4$ followed by separation by gas chromatography with subsequent analysis by flame ionization detection. This instrumentation has been used to measure Carbon-14 at the 100 ppb level with an uncertainty of a factor of two.

It is apparent that none of the presently available analytical instrumentation is suitable for real time measurement of $^{14}$CO$_2$. Even the best techniques have a sensitivity limit near 100 ppb. The instrumentation is extremely sophisticated, expensive, and is unlikely to be applicable for routine use for widespread effluent analysis.

II. Experimental

Current techniques involving scrubbing and radio counting or gas chromatographic separation with radio counting or flame ionization detection appear to fall short of the 1-10 ppb limit even with more and more sophisticated adaptations of the instrumentation. For this reason, we chose to concentrate upon optical techniques. Vacuum ultraviolet, visible and conventional infrared techniques were rejected for a variety of reasons. Several infrared laser techniques were evaluated in detail and the scanning infrared diode laser technique was chosen for development.

In order to make analytical measurements with an ultra high resolution source such as the laser diode, several parameters must be known with high precision. These include:

a. Vibrational and rotational line positions in the accessible spectral region;

b. Similar information for all other isotopic species and possible interferents;
c. Absorption coefficients and linestrengths for resonances in the chosen spectral region.

Much of this information is available for $^{14}\text{C}^{16}\text{O}_2$ and other carbon and oxygen isotopic species for CO$_2$. Recently, additional spectroscopic information has become available concerning the spectra of possible interfering gases in the CO$_2$ region of interest. This includes such gases as H$_2$O, N$_2$O, NO$_2$, CO and CH$_4$. This information is important because it allows one to specify the spectral region to cover. The individual laser diodes will scan only over a limited frequency range ($\pm 15$ cm$^{-1}$). With this new information it was possible to make an informed choice of the P-branch line to monitor and thus to specify the diode for purchase.

**Experimental Design**

The laser diode spectrometer is shown in Figure 1.

**Figure 1. Optical Schematic of the Laser Diode Spectrometer**

The frequency of the laser is controlled by temperature and current and, in the case of $^{14}\text{CO}_2$, can be tuned from 2200 cm$^{-1}$ to 2250 cm$^{-1}$ with a $1 \times 10^{-4}$ cm$^{-1}$ bandwidth. The light is collimated by a lens and can then be sent through an etalon (which provides a relative frequency standard) or a reference gas cell (which provides absolute frequency standards). It then enters a sample chamber or a 100 meter White cell. The White cell is simply a 100 pass system, 1 meter in length, providing a total path length of 100 meters in order to enhance sensitivity. The total hold up volume is 12 liters. The beam then enters a monochromator to isolate one laser mode and finally is detected by a In:Sb solid state detector.

Gas handling is provided by conventional vacuum manifolds and pressures are measured by Baratron Capacitance Manometer.

It has been shown by Reid$^{(11)}$ and others$^{(12)}$ that introducing a modulation frequency in the current to the laser allows one to dither the laser frequency about an absorption feature.
Using this technique and detecting the signal with a lock-in amplifier at twice the modulation frequency, a so-called second derivative spectrum can be obtained. This technique results in a dramatic increase in the signal to noise ratio as shown in Figure 2.

![Figure 2](image)

Figure 2. These plots demonstrate three detection schemes for scanning infrared laser diode absorption spectra. The three traces are taken under identical experimental conditions. The dramatic noise reduction in the spectra is apparent with the second harmonic detection scheme.

It should be noted that although the signal in its second derivative mode appears complex, the height of the signal is still proportional to concentration. Table I gives estimates of sensitivities for particular species using this method of detection.

### Table I

**Minimum Detectable Concentration**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Absorption Coefficient of Strong Lines (\text{m}^{-1}\text{ppb}^{-1})</th>
<th>Approximate Wavenumber of Lines (\text{cm}^{-1})</th>
<th>Sensitivity (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)</td>
<td>(3 \times 10^{-6})</td>
<td>1300</td>
<td>0.03</td>
</tr>
<tr>
<td>SO(_2)</td>
<td>(3.5 \times 10^{-7})</td>
<td>1370</td>
<td>0.3</td>
</tr>
<tr>
<td>NO(_2)</td>
<td>(5 \times 10^{-6})</td>
<td>1600</td>
<td>0.02</td>
</tr>
<tr>
<td>NO</td>
<td>(3 \times 10^{-6})</td>
<td>1880</td>
<td>0.03</td>
</tr>
<tr>
<td>CO</td>
<td>(10^{-5})</td>
<td>2120</td>
<td>0.01</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>(10^{-4})</td>
<td>2350</td>
<td>0.001</td>
</tr>
</tbody>
</table>
III. Results

Figure 3 shows a typical absorption trace for 1% $^{14}$CO$_2$, in natural abundance CO$_2$, with the etalon fringe scan superimposed. With this method of detection sensitivity is limited to absorptions on the order of 5% due to S/N constraints and the problem of sloping background.

![Figure 3](image)

**Figure 3.** Spectral absorption scan near 2241 cm$^{-1}$ showing the $^{14}$CO$_2$ R (20) and $^{13}$CO$_2$ P (46) lines. The unlabeled feature near the center of the scan is a $^{13}$CO$_2$ line at 2240.95 cm$^{-1}$. The lower trace shows an etalon fringe scan. The etalon free spectral range is 0.04795 cm$^{-1}$. These fringe patterns are used for wavelength calibration.

Figure 4 shows a scan of a synthetic effluent gas sample with components and percentages corresponding to those analyzed in the effluent from the Exxon Idaho WCF (13). The amount of $^{14}$CO$_2$ is 80 ppb, 800 pci/cm$^3$. The lower trace is a conventional laser diode absorption spectrum. Starred features are due to absorption by N$_2$O. Absorption features due to $^{14}$CO$_2$ are barely observable in this trace. The upper trace is the same spectrum in the second derivative mode. In this case the $^{14}$CO$_2$ feature clearly seen and resolved from surrounding features. During these tests, we have demonstrated that all the N$_2$O features can be removed by first flowing the effluent through a 5% Pt:Pd catalyst at 350°C. The N$_2$O is oxidized to NO$_2$ quantitatively and no absorption features are then detectible which correspond to N$_2$O. In this way a further improvement in $^{14}$CO$_2$ sensitivity is obtained. The presence of the other gases have no effect on the $^{14}$CO$_2$ sensitivity since they have no absorption features in this region.
In these scans, it was found that an additional source of noise was present due to optical "fringing". This comes about because a small fraction of the laser light is reflected back into the laser setting up interference patterns due to the coherent nature of the light. Reid(14) has recently shown that a second modulation frequency with a current amplitude equal to exactly one of these fringe spacings essentially washes out this pattern and results in an additional increase in sensitivity. Using this technique, Reid estimates a sensitivity of 10 ppt of $^{14}$CO$_2$ in a background of natural abundance CO$_2$ with a path length of 1 meter. Initial experiments have been carried out in our laboratory utilizing this technique. Final figures for sensitivity are not available at this time but we estimate an ultimate sensitivity on the order of 0.1 ppt of $^{14}$CO$_2$. It should be possible using instrumentation similar to this and employing the multiple modulation techniques of Reid to routinely monitor concentrations in the few ppt range.

One of the more frustrating problems in the R&D involving scanning diode laser spectrometers is acquiring the laser diodes themselves. Often, operating characteristics are not adequate for making precise measurements such as these. The manufacturer typically has to reject dozens of diodes before selection of a satisfactory one can
be made. This has finally become an area of rapid development, however. The number of laser diode manufacturers has risen from 1 to 3 in the last two years and two Japanese manufacturers are now entering the market. This has already had a positive effect on pricing and hopefully in the near future it will be possible to simply and reliably specify and purchase a laser diode with the desired operating characteristics.

Monitoring Other Isotopes

Since the frequency of the diode laser spectrometer depends on the choice of the laser diode, one can choose the particular regions of interest simply by changing diodes. Because of the ease with which this can be accomplished, the diode laser spectrometer is capable of monitoring several species. Additional diodes are installed in our system to enable us to monitor H129I, TF, and TCl. Figure 5 gives an example of the absorption spectrum of 90% H129I and 10% H127I at a total pressure of 80 mtorr. The arrow corresponds to the predicted position of H131I.

![HI Absorption Spectrum](image)

**Figure 5.** Absorption spectrum of 90% H129I and 10% H127I. The expected position of H131I is labeled.

In this case, the absorptions are not a single line, but are combinations of many different lines due to interactions between the rotational angular momentum of HI and the nuclear electric quadrupole moment of 129I and 127I. It is not warranted to go into this coupling in detail, except to show that the two isotope splittings are well resolved and can be used as a method of detection. Figure 6 shows a similar spectrum for a sample of 2% H129I in H127I. Even at this level of dilution, we have found no interference problems in monitoring H129I.
Since $^{129}\text{I}$ in nuclear waste offgases is predominantly in the form of alkyl iodides, we have developed techniques which allow us to convert alkyl iodides to HI. The alkyl iodide is quantitatively converted to I$_2$ by flowing the sample through a quartz tube maintained at 1150°C. The I$_2$ is trapped on a charcoal bed at room temperature. In order to liberate I$_2$, the charcoal is heated to $\sim$600°C in a flow of H$_2$. This stream passes through a gold catalyst in an alumina furnace maintained at 1000°C. This results in the conversion of H$_2$ + I$_2$ to HI with an efficiency of 35%. Tests to determine the ultimate sensitivity of this method of $^{129}\text{I}$ detection had been scheduled for FY 81.

Figure 7 shows a conventional infrared absorption spectrum of TF. This spectrum is conveniently overlapped by one of the diodes currently being used. Since Tritium occurs mainly in the form of HTO, the tritiated water must be converted to TF. This is conveniently accomplished by reacting HTO with F$_2$O to give TF(HF) + O$_2$. In addition, TCL can be monitored by reacting HTO with SiCl$_4$ to give TCL(HCl) + SiO$_2$. Due to the large isotope shift of HF from TF, interferences from the stable isotopes will not be a problem. Tests of other possible interferences and sensitivity for Tritium detection will be undertaken in FY 81.
Conclusion

It is evident that the diode laser spectrometer provides a sensitive, versatile technique to monitor airborne radionuclides in the ppb and lower range. In all the areas discussed, internal reference standards are also available due to nearby absorption features from stable isotopes (i.e., $^{127}$I lines can be used to calibrate $^{129}$I and $^{131}$I concentrations). In all cases, the technique is near real-time, having a sampling rate of, perhaps, one sample every few minutes.

This technique is also attractive since one instrument may be used to monitor a variety of isotopic species without time consuming modifications to the instrument.

Further development work is necessary to determine interference and sensitivities for various isotopes, but the application of long path length diode laser absorption to the detection and monitoring of airborne nuclear wastes is quite promising.
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3. "C-14 Gaseous Effluents from Boiling Water Reactors"
C. Kunz, W. E. Mahoney, and T. W. Miller

4. C. O. Kunz, W. E. Mahoney and T. W. Miller

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DISCUSSION

THOMAS: Would 1-2% water vapor be an interference for analyzing tritium or iodine in this monitor?

BARONAVSKI: No, none at all. The HTO absorption falls totally out of the region of TF, and the HI-129 is no problem. We have already looked at that. We can tolerate up to 10 torr of water. We do not want to run our samples at too high a pressure because of line broadening, as this smears out some of the resolution. Therefore, we always run our samples at about 10 torr, or less. We have put as much as 10 torr of pure water vapor in and we have seen no absorption in any of the regions we have looked at. So, I do not think that is going to be any problem at all.

THOMAS: So you would not have to pretreat your samples to remove any of the water unless they were about 100% relative humidity?

BARONAVSKI: We would pretreat them in terms of reacting the HTO to get TF, if that is what you mean. We would have to do that in order to monitor TF. But other than that, we would not have to pretreat the samples at all.

THOMAS: At what temperature do you operate the cell?

BARONAVSKI: The cell currently is only run at ambient temperature. It can be cooled or it can be heated, but it is a little bit tricky.
Abstract

Although no restrictions have been placed on the release of $^{14}$C, it has been identified as a potential health hazard due to the ease in which it may be assimilated into the biosphere. The intent of the Carbon-14 Immobilization Program, funded through the Airborne Waste Program Management Office, is to develop and demonstrate a novel process for restricting off-gas releases of $^{14}$C from various nuclear facilities. The process utilizes the $\text{CO}_2$–$\text{Ba(OH)}_2$ hydrate gas-solid reaction to directly remove and immobilize $^{14}$C. The reaction product, $\text{BaCO}_3$, possesses both the thermal and chemical stability desired for long-term waste disposal. The process is capable of providing decontamination factors in excess of 1000 and reactant utilization of >99% in the treatment of high-volumetric, airlike (330 ppm $\text{CO}_2$) gas streams.

Experimental studies have been conducted on fixed and fluidized beds of $\text{Ba(OH)}_2$ hydrates. For these studies, commercial-grade $\text{Ba(OH)}_2$$\cdot$$\text{H}_2\text{O}$, $\text{Ba(OH)}_2$$\cdot$$5\text{H}_2\text{O}$, and $\text{Ba(OH)}_2$$\cdot$$8\text{H}_2\text{O}$ and analytical-grade $\text{Ba(OH)}_2$$\cdot$$8\text{H}_2\text{O}$ have been examined. Studies at ambient conditions have indicated $\text{Ba(OH)}_2$$\cdot$$8\text{H}_2\text{O}$ to be the active species. Therefore, process operating conditions will likely be required which favor the formation of $\text{Ba(OH)}_2$$\cdot$$8\text{H}_2\text{O}$. The dissociation water vapor pressure for $\text{Ba(OH)}_2$$\cdot$$8\text{H}_2\text{O}$ at 25°C is 1.10 kPa (8.26 mm Hg). Although both commercial- and analytical-grade $\text{Ba(OH)}_2$$\cdot$$8\text{H}_2\text{O}$ have been found to be reactive toward $\text{CO}_2$, they are considerably less reactive than either $\text{Ba(OH)}_2$$\cdot$$\text{H}_2\text{O}$ or $\text{Ba(OH)}_2$$\cdot$$5\text{H}_2\text{O}$ which have been hydrated to $\text{Ba(OH)}_2$$\cdot$$8\text{H}_2\text{O}$. We have observed that during the fixed-bed treatments of humidified-air gas streams, the two reactants undergo a conditioning period during which the $\text{CO}_2$ removal efficiency of the bed dramatically improves. However, this activation step is accompanied by a twofold increase in bed volume and degradation of the reactant particles. The resultant bed is extremely active for $\text{CO}_2$ removal, but gas throughput is restricted because of increased pressure-drop problems. For the operation of a fluidized bed, this would likely not present a problem. However, because of the many merits of the simpler fixed-bed concept, considerable effort has been directed toward reducing the magnitude of the pressure drop problem. Recent experimental results have indicated that for the treatment of an air-based off-gas stream, packed beds of commercially available $\text{Ba(OH)}_2$$\cdot$$8\text{H}_2\text{O}$ flakes possess acceptable $\text{CO}_2$ removal, bed utilization, and pressure drop properties. Under appropriate conditions, we have observed a pressure drop of 3.64 kPa/m (0.14 psi/ft) at a superficial gas velocity of 13 cm/s.

I. Introduction

In the radiation field which exists within a nuclear reactor, radioisotope $^{14}$C is produced by neutron interactions with $^{14}$N, $^{15}$N, $^{16}$O, $^{17}$O, and $^{13}$C which is present in the fuel, the cladding, and the primary cooling system. (1-9) Although it is a weak beta emitter, $^{14}$C poses a long-term health hazard due to its long half-life of $5730$ yr and the ease with which it may be assimilated into living matter. (10-14)

An appreciable fraction of the $^{14}$C produced would be expected to be converted to gaseous effluent during normal operation of a light-water reactor, extensive fuel element failure, storage of spent fuel, and upon fuel reprocessing. The $^{14}$C would exist as either $\text{CO}_2$ or low-molecular-weight hydrocarbons with the most probable method of treatment being the oxidation of the hydrocarbons to $\text{CO}_2$ and subsequent fixation of the $\text{CO}_2$. Likely $\text{CO}_2$ gas concentrations would range from 10 to 330 ppm with gas flow rates of up to $20 \text{ m}^3/\text{min}$ ($700 \text{ ft}^3/\text{min}$) anticipated. Expected release rates from various nuclear facilities are presented in Table I.

<table>
<thead>
<tr>
<th>Table I. Approximate production and release rates of $^{14}$C in the Nuclear Fuel Cycle(2)</th>
</tr>
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<tbody>
<tr>
<td>Nuclear Reactors</td>
</tr>
<tr>
<td>LWR</td>
</tr>
<tr>
<td>CANDU</td>
</tr>
<tr>
<td>Reprocessing Plant</td>
</tr>
<tr>
<td>LMFBR</td>
</tr>
<tr>
<td>LWR</td>
</tr>
<tr>
<td>HTGR</td>
</tr>
</tbody>
</table>

For the removal and fixation of $^{14}$C in selected off-gas streams at nuclear facilities, we have established the following criteria with respect to process development. First, the process removal efficiency must be consistent with or greater than anticipated NRC release criteria. Second, the final product must be an acceptable form for final waste disposal. Third, the process must possess excellent on-line reliability characteristics. Fourth, it is desirable that the process operate at ambient conditions. Fifth, maximum process costs should not exceed $\$100-200/\text{man-rem}$.

II. Suggested Technologies for $^{14}$CO$_2$ Control

Suggested technologies for $^{14}$C control have generally followed commercially available technology for $\text{CO}_2$ control. The processes range from $\text{CO}_2$ absorption in amine-bearing solutions to physical adsorption on molecular sieves to chemical reaction with a NaOH solution and carbonate interchange with $\text{Ca(OH)}_2$, the double alkali process. (15) However physical absorption, adsorption, and reaction with NaOH solution share a common trait in that they are $\text{CO}_2$ removal processes, but they do not chemically fix the $\text{CO}_2$ for final disposal, a requisite for the disposal of nuclear waste. Therefore, suggested technologies for the treatment of dilute $\text{CO}_2$-bearing gases have generally employed a removal or an enrichment step to increase the $\text{CO}_2$ gas concentration, followed by a final fixation step whereby the
CO₂ is reacted with Ca(OH)₂ slurry.\(^{15-20}\) The product, CaCO₃, possesses excellent thermal and chemical stability, making it suited for long-term waste disposal (thermal decomposition at 825°C and water solubility of 0.0153 g/L at 25°C).\(^{21}\) However for the treatment of high-volumetric, low-CO₂-content gas streams, this process suffers severely as an enrichment step is required to restrict the overall size of the Ca(OH)₂ slurry reactor. Other areas of concern with this technology are the generation and recycle of aqueous wastes and the need for solid-liquid separation equipment.

For the treatment of a high-volumetric, dilute CO₂-bearing off-gas stream, many potential advantages could be realized if a suitable technology utilizing a gas-solid reaction for \(^{14}\)C removal and fixation existed. However, widely acceptable CO₂ sorbents such as ascarite (NaOH on asbestos) and LiOH·H₂O, which has been used extensively for CO₂ control in life support systems, lack sufficient carbonate stability for final waste disposal. Studies in CO₂ removal have been conducted on soda lime [NaOH–Ca(OH)₂ mixture] and baralyme [Ca(OH)₂–Ba(OH)₂ mixture] with reasonable success.\(^{23-28}\) However, the solubility of Na₂CO₃ in the former and poor reactant utilization in the latter make the use of these reactants doubtful. An examination of the carbonate products of potential Group 1 (alkali metals) hydroxides (Table II) indicates that they may be categorically classified as possessing excessive solubility in water for long-term waste disposal. However, the higher-molecular-weight carbonates of the Group II (alkaline earths) are considerably more stable. As shown in Table II, the carbonates of calcium, strontium, and barium possess excellent solubility characteristics and furthermore, decompose at considerably greater temperatures.

**Table II. Solubility and decomposition properties of Group 1 (alkali metal) and Group 2 (alkaline earth) carbonates at low CO₂ partial pressures \(^{21,22}\)**

<table>
<thead>
<tr>
<th>Carbonates</th>
<th>Molal solubility</th>
<th>Decomposition temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25°C</td>
<td>100°C</td>
</tr>
<tr>
<td>Group 1 carbonates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li₂CO₃</td>
<td>0.18</td>
<td>0.10</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>2.80</td>
<td>4.26</td>
</tr>
<tr>
<td>K₂CO₃</td>
<td>8.10</td>
<td>4.41</td>
</tr>
<tr>
<td>Rb₂CO₃</td>
<td>19.48</td>
<td>--</td>
</tr>
<tr>
<td>Cs₂CO₃</td>
<td>8.00</td>
<td>--</td>
</tr>
<tr>
<td>Group 2 carbonates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgCO₃</td>
<td>0.00126(^{a})</td>
<td>--</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>0.00013</td>
<td>0.000375</td>
</tr>
<tr>
<td>SrCO₃</td>
<td>0.000075</td>
<td>0.00044</td>
</tr>
<tr>
<td>BaCO₃</td>
<td>0.000124</td>
<td>0.000332</td>
</tr>
</tbody>
</table>

\(^{a}\)Cold water.
It has been suggested in the literature, and confirmed experimentally at ambient conditions in our lab, that a CaCO₃ coating forms about the Ca(OH)₂ reactant thereby resulting in severe diffusional limitations. Some success has been reported at higher temperatures. A German patent was issued in which thermal ramping was used to enhance the reactivity and conversion of the Ca(OH)₂ reactant. Process temperatures were 100 to 200°C. Work performed by Ontario Hydro has indicated that the reaction proceeds more readily at 400°C, but reactant conversions in excess of 60% have been uncommon.

The alkaline earth hydroxides of strontium and barium differ from the other alkaline earth hydroxides in that they may exist in a hydrated form. The most commonly reported coordination numbers are 1 and 8, although 2 and 3 waters of hydration have been reported for Ba(OH)₂. Our studies have concentrated on the use of Ba(OH)₂ hydrates since the hydrates of Sr(OH)₂ are not as available in commercial quantities.

To determine the likelihood of a reactant being coated by a nonporous product which would result in severe diffusional limitations of the gaseous reactant, a comparison of the molar crystal volume ratios of the product and reactant, referred to as the Pilling-Bedworth ratio, is often beneficial. The Pilling-Bedworth ratios for several alkali and alkaline earth hydroxides and their carbonate products are presented in Table III. With the exception of the Ba(OH)₂ and Sr(OH)₂ data, the table was taken from a paper by Markowitz. A Pilling-Bedworth ratio >1 indicates a high probability of diffusional limitations, and a value of <1 indicates that product porosity may exist. Apparent exceptions to this relationship may result for various mixtures where synergistic effects or physical changes of the solid such as sintering or melting may occur. From Table III, one would anticipate that LiOH₂•H₂O, Sr(OH)₂•8H₂O, Ba(OH)₂•H₂O, and Ba(OH)₂•8H₂O would be efficient CO₂ absorbents if the chemical reactions were kinetically favored. One might also predict Ba(OH)₂•8H₂O to be more efficient than Ba(OH)₂•H₂O for CO₂ removal. The Pilling-Bedworth ratio of 1.18 for Ca(OH)₂ is consistent with the reported formation of an impervious shell about the Ca(OH)₂ particle, thus resulting in diffusional limitations. Similarly, work performed by Boryta and Maas and the Naval Research Laboratory have indicated LiOH•H₂O, Pilling-Bedworth ratio of 0.64, to be the reactive species in CO₂ removal studies and LiOH, Pilling-Bedworth ratio of 1.07, to be unreactive.

III. Literature Review

Although hydrates of Ba(OH)₂ have been cited in the literature as being reactive toward CO₂ in ambient air, the extent of this reactivity had not been examined until this study. The stoichiometry of the overall reaction may be represented by

\[
\text{Ba(OH)₂•xH₂O(s) + CO₂(g) + BaCO₃(s) + (x+1)H₂O(g),}
\]

where x is the initial degree of hydration.

In the opinion of this author, the most credible study conducted to date on the dissociation vapor pressures of Ba(OH)₂ hydrates was that of Kondakov, Kvtumenenko, and Bundel. The results were published in 1964. In this study, the water vapor pressure of Ba(OH)₂•xH₂O samples with x values of 0.3896, 1.342, 2.260, 3.282, 4.196, 5.042, 5.882, and 6.763 were determined. When the results
Table III. Molar volume relationships among some possible carbon dioxide absorbents

<table>
<thead>
<tr>
<th>Substance</th>
<th>Formula weight</th>
<th>Density (g/cm³)</th>
<th>Molar volume (cm³/g-mole)</th>
<th>Pilling-Bedworth ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiOH</td>
<td>23.95</td>
<td>1.43</td>
<td>16.75</td>
<td>1.07</td>
</tr>
<tr>
<td>LiOH•H₂O</td>
<td>41.96</td>
<td>1.51</td>
<td>27.79</td>
<td>0.64</td>
</tr>
<tr>
<td>Li₂CO₃</td>
<td>73.89</td>
<td>2.07</td>
<td>35.70</td>
<td></td>
</tr>
<tr>
<td>NaOH</td>
<td>40.01</td>
<td>2.13</td>
<td>18.78</td>
<td></td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>106.00</td>
<td>2.51</td>
<td>42.25</td>
<td></td>
</tr>
<tr>
<td>Na₂CO₃•H₂O</td>
<td>124.02</td>
<td>2.25</td>
<td>55.12</td>
<td></td>
</tr>
<tr>
<td>Mg(OH)₂</td>
<td>58.34</td>
<td>2.39</td>
<td>24.41</td>
<td>1.14</td>
</tr>
<tr>
<td>MgCO₃</td>
<td>84.33</td>
<td>3.04</td>
<td>27.77</td>
<td></td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>74.10</td>
<td>2.34</td>
<td>31.63</td>
<td>1.18</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>100.09</td>
<td>2.71</td>
<td>36.92</td>
<td></td>
</tr>
<tr>
<td>Sr(OH)₂•8H₂O</td>
<td>265.76</td>
<td>1.90</td>
<td>139.87</td>
<td>0.29</td>
</tr>
<tr>
<td>SrCO₃</td>
<td>147.63</td>
<td>3.70</td>
<td>39.90</td>
<td></td>
</tr>
<tr>
<td>Ba(OH)₂•3H₂O</td>
<td>315.48</td>
<td>2.10</td>
<td>150.23</td>
<td>0.30</td>
</tr>
<tr>
<td>Ba(OH)₂•1H₂O</td>
<td>189.48</td>
<td>3.65</td>
<td>51.8</td>
<td>0.86</td>
</tr>
<tr>
<td>BaCO₃</td>
<td>197.35</td>
<td>4.43</td>
<td>44.47</td>
<td></td>
</tr>
</tbody>
</table>

were plotted (log p vs 1/T), three distinct lines were obtained, as shown in Fig. 1. The lines correspond to Ba(OH)₂ hydrate samples in which Ba(OH)₂•H₂O, Ba(OH)₂•3H₂O, and Ba(OH)₂•8H₂O were the contributing species to the water vapor pressure within the system. The controlling decomposition reactions and their respective dissociation vapor pressure equations were found to be the following:

\[ \text{Ba(OH)}_2\cdot\text{1H}_2\text{O(s)} \rightarrow \text{Ba(OH)}_2\cdot\text{H}_2\text{O(s)} + \text{H}_2\text{O(g)} \]  

\[ \log P = \frac{-61353}{19.155T} + 12.421 \]  

\[ \text{Ba(OH)}_2\cdot3\text{H}_2\text{O(s)} \rightarrow \text{Ba(OH)}_2\cdot\text{1H}_2\text{O(s)} + 2\text{H}_2\text{O(g)} \]  

\[ \log P = \frac{-62618}{19.155T} + 13.823 \]  

\[ \text{Ba(OH)}_2\cdot8\text{H}_2\text{O(s)} \rightarrow \text{Ba(OH)}_2\cdot3\text{H}_2\text{O(s)} + 5\text{H}_2\text{O(g)} \]  

\[ \log P = \frac{-58230}{19.155T} + 13.238 \]

where

\[ P = \text{vapor pressure, Pa or nt·m}^{-2} \]

\[ T = \text{temperature, K.} \]

1099
Fig. 1. Dissociation vapor pressures for \( \text{Ba(OH)}_2 \) hydrates.
Using the Van't Hoff equation, the data were analyzed for thermodynamic consistency. Based upon the entropy change for the formation of the trihydrate, they concluded that the trihydrate may be less stable than the other crystalline hydrates. However, other investigators under highly controlled conditions have reported Ba(OH)$_2$$\cdot$2H$_2$O and amorphous compounds to exist.

With the exception of Ba(OH)$_2$$\cdot$2H$_2$O, the thermodynamics of the CO$_2$-barium hydroxide hydrate gas-solid reaction may be calculated from published values.$^{(34-40)}$ Presented in Table IV are the thermodynamic calculations for the following reactions:

\[
\begin{align*}
\text{Ba(OH)$_2$} & + \text{CO}_2 \rightarrow \text{BaCO}_3 + \text{H}_2\text{O}, & \Delta H = -115 \text{ kJ/mol} \quad (5) \\
\text{Ba(OH)$_2$$\cdot$H$_2$O} & + \text{CO}_2 \rightarrow \text{BaCO}_3 + 2\text{H}_2\text{O}, & \Delta H = -53 \text{ kJ/mol} \quad (6) \\
\text{Ba(OH)$_2$$\cdot$3H$_2$O} & + \text{CO}_2 \rightarrow \text{BaCO}_3 + 4\text{H}_2\text{O}, & \Delta H = -73 \text{ kJ/mol} \quad (7) \\
\text{Ba(OH)$_2$$\cdot$8H$_2$O} & + \text{CO}_2 \rightarrow \text{BaCO}_3 + 9\text{H}_2\text{O}, & \Delta H = 364 \text{ kJ/mol} \quad (8)
\end{align*}
\]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta G$ (kJ/mol)</th>
<th>$\Delta H$ (kJ/mol)</th>
<th>$\Delta S$ (J/mol*K)</th>
<th>$K_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>-85.7</td>
<td>-114.6</td>
<td>-37.2</td>
<td>1.05$\times$10$^{15}$</td>
</tr>
<tr>
<td>6</td>
<td>-66.5</td>
<td>-53.0</td>
<td>104.6</td>
<td>4.52$\times$10$^{11}$</td>
</tr>
<tr>
<td>7</td>
<td>-41.6</td>
<td>-72.6</td>
<td>442.3</td>
<td>1.94$\times$10$^{7}$</td>
</tr>
<tr>
<td>8</td>
<td>15.9</td>
<td>364.4</td>
<td>1230.0</td>
<td>0.00187</td>
</tr>
<tr>
<td>9</td>
<td>-61.9</td>
<td>-31.8</td>
<td>161.3</td>
<td>6.84$\times$10$^{10}$</td>
</tr>
</tbody>
</table>

At 298 K and 1 atm, the fugacities of the gas species may be approximated by their partial pressures (atm), and the fugacities of the crystalline species, with respect to their reference states, is equal to $\sim$. If the water product is present as vapor, the equilibrium constant, $K_{eq}$, is equal to $[P(H_2O)]^{x+1}/[P(CO_2)]$, where $x$ is the hydration number of the reacting species and $P(H_2O)$ and $P(CO_2)$ are the partial pressures of water and carbon dioxide that exist within the system. The maximum partial pressure water vapor that can exist within the system at a fixed temperature is that at complete saturation. At 25°C, this value is 3.165 kPa or 23.75 mm Hg. Therefore, based upon the previously calculated equilibrium constants for the speculated reactions, the corresponding CO$_2$ partial pressure at equilibrium may be calculated for the possible carbonation reactions. These values are presented in Table V. With respect to the preceding analysis, if any of the speculated reaction mechanisms were equilibrium controlled, the effluent CO$_2$ concentration would be less than 15 parts per trillion.
Table V. Equilibrium values for the CO₂-Ba(OH)₂ hydrate gas-solid reaction

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Kₑq</th>
<th>Reactant hydration</th>
<th>Pₑq CO₂ Pa</th>
<th>Pₑq CO₂ mm Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1.0·10¹⁵</td>
<td>0</td>
<td>3.1·10⁻¹²</td>
<td>2.4·10⁻¹⁴</td>
</tr>
<tr>
<td>6</td>
<td>4.52·10¹¹</td>
<td>1</td>
<td>2.2·10⁻¹⁰</td>
<td>1.7·10⁻¹²</td>
</tr>
<tr>
<td>7</td>
<td>1.94·10⁷</td>
<td>3</td>
<td>5.0·10⁻⁹</td>
<td>3.7·10⁻¹¹</td>
</tr>
<tr>
<td>8</td>
<td>1.87·10⁻³</td>
<td>8</td>
<td>1.5·10⁻⁶</td>
<td>1.1·10⁻⁸</td>
</tr>
<tr>
<td>9</td>
<td>6.84·10¹⁰</td>
<td>8</td>
<td>1.5·10⁻⁶</td>
<td>1.1·10⁻⁸</td>
</tr>
</tbody>
</table>

Based upon a dissociation pressure for Ba(OH)₂·8H₂O of 1.1 kPa (8.26 mm Hg) at 298 K, any water vapor pressure greater than this value would override the thermodynamic constraints for formation of Ba(OH)₂·8H₂O. However, the kinetics of this exothermic transformation are unknown. If the gas surrounding the particle is water saturated, the excess water of reaction (nine molecules of water per molecule of CO₂ reacted) must remain as a liquid in the pore structure and may have a deleterious effect on the overall reaction. Thermodynamic and equilibrium values for this reaction sequence are also presented in Tables IV and V for the following reaction:

\[
\text{Ba(OH)₂·8H₂O(s) + CO₂(g) → BaCO₃(s) + 9H₂O(l)} \quad \Delta H = -32 \text{ kJ/mol}.
\]  (9)

Again, the reactions will be equilibrium controlled only for very low CO₂ partial pressures.

When no work is being performed on or by the system, the enthalpy change is a measure of the endo- or exothermicity of the reaction at 298 K. Although hydroxide-carbonate reactions are generally regarded as exothermic, as reflected by the stability of the carbonate product, the waters of reaction (when released as a vapor) tend to make the reaction less exothermic. If the surrounding gas is water saturated and heat is not removed from the system by vaporization of the released waters of hydration, the reaction becomes more exothermic. Therefore, for situations in which the feed gas is rich in CO₂, the gas may quickly become saturated with water. In this case, part of the column may operate under endothermic conditions (Reaction 8) and another section under exothermic conditions (Reaction 9).

IV. Experimental Studies

Experimental studies are being conducted to develop a better understanding of the CO₂ - Ba(OH)₂ hydrate gas-solid reaction and to develop a process capable of treating a high-volumetric, low-CO₂-content gas stream. Studies have been conducted on packed and fluidized beds of Ba(OH)₂ hydrate. Presently, the packed-bed concept is preferred due to overall operational simplicity.
Potential Ba(OH)$_2$ Hydrate Reactants

As previously mentioned, stable Ba(OH)$_2$ hydrate species with hydration of 1, 2, 3, and 8 have been reported. To date, we have examined the reactivity of reagent-grade Ba(OH)$_2$•8H$_2$O and commercially available Ba(OH)$_2$•H$_2$O, Ba(OH)$_2$•5H$_2$O, and Ba(OH)$_2$•8H$_2$O. A photograph of the materials is presented in Fig. 2. X-ray diffraction patterns were obtained for each material form, and the results presented in Table VI. Considerable difficulty was encountered in analyzing the diffraction pattern for the commercial Ba(OH)$_2$•8H$_2$O flakes. Reactant analyses were conducted on two 200-lb drums of the commercial Ba(OH)$_2$•8H$_2$O. These results are presented in Table VII.

Table VI. X-ray diffraction analyses of Ba(OH)$_2$ hydrate samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Observed line intensities</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba(OH)$_2$•H$_2$O</td>
<td>Ba(OH)$_2$•H$_2$O - strongest</td>
</tr>
<tr>
<td>Ba(OH)$_2$•5H$_2$O</td>
<td>Ba(OH)$_2$•3H$_2$O</td>
</tr>
<tr>
<td>Ba(OH)$_2$•8H$_2$O</td>
<td></td>
</tr>
<tr>
<td>Ba(OH)$_2$•8H$_2$O - commercial</td>
<td>Unidentified</td>
</tr>
<tr>
<td>Ba(OH)$_2$•8H$_2$O - analytical</td>
<td>Ba(OH)$_2$•8H$_2$O</td>
</tr>
</tbody>
</table>

Table VII. Reactant analyses on commercial Ba(OH)$_2$•8H$_2$O

<table>
<thead>
<tr>
<th>Drum No.</th>
<th>Average composition</th>
<th>Standard deviation</th>
<th>Number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ba(OH)$_2$•7.54H$_2$O</td>
<td>0.0966</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>Ba(OH)$_2$•7.47H$_2$O</td>
<td>0.0830</td>
<td>20</td>
</tr>
</tbody>
</table>

From the results, one cannot statistically reject the hypothesis that the mean compositions for the drums are the same. In a similar manner, the standard deviation attributed to the experimental technique was determined to be 0.077. This value was obtained by repetitive titrations of analytical-grade Ba(OH)$_2$•8H$_2$O.
Fig. 2. Commercial and analytical Ba(OH)₂ hydrates.
Therefore, the deviation about the mean which was observed for the two drums of commercial-grade Ba(OH)$_2$•8H$_2$O may be attributed to the analytical technique and not the sample position in the drum. Vendor specifications for the commercial-grade Ba(OH)$_2$•8H$_2$O indicate the reactant composition to be between Ba(OH)$_2$•7.13H$_2$O and Ba(OH)$_2$•7.86H$_2$O. The mean of these values is Ba(OH)$_2$•7.50H$_2$O, which agrees well with the analyses reported above. It is interesting to note that Michaud reported a Ba(OH)$_2$•3H$_2$O – Ba(OH)$_2$•8H$_2$O eutectic to exist during solubility studies on the Ba(OH)$_2$ hydrate–water system. The stoichiometric composition of the eutectic corresponds to Ba(OH)$_2$•7.12H$_2$O, which agrees with the lower specification cited by the vendor. This eutectic consists of 18 mole % Ba(OH)$_2$•3H$_2$O. Therefore, the samples of commercial Ba(OH)$_2$•8H$_2$O used in our studies appear to consist of 47 mole % eutectic and 53 mole % Ba(OH)$_2$•8H$_2$O. The total amount of Ba(OH)$_2$•3H$_2$O in these samples would then be 10 mole %.

Discussions with the vendor have indicated that the flakes are prepared by distributing a hot magma solution of Ba(OH)$_2$ hydrate (~0.3 mm thick) on a conveyor belt which is cooled on the underside by a water bath. As shown in Fig. 3, the two sides of the resultant flake are quite different – the side next to the belt is very smooth; the outer side, somewhat rough. Presented in Fig. 4 is a photo obtained by the transmission of light through the flake. Of particular interest are the star-shaped patterns appearing in the material. Based upon the observations of Flemings in Solidification Processes for a similar solidification process in which eutectic and pure species are present, we speculate the dendritic-like stars to be Ba(OH)$_2$•8H$_2$O. This material preferentially crystallizes next to the cool surface at the conveyor belt and then extends in a dendritic manner up through the flake. The eutectic then precipitates out and fills in the voids. The stoichiometric composition of the commercial Ba(OH)$_2$•8H$_2$O is 47% eutectic, 53% Ba(OH)$_2$•8H$_2$O.

Experimental Equipment

A schematic of the experimental equipment is presented in Fig. 5. The equipment may be used for either differential-bed or extended-length packed-bed studies. The feed gas is metered through rotameters and fed to a humidifier. The extent of humidification is controlled by the temperature and pressure of the humidifier. The gas is then passed through a preheater and to the reactor. At the base of the 10.2-cm (4-in.)-ID glass reactor, the gas is dispersed by Pall rings before passing through the bed. The Ba(OH)$_2$ hydrate reactant is supported in the glass column by 100-mesh wire screen. The reactor is jacketed to ensure a uniform temperature profile. The minimal bed depth for differential reactor studies is 6 mm (¼ in.). The common length for the extended-length packed-bed studies is 51 cm (20 in.). For these studies, a differential pressure (D/P) cell was used to monitor the pressure drop increase across the bed as a function of time. To ensure a positive pressure system for gas analyses, the pressure at the top of the bed is maintained at 108 kPa (1 psig). A small portion of the effluent gas is passed through a filter and to a metal bellows pump for pressurization to 145 kPa (7 psig). Following pressurization, the gas flows through two knockout vessels for water removal and then to the off-gas analytical system.

The analytical system consists of a flowthrough Wilks-Foxboro Miran lA infra-red analyzer that is located in a glove box. Because the window to the flow cell and IR light source of the analyzer are separated by the surrounding gas, we have found it necessary to place the analyzer in a controlled environment because of fluctuations in the ambient CO$_2$ concentration and hence, the drifting of the baseline. The glove box is continuously purged with argon. The infra-red spectrometer wavelength is set at 4.25 µm and the pathlength at 20.25 m. The cell pressure is
Fig. 3. Top and bottom views of commercial Ba(OH)$_2$·8H$_2$O flakes; 2.85 by 3.75 in. original photograph, magnification - 12.75X.
Fig. 4. Ba(OH)$_3$:8H$_2$O flake; 2.85 by 3.75 in. original photograph, magnification - 12.75X.
Fig. 5. Schematic of the experimental equipment for CO₂ removal studies.
maintained at 136 kPa (5 psig), and the cell is jacketed and maintained at 50°C to avoid water condensation within the cell. No interference from high water concentrations has been observed at extremely low CO₂ concentrations. The instrument has been calibrated over the concentration range of 100 ppb to 330 ppm CO₂ using calibration gases obtained from the Bureau of Mines Helium Operations Plant in Amarillo, Texas, and from commercial vendors. The calibration gases obtained from the Bureau of Mines are excellent sub-ppm standards as they have been analyzed by a freeze-out preconcentration technique followed by mass spectroscopy analysis.

The runs are generally continued through column loading (complete breakthrough of CO₂). The product is then analyzed by a standard acid-base titration with a Brinkmann automatic titrator. The reactant conversion is determined from the titration results, and the extent of hydration is calculated by an overall mass balance on the analyzed sample.

**Ba(OH)₂•H₂O Studies**

Due to the lack of reactivity and poor product conversion associated with the carbonation of Ca(OH)₂, the prime objective in initial studies on the hydrates of Ba(OH)₂ was to establish the reactivity of the various hydrated species. As indicated in Fig. 6, beds of Ba(OH)₂•H₂O were superior to either beds of Ba(OH)₂•8H₂O or Ba(OH)₂•5H₂O for the treatment of a humidified 4.8% CO₂ gas stream. Therefore, initial experimental emphasis was placed upon the use of Ba(OH)₂•H₂O for CO₂ removal and fixation. The results of these studies indicated CO₂ removal from air (330 ppm CO₂) concentrations to <50 ppb to be possible. Reactant utilization in excess of 99% was routinely obtained, and the mass transfer zone was extremely short. As may be observed in Fig. 2, the reactant is particulate in nature.

However, these runs were characterized by a twofold increase in bed volume and accompanying increases in pressure drop across the bed. As indicated in Fig. 7, when a bed of Ba(OH)₂•H₂O was contacted with a dry feed gas, poor removal was noted. However, when the water vapor pressure of the feed gas exceeded the dissociation vapor pressure of Ba(OH)₂•8H₂O (Fig. 8 or Fig. 7), the reaction proceeded quite rapidly. The formation of Ba(OH)₂•8H₂O was confirmed by x-ray diffraction analysis. As shown in Run 10 (Fig. 8), a packed bed of Ba(OH)₂•H₂O undergoes a conditioning period when contacted with a humid CO₂-bearing gas, during which the activity of the bed decreases and then increases. The initial reactivity is attributed to the presence of a small amount of Ba(OH)₂•8H₂O which is gradually depleted. In time, moisture from the air converts the rest of the bed to active Ba(OH)₂•8H₂O. As indicated by Run 22 (Fig. 8), the bed may also be preconditioned by a humid inert gas. In both cases, a factor of 2.5 increase in bed volume, resulting from Ba(OH)₂•8H₂O formation was observed, and reactant conversions in excess of 99% were obtained. The bed expansion did result in a significant pressure drop increase across the bed. Therefore, the increase in reactivity of Ba(OH)₂•H₂O over that of either Ba(OH)₂•5H₂O or Ba(OH)₂•8H₂O is now attributed to the existence of a more active (greater surface area) form of Ba(OH)₂•8H₂O. Similar results were obtained on fluidized-bed studies with humidified air (330 ppm) CO₂ as a feed gas and Ba(OH)₂•H₂O as a reactant. Initial results were promising although the entrainment of fines in the off-gas presented and will present a considerable problem for process operation. Therefore, because of operational simplicity, the fixed-bed approach has been designated as the desired mode of gas-solid contacting.

For the treatment of an airlike (330 ppm CO₂) gas stream, initial studies on packed beds of commercially designated Ba(OH)₂•5H₂O flakes were discontinued as the material degraded upon conversion to octahydrate. This degradation resulted in severe pressure drop problems. Attempts to press either Ba(OH)₂•H₂O or
Fig. 6. Comparison of Ba(OH) hydrates in packed beds with a humidified 4.8% CO₂ feed gas.
Fig. 7. The effect of water vapor pressure on the reactivity of Ba(OH)$_2$·H$_2$O beds.
Fig. 8. The effects of bed preconditioning on Ba(OH)$_2$·H$_2$O with humidified nitrogen.
Ba(OH)$_2$•5H$_2$O into pellets also failed as the pellets degraded upon conversion to the octahydrate. As a result of these observations, the research effort was then redirected toward the development of a sufficiently active Ba(OH)$_2$•8H$_2$O species which, when placed in a packed bed, resulted in acceptable operational characteristics, particularly with respect to pressure drop.

**Commercial Ba(OH)$_2$•8H$_2$O Flake**

Present efforts are directed toward the use of the flakes of commercial Ba(OH)$_2$•8H$_2$O in packed-bed reactors. Although these flakes possess considerably less reactivity than hydrated Ba(OH)$_2$•H$_2$O, the material has been found to have sufficient reactivity for the treatment of dilute CO$_2$ gas streams. The bulk of these runs have been conducted on 10.2-cm-ID by 51-cm-long (4-in.-ID by 20-in.-long) packed beds which contain 4200 g of reactant. The initial void volume of the bed is 52%. However, negligible bed expansion is noted upon complete conversion to carbonate, and the final void volume is 77% due to the lower molar volume of the product. Although several gas superficial velocities have been examined, a nominal superficial velocity of 10 cm/s has been established as a reasonable process standard based upon desired scale-up criteria. The bulk of the data to be presented, however, was obtained at a superficial velocity of 13 cm/s. For these studies, variables of particular interest are the effect of water vapor pressure and column temperature upon the removal efficiency of the bed, and the final pressure drop across the bed upon 100% conversion.

Results of a run operated at near optimal conditions are shown in Fig. 9. The CO$_2$ breakthrough was reasonably sharp with a mass transfer zone of 18 cm. The initial pressure drop across the bed was 1.01 kPa/m (0.04 lb•in.$^{-2}$ft$^{-1}$) and gradually increased to 3.64 kPa/m (0.14 lb•in.$^{-2}$ft$^{-1}$). The final bulk conversion of the bed upon completion of the run was greater than 99%. The final product was a free-flowing solid which was easily removed from the column (Fig. 10).

As previously mentioned, it is believed that the conditions for the preceding run were near optimal as results have indicated an operating envelope to exist. The relative humidity for this run was 40%, which corresponded to an inlet water pressure of 1129 Pa (8.47 mm Hg). The dissociation vapor pressure of Ba(OH)$_2$•8H$_2$O at these conditions is 918 Pa (6.89 mm Hg). Results obtained under similar conditions with water vapor pressures less than that of the dissociation vapor pressure for Ba(OH)$_2$•8H$_2$O have resulted in bed deactivation and early CO$_2$ breakthrough, indicating Ba(OH)$_2$•3H$_2$O to be considerably less reactive than Ba(OH)$_2$•8H$_2$O. This deactivation step appears to be kinetically controlled. Studies are presently under way to develop a better understanding of the deactivation phenomenon. Although prolonged operation at vapor pressures below the dissociation vapor pressure of Ba(OH)$_2$•8H$_2$O does not appear feasible.

Experimental studies have also indicated that there may be an upper relative humidity or water vapor pressure, above which it may not be desirable to operate as pressure drop problems are compounded. As previously cited, the flakes of commercial Ba(OH)$_2$•8H$_2$O are composed of 53 mole % Ba(OH)$_2$•8H$_2$O and 47 mole % Ba(OH)$_2$•8H$_2$O-Ba(OH)$_2$•3H$_2$O eutectic. Results have indicated that when a flake is exposed to a high-humidity gas stream, a transformation takes place whereby the flake preferentially curls on one side and becomes a more active species (Fig. 11). Work is in progress to develop a better understanding of the mechanism for this transformation, although conversion of Ba(OH)$_2$•3H$_2$O to Ba(OH)$_2$•8H$_2$O and capillary condensation of H$_2$O vapor within the pores of the flakes appear to be likely candidates. The resulting material is more active, but pressure drop problems are also much greater due to ensuing particle degradation. Studies are underway to
REACTANTS:
Ba(OH)$_2$·8H$_2$O FLAKES - 4229.6 g
330 ppm$_v$ CO$_2$ - 4.04 m$^3$·h$^{-1}$ (2.37 ft$^3$·min$^{-1}$)
SUPERFICIAL VELOCITY - 13.8 cm·s$^{-1}$
BED DEPTH - 50.8 cm (20 in.)
COLUMN TEMPERATURE - 22.7°C
RELATIVE HUMIDITY at 22.7°C - 41%
H$_2$O VAPOR PRESSURE - 1129 Pa
DISSOCIATION VAPOR PRESSURE - 918 Pa
FINAL CONVERSION - +99%
MAXIMUM PRESSURE DROP - 2.8 kPa·m$^{-1}$
(0.14 lb$_f$·in.$^{-2}$·ft$^{-1}$)

Fig. 9. Near optimal conditions for CO$_2$ removal from air (330 ppm$_v$) with Ba(OH)$_2$·8H$_2$O flake bed.
Fig. 10. Commercial Ba(OH)$_2$·8H$_2$O reactant and BaCO$_3$ product flakes.
Fig. 11. Top and bottom views of commercial Ba(OH)$_2$·8H$_2$O subjected to high humidity; 2.85 by 3.75 in. original photograph, magnification — 16.5 and 13X, respectively.
determine the severity of the problem as the humidity or water vapor pressure is increased while other system parameters remain constant.

V. CONCLUSION

For the treatment of an air-based off-gas stream, the use of packed beds of Ba(OH)$_2$•8H$_2$O flakes to remove CO$_2$ has been demonstrated. However, the operating conditions must be maintained between certain upper and lower limits with respect to the partial pressure of water. If the water vapor pressure in the gas is less than the dissociation vapor pressure of Ba(OH)$_2$•8H$_2$O, the bed will deactivate. If the vapor pressure is considerably greater, pressure drop problems will increase with increasing humidity as the particles curl and degrade. Results have indicated that when operated in the proper regime, the bulk of the increase in pressure drop results from the conversion of Ba(OH)$_2$•8H$_2$O to BaCO$_3$ and not from the hydration of the commercial Ba(OH)$_2$•7.5H$_2$O (i.e., Ba(OH)$_2$•7.50H$_2$O) to Ba(OH)$_2$•8H$_2$O.

VI. REFERENCES


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1,4-DIPHENYLBUTADIYNE AS A POTENTIAL TRITIUM GETTER*

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Abstract

Research on the acetylene compound 1,4-diphenylbutadiyne is an effort to develop an air-operative tritium gas scavenger. T$_2$ adds to the acetylene bond of the organic in the presence of a metal catalyst. The catalyst also stimulates the oxidation reaction as well. The butadiyne compound has shown good reaction efficiency at 300ppm T$_2$ in static dry air. At this concentration 75% of the scavenged tritium was in the organic. Our work has expanded to the investigation of liquid acetylenes, metal acetylene complexes, organometallics and acetylene based alcohols. The best of these compounds has gotten 100% of 10-500ppm T$_2$ for both static and dynamic air flow conditions. Gas mixtures as low as 1ppm will be evaluated in future work.

Introduction

Tritium gas is less hazardous than tritiated water. The new factor of 25,000 separating the permissible air concentrations for HT and HTO for occupational workers has created interest in engineering alternatives for both in-plant tritium control as well as waste management schemes.¹

The current technology used in tritium control deliberately converts HT to HTO. Most tritium air cleaning systems consist of a catalyst bed followed by a water trapping device containing a bed of molecular sieve adsorbant. Several publications exist describing the performance of catalytic reactor-adsorber bed decontamination systems of various sizes.²-⁶ Reported differences in moisture collection efficiencies and break through times need to be reconciled for systems whose design parameters make easy extrapolations to large scale systems possible. With a factor of 10⁴ separating the relative radiotoxicity of HT to HTO, adding an additional factor of 10² for protective clothing,⁷ a system which operates at an oxide removal efficiency less than 10⁵ to 10⁶ can actually increase the tritium hazard within the recirculating clean-up volume. There is no substance used presently that will react with tritium in the presence of air. We have concentrated on the hydrogenation of acetylene.

*Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore Laboratory under contract number W-7405-ENG-48.
The first organic getter was studied at Sandia, Albuquerque. The getter was intended for hydrogen in atmospheres not containing oxygen. The researchers selected DPPE (dimerized phenylpropargyl ether), C$_{18}$H$_{14}$O$_2$, 2,4-hexadiyne; 1,6-diol, 1,6-diphenyl- which possesses two carbon-carbon triple bonds. The H$_2$ reacted efficiently at room temperature in the presence of palladium catalyst on calcium carbonate. There was some evidence of reaction in air, however no catalyst blank was run for comparison. The compound reacted incompletely with pure tritium then outgassed due to possible radiation damage.

We initially selected 1,4-diphenylbutadiyne, C$_{16}$H$_{10}$, m.p. 87°C, which is a hydrocarbon of the structure C$_6$H$_5$-C≡C-C≡C$_6$H$_5$. As is the case with the Sandia compound, the phenyl groups are present to add radiation stability. We have replaced the ether linkages on the Sandia compound with carbon-carbon bonds to further improve stability. Mike Smith, of Bendix, determined that DPPE's ether linkages are subject to breakage during conventional hydrogenation and selected the hydrocarbon as an improved hydrogen getter.

In addition to the butadiyne compound, we have collected data on the acetylene based alcohol 4-phenyl-3-butyn-l-ol, C$_{10}$H$_{10}$O, m.p. < 20°C of the structure C$_6$H$_5$-C≡C-CH$_2$CH$_2$OH. This alcohol has shown improved performance over the butadiyne compound at low concentrations of T$_2$ (10ppm).

**Experimental Results**

1,4-diphenylbutadiyne and 4-phenyl-3-butyn-l-ol have been evaluated at room temperature and 1 atmosphere pressure. Tritium concentrations ranging from 10-500ppm T$_2$ in dry air have been used in static and dynamic airflow tests. Substrates used to support the catalyst and organic include calcium carbonate, carbon, Chromosorb W, Fluorapak 80 (a nylon), Porasil B and GC22 firebrick (chromatographic column supports).

Samples of 20% 1,4-diphenylbutadiyne/1% palladium or platinum catalyst have removed 100% of 300-500ppm T$_2$ in static dry air. The efficiencies of the organic reaction vary from 0.6% to 74.8%; see Table 1.

The variation in the organic reaction efficiency (ORE) has been correlated to effects produced by not only the catalyst and the substrate but also by the solvent used to reduce the catalyst and the addition of wetting agents used to aid the dispersion of the metal catalyst on the substrate. The mechanisms by which these parameters affect the organic reaction are not fully understood.

The reaction of tritium with 60% 1,4-diphenylbutadiyne (DPBD)/5% palladium catalyst on calcium carbonate, showed the reaction to be dominated by the formation of HTO with only 11% of the input tritium reacting with the organic. Examination of this material by electron microscopy (SEM) and x-ray photoelectron microscopy (ESCA) revealed that the organic was unevenly distributed over the palladium/calcium carbonate (Fig. 1).
This resulted in areas of catalyst and substrate left uncovered. We know that palladium atoms quickly acquire oxygen atoms at their surface. An overlying layer of the organic attempts to keep the $O_2$ away from the catalyst surface once the metal has been reduced. The lighter mass $T_2$ will permeate the organic up to an order of magnitude faster than $O_2$; the principle in membrane separation.13

Tests using firebrick as a substrate for 20% DPBD/1% palladium showed an improved organic reaction efficiency of 300%; 36% of the input $T_2$ reacted with the organic. The rest of the $T_2$ formed HTO and was adsorbed on the substrate. Analysis of the remaining gas by mass spectrometry showed no $T_2$ remained unreacted in the gas phase. The rigid honey-combed structure of the firebrick provided an improved surface for the dispersion of the catalyst and subsequent coating with the organic; see Fig. 2.
With the same formulation of organic and substrate, platinum catalyst was substituted for palladium. The ORE increased from 36% to 47%. Again, the rest reacted to form HTO which was strongly adsorbed by the firebrick. No T₂ remained in the gas phase. Our best results at 300ppm T₂ in static dry air were obtained using 20% DPBD/1% Pt on firebrick. Among the experiments using material of this composition, experiments 42, 54 and 55 show extreme differences in performance. Effects produced by changing the solvent in which the catalyst was reduced, plus the addition of a wetting agent, Aerosol-OT, resulted in the highest and the lowest efficiencies obtained to date. Two materials of identical formulation were evaluated in experiments 42 and 55. Both catalysts were reduced from K₂PtCl₄ in methanol using sodium borohydrate. The only exception was that the material used in Exp. 55 had Aerosol-OT added with the catalyst at time of synthesis. The ORE for Exp. 42 was 47% whereas for Exp. 55 it was 0.6%. A material of the same proportions of organic/catalyst/substrate was evaluated in experiment 54. This material also had the wetting agent added with the catalyst during synthesis. The only difference here was that the reduction of platinum from K₂PtCl₄ was performed in MLM (ethylene glycol monomethyl ether) instead of methanol. We measured 75% of the input T₂ in the organic for this sample. The remaining T₂ formed HTO; no T₂ remained unreacted in the gas phase. We observed that the use of Aerosol-OT poisoned the addition reaction of tritium with the organic when the reduction of platinum was done in methanol, yet greatly enhanced the addition reaction when platinum was reduced in MLM. The remaining data in Table 1 ranges from a 50:50 split in the distribution of tritium activity in the organic and aqueous phases for platinum on firebrick to a complete dominance of the water forming reaction for other catalysts and substrates. Most experiments were 48 hours in duration.
Two experiments of 300ppm $T_2$ in argon were completed to measure the extent of water formation in inert atmosphere. Experiments 35 and 36 using 300ppm $T_2$ in argon showed 2:1 dominance of the water forming reaction over the organic. This water probably was a result of exchange with trace quantities of water present in the substrate material despite the efforts to ensure dryness. A blank was run using only 1% palladium on firebrick in 500ppm $T_2$ in air. We found that 74% on the input $T_2$ had reacted to form water (HTO, $T_2O$) under these conditions.

In an attempt to bring the metal atom closer to the triple bond we made some preliminary investigation into organometallic catalysts. Vaska's catalyst, chlorocarbonylbis(triphenylphosphine) iridium (I), with the formula $\text{IrCl(CO)(PPh}_3)_2$, where Ph indicates a phenyl group, is known to add H$_2$ (and O$_2$) directly to the metal atom with a weak bond.$^{14-16}$ The H$_2$ can be regenerated when irradiated with ultraviolet light so that this class of compound could be an easy-regenerative getter.

Experiments 38 and 44 were tests on the iridium complex in combination with 1,4-diphenylbutadiyne on firebrick. With no UV activation prior to $T_2$ exposure (Exp. 38), the iridium complex put 11% of the tritium in the organic phase and 53% in the aqueous phase, leaving 6% $T_2$ unreacted. Quite different results were produced using UV activation, (Exp. 44), where 17% of the tritium was found in the organic; 8% in the aqueous phase, leaving 59% $T_2$ unreacted. However, tests on Vaska's catalyst without DPBD showed no improvement. It may be that the iridium had already reacted with the acetylene triple bond, thereby blocking out the $T_2$.$^{17}$ In the case of no UV activation, hydrogen was never purged from the metal, thus preventing any $T_2$ addition there. The beta activity was enough to initiate the water reaction.$^{18}$

Nearly all compounds tested were activated with 10 mole% hydrogen before exposure to $T_2$. This reduces the metal catalyst from the oxide and shortens the induction time of the reaction. Those compounds that reacted quickly with hydrogen performed well with tritium. It was apparent that those compounds that did not take up H$_2$ would not react with $T_2$. Hydrogen activation therefore was used as a means of screening out compounds whose reactivity was poor. Among those compounds which performed poorly with hydrogen were the iridium organometallics and the metal-acetylene complexes. Among the metal acetylenes tested were (Diphenylacetylene)bis(triphenylphosphine)platinum(0) of the structure:
and bis(phenylacetylene)bis(triphenyl-phosphine)platinum(II) of the structure:

![Chemical Structure](image)

After 17 hours these compounds still showed no reactivity to hydrogen.

Scavenging T₂ at concentrations 30 times more dilute has proven more difficult. Using 10ppm T₂ in dry air, 20% DPBD/1% Pt on firebrick, with Aerosol-OT was evaluated under both static and dynamic airflow conditions, see Tables II and III.

In static air this material reacted 7.9% of the input T₂ with the organic in 48 hours and 10.2% in 24 hours; see Table II. The wetting agent was put on with the organic instead of with the catalyst, then exposed to 10ppm T₂ in static air for 6 hours. 7.9% of the input T₂ reacted with the organic (Exp. 75) showing the same organic reaction efficiency obtained for a 48 hour test on the same material. A new wetting agent, Aerosol AY, was added with catalyst in the formulation of the material, then exposed to 10ppm T₂ in static air for 6 hours. The performance of this material in 6 hours was equivalent to the performance of 20% DPBD/1% Pt on firebrick with Aerosol-OT in 24 hours.

Twenty percent 4-phenyl-3-butyn-1-ol/1% Pt on firebrick was also tested at 10ppm T₂ in static air. The Aerosol-OT had been applied with the organic. The other synthesis parameters remained the same. After 6 hours exposure to tritium in air at this concentration, the organic scavenged 17.9% of the input T₂. Without the addition of the wetting agent, the ORE was 15.0% (Table 2).

An all glass system was designed to evaluate the performance of organic getters at low concentrations of T₂ under dynamic airflow. The system shown in Fig. 3 has a total volume of 1.1 liters.
A test was made to determine the uptake of $T_2$ by the system (glass, grease and pump). Analysis of the gas mixture before and after a 24 hour test showed no change in $T_2$ concentration when the airflow was maintained at 10 lpm. Only our best candidates, 1,4-diphenylbutadiyne and 4-phenyl-3-butyn-1-ol (PBol) have been tested on this system to date. This data is shown in Table III.

4-phenyl-3-butyn-1-ol has outperformed the DPBD material at both high and low flow rates (10 lpm vs. 1 lpm) using 10ppm $T_2$ in air. At 3 liters/minute flow 20% PBol/1% Pt on firebrick had an organic reaction efficiency of 24.8%. This is the best efficiency achieved to date for our organic getters at 10ppm $T_2$ in air. Work at this concentration, under dynamic flow conditions is still in the preliminary stages.
Discussion

The mechanisms of conversion of tritium gas to tritiated water have been studied for several gas mixtures. The physical and chemical processes involved in the self-radiolysis of such mixtures have been described and the rate constants presented (Table IV).\textsuperscript{19-22}

For tritium mixtures without water vapor, the formation of tritium atoms through ion molecule reactions is an important process for the final formation of HTO. The kinetics of the conversion of tritium to HTO depends considerably on the concentration of reacting components, the composition of the gas phase, the temperature and the presence of catalysts.\textsuperscript{22}

We know that tritium molecules in a mixture decay by emitting beta particles (electrons) with an average energy of 5.7 KeV. These beta particles lose energy through collisions with the mixture molecules and disappear by recombination with positive ions or by attachment to neutral molecule. These molecules undergo ionization or excitation depending on the energy of the primary electrons.\textsuperscript{23} A primary electron with an average energy of 5.7 KeV produces approximately 170-190 ions depending on the ionization efficiency of the mixture.\textsuperscript{24} The positive ions collide with neutral molecules and undergo charge transfer or initiate ion-molecule reactions.\textsuperscript{25} These processes result in the formation of free radicals (T, CT) which are responsible for the formation of the final products.

Experiments with mixtures of tritium, oxygen and nitrogen performed by Caseletto, et al.,\textsuperscript{19} at 700mm total pressure showed the main ionic and excitation process to be:

1) \[ \text{N}_2 + e \rightarrow \text{N}_2^+ + 2e , \]
\[ + \text{N}_2^* + e , \]

2) \[ \text{O}_2 + e \rightarrow \text{O}_2^+ + 2e , \]
\[ + \text{O}_2^* + e , \]

3) \[ \text{T}_2 + e \rightarrow \text{T}_2^+ + 2e , \]
\[ + \text{T}_2^* + e . \]

Since \text{N}_2 is the major component in air, \text{N}_2^+ ions are the main positive ions in the mixture. They probably undergo the reactions:\textsuperscript{33-34

1128
The tritium atoms produced in reaction (2) initiate a number of free radical reactions, the most important of which are:

\[
\begin{align*}
\text{T} + \text{O}_2 + \text{T}_2 \rightarrow & \text{T}_2\text{O} + \text{T}, \quad K_3 = 4.0 \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}; (3) \\
\text{T} + \text{TO}_2 \rightarrow & \text{T}_2 + \text{O}_2, \quad K_4 = 1.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}; (4) \\
& \rightarrow \text{OT} + \text{OT}, \quad K_5 = 1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}; (5) \\
& \rightarrow \text{T}_2\text{O} + \text{O}, \quad K_6 = 1.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}; (6) \\
\text{OT} + \text{T}_2 \rightarrow & \text{T}_2\text{O} + \text{T}, \quad K_7 = 6.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}; (7) \\
\text{OT} + \text{TO}_2 \rightarrow & \text{OT} + \text{O}_2, \quad K_8 = 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}; (8)
\end{align*}
\]

A small number of tritium atoms are removed through the reaction:

\[
\text{T} + \text{T} + \text{N}_2 \rightarrow \text{T}_2 + \text{N}_2
\]

which is a much slower process than reaction (3). Substituting these rate constant values into the expression for the rate of formation of water presented by Papagiannakopoulos and Easterly:

\[
\frac{d[T_2\text{O}]}{dt} = 1.5 \times 10^{-8} [T_2] \text{ sec}^{-1}
\]

This reaction rate constant of \(1.5 \times 10^{-8} \text{ sec}^{-1}\) is in good agreement with the experimental found value of \(5.2 \times 10^{-8} \text{ sec}^{-1}\) by Caseletto et al. in their experiments with mixtures of tritium, oxygen and nitrogen. By this relation we would expect HTO to be formed faster at higher concentrations. Substituting the \(T_2\) concentrations used in the work of this report into the rate equation for the formation of water under self-radiation we calculate:
300ppm $T_2$ (static) - $2.0 \times 10^{-5}$ moles liter$^{-1}$
\[
\frac{d[T_2O]}{dt} = 3.0 \times 10^{-13} \text{ molecules cm}^{-1} \text{ sec}^{-1}
\]

10ppm $T_2$ (static) - $4.6 \times 10^{-7}$ moles liter$^{-1}$
\[
\frac{d[T_2O]}{dt} = 6.9 \times 10^{-15} \text{ molecules cm}^{-1} \text{ sec}^{-1}
\]

10ppm $T_2$ (dynamic) - $4.0 \times 10^{-10}$ moles liter$^{-1}$
\[
\frac{d[T_2O]}{dt} = 5.9 \times 10^{-18} \text{ molecules cm}^{-1} \text{ sec}^{-1}
\]

As would be expected, the observed trend for catalyzed systems is in disagreement with the self-oxidation system. Our data shows the oxidation reaction to be more efficient at lower $T_2$ concentrations (higher $O_2$).

Comparing the water and organic reactions we find that the thermodynamic values do not tell us much. The heat of formation of $D_2O$ is $-295$ kJ/mole at 298K with an equilibrium constant of $K_{eq} = 10^{42}$. The hydrogenation of aliphatic alkynes has a heat of reaction of about $-140$kJ/mole and an equilibrium constant of $K_{eq} = 10^{23.6}$. Both reactions want to run to absolute completion.

Comparing the rate constants for a number of reactions between hydrogen atoms and hydrocarbons$^{27-32,35}$ we see that the basic water forming reactions are not fast compared to the organic reactions:

\[
H + C_2H_2 \rightarrow C_2H_3, \quad k = 2.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}; \quad (11)
\]

\[
H + C_2H_4 \rightarrow C_2H_5, \quad k = 1.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}; \quad (12)
\]

\[
H + C_3H_3 \rightarrow C_3H_5, \quad k = 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}; \quad (13)
\]

\[
H + C_3H_6 \rightarrow C_3H_7, \quad k = 1.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}; \quad (14)
\]

\[
H + C_4H_8 \rightarrow C_4H_9, \quad k = 1.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}; \quad (15)
\]

\[
H + C_4H_6 \rightarrow C_4H_7, \quad k = 8.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}; \quad (16)
\]

\[
H + C_6H_{12} \rightarrow C_6H_{13}, \quad k = 1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}; \quad (17)
\]
Ethene is known to be used as an inhibitor of the water forming reaction by reaction (12) above.\textsuperscript{32}

What makes the formation of water so efficient is the reaction on or near the catalyst. The mechanism is unknown. The catalyst provides an environment in which thermal energy is used to successfully pump up the evenly spaced vibrational levels of H\textsubscript{2} and O\textsubscript{2} until dissociation occurs. The dissociation energies of H\textsubscript{2} and O\textsubscript{2} are 436 and 498 KJ/mole, meaning that atoms of both will be formed simultaneously. We conclude that there is no easy way to compare the rates of the water and organic reactions from first principles.

Two important points do emerge. The first is to try to keep O\textsubscript{2} away from the catalyst surface. To this end the organic should completely surround the catalyst particle. The lighter mass T\textsubscript{2} will permeate the organic up to an order of magnitude faster than O\textsubscript{2}; the principle used in membrane gas separation.\textsuperscript{14} The second point is that distance between the catalyst and the organic should be as short as possible so that a tritium atom will meet few oxygen atoms or molecules while diffusing. The catalyst particle should be as small as possible and evenly dispersed on the substrate. In the case of our Pt or Pd catalysts, this depends on minute details in the synthesis that are largely trial and error.

The ability of the wetting agents to produce enhanced effects in the organic reaction is evident. These effects may be a result of improved catalyst dispersion or of improved covering of the substrate and catalyst by the organic or both. Samples of both 1,4-diphenylbutadiyne and 4-phenyl-3-butyn-1-ol with 1% platinum on firebrick plus wetting agent were subjected to analysis using electron micro-probe x-ray spectroscopy. No platinum peak was found in either case. This suggests that the platinum may be deeply embedded in the firebrick with the aid of the surfactant. It also suggests that the substrate and catalyst are effectively coated with more than 1 x 10\textsuperscript{-6} layer of organic.

**Future Work**

Our future work with organic getter systems will include further investigation of heterogeneous catalysis using organic/Pt getters and optimizing their performance for 1-10ppm T\textsubscript{2} in air. Liquid acetylenes and acetylene based alcohols will be evaluated to determine the contributing effect of the OH group in 4-phenyl-3-butyn-1-ol, our best candidate. In addition, we plan to develop a homogeneous catalysis system to assess these same materials. Attention will be given to a few specialized wetting agents and their affect on the efficiency of the organic reaction. Upon selection of the best material,
investigation into the disposal of organic getters will begin. This includes tests on the stability and hydrophobic nature of the materials chosen.

**Experimental Procedure**

A weighed amount of organic getter material is placed in a 50cc glass reaction flask and attached to the vacuum manifold for hydrogen activation. The sample is pumped on for 30-90 minutes at $10^{-3}$ torr. A pressure of hydrogen is then added to the sample to reduce 10% of the acetylene bonds. This "hydrogen activation" shortens the induction time of the reaction of tritium with the organic and was performed for all samples except the organometallics. When the pressure of hydrogen returns to zero the sample vessel is valved off and removed from the activation system. It is then attached to the getter system comprised of a copper manifold equipped with a 1000 torr baratron pressure transducer, a cryo-sorption pump, a mechanical pump and a gas cylinder containing T$_2$ in dry air. The system is pumped down to $10^{-4}$ torr then leak checked with helium. A pressure of tritium feed gas is then added to the manifold so that when expanded into the sample vessel it will produce reaction pressures close to 1 atmosphere. When the expanded gas reaches equilibrium, the valve to the sample vessel is closed and the reaction is allowed to proceed at room temperature for the duration of the test. The gas remaining in the manifold is then evacuated by the cryo-sorption pump. After the test the sample vessel is removed from the system for mass spec analysis of the gas remaining.

The reacted getter material is then placed in a 50cc glass column equipped with a coarse frit for support and a stopcock. The sample is first washed with 250cc of mixed solvent (90% methylene chloride, 10% diethyl ether) to dissolve and elute the organic getter. An aliquot of this solution is taken and the tritium is measured by liquid scintillation counting. The substrate is dried with a stream of argon then washed with 100cc deionized H$_2$O or 2M HCl to elute the tritium in the aqueous phase. An aliquot of this solution is taken and counted. Because water is slightly soluble in the organic solvent determined to be optimum for dissolving the organic getter and because some color present in the acid wash indicated that some organic may be present in this phase an aliquot of both fractions is taken and solvent extraction is performed to remove any HTO present in the organic fraction and any organic in the acid fraction. The activity separated by these washes is then added to their respective fractions to yield the total amount activity in each phase. The firebrick substrate is dissolved in a solution of concentrated hydrofluoric acid and nitric acid; an aliquot is taken and counted. The total activity found in each fraction is expressed as a mole percent of input tritium. The sum of these values in addition to the activity remaining in the gas phase gives the total closure number. Closure has varied from 11% to 100%. Low closure numbers may result from a loss of detectable tritium in the firebrick substrate as it is not completely dissolved by the HF and HNO$_3$. Sorption of tritium into the glass of the reaction vessel has been investigated and found to be less than 10%.
Acknowledgements

We wish to thank Gene Nardella and Jack Baublitz of the Office of Fusion Energy, Department of Energy, for their support of this work.

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Table I. Results for 1,4-Diphenylbutadiyne at 20°C and 1 ATM OF 300-500 ppm T₂ in static dry air

<table>
<thead>
<tr>
<th>Exp.</th>
<th>DPBD (w/w%)</th>
<th>Catalyst (w/w%)</th>
<th>Substrate</th>
<th>Initial Moles</th>
<th>% T in Phase</th>
<th>T₂</th>
<th>PPM</th>
<th>T₂</th>
<th>PPM</th>
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<td></td>
<td></td>
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<td>Gas</td>
<td>Source</td>
<td>Solvent</td>
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<td>60</td>
<td>5% Pd</td>
<td>CaCO₃</td>
<td>3</td>
<td>7</td>
<td>5</td>
<td>10.5</td>
<td>61.9</td>
<td>--</td>
</tr>
<tr>
<td>35</td>
<td>60</td>
<td>5% Pd</td>
<td>CaCO₃</td>
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<td>a</td>
<td>10.6</td>
<td>22.4</td>
<td>--</td>
<td>--</td>
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<tr>
<td>34</td>
<td>20</td>
<td>1% Pd</td>
<td>Fluoropak 80</td>
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<td>5</td>
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<td>33</td>
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<td>1% Pd</td>
<td>Chromosorb W</td>
<td>8</td>
<td>12</td>
<td>5</td>
<td>6.5</td>
<td>36.7</td>
<td>13.0</td>
</tr>
<tr>
<td>36</td>
<td>20</td>
<td>1% Pd</td>
<td>Chromosorb W</td>
<td>8</td>
<td>9</td>
<td>a</td>
<td>21.9</td>
<td>42.1</td>
<td>4.5</td>
</tr>
<tr>
<td>46</td>
<td>20</td>
<td>5%</td>
<td>Carbon</td>
<td>7</td>
<td>12</td>
<td>5</td>
<td>5.3</td>
<td>43.6</td>
<td>--</td>
</tr>
<tr>
<td>40</td>
<td>20</td>
<td>1% Pd</td>
<td>FIREBRICK</td>
<td>3</td>
<td>11</td>
<td>5</td>
<td>6.1</td>
<td>62.1</td>
<td>14.0</td>
</tr>
<tr>
<td>43</td>
<td>20</td>
<td>1% Pd</td>
<td>FIREBRICK</td>
<td>6</td>
<td>10</td>
<td>5</td>
<td>39.4</td>
<td>42.3</td>
<td>8.1</td>
</tr>
<tr>
<td>42</td>
<td>1% Pd</td>
<td>FIREBRICK</td>
<td>6</td>
<td>12</td>
<td>4</td>
<td>19.5</td>
<td>45.6</td>
<td>3.0</td>
<td>ND</td>
</tr>
<tr>
<td>47</td>
<td>1% Pd</td>
<td>FIREBRICK</td>
<td>4</td>
<td>11</td>
<td>5</td>
<td>46.6</td>
<td>48.4</td>
<td>5.0</td>
<td>ND</td>
</tr>
<tr>
<td>48</td>
<td>1% Pd</td>
<td>FIREBRICK</td>
<td>6</td>
<td>9</td>
<td>2</td>
<td>0.6</td>
<td>59.5</td>
<td>23.4</td>
<td>ND</td>
</tr>
<tr>
<td>54</td>
<td>20</td>
<td>1% Pt</td>
<td>FIREBRICK</td>
<td>6</td>
<td>9</td>
<td>3</td>
<td>74.8</td>
<td>4.8</td>
<td>104</td>
</tr>
<tr>
<td>60</td>
<td>1% Pt</td>
<td>FIREBRICK</td>
<td>6</td>
<td>9</td>
<td>3</td>
<td>33.1</td>
<td>55.4</td>
<td>4.0</td>
<td>ND</td>
</tr>
<tr>
<td>61</td>
<td>1% Pt</td>
<td>FIREBRICK</td>
<td>6</td>
<td>10</td>
<td>3</td>
<td>30.4</td>
<td>52.2</td>
<td>5.0</td>
<td>ND</td>
</tr>
<tr>
<td>41</td>
<td>1% Ni</td>
<td>FIREBRICK</td>
<td>5</td>
<td>11</td>
<td>5</td>
<td>3.7</td>
<td>20.1</td>
<td>0.2</td>
<td>85.2</td>
</tr>
<tr>
<td>47</td>
<td>1%Au</td>
<td>FIREBRICK</td>
<td>4</td>
<td>11</td>
<td>3</td>
<td>2.4</td>
<td>11.4</td>
<td>0.4</td>
<td>59.3</td>
</tr>
<tr>
<td>48</td>
<td>20</td>
<td>5% Au/1% Pd</td>
<td>FIREBRICK</td>
<td>3</td>
<td>13</td>
<td>3</td>
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<td>51.5</td>
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<td>38</td>
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<td>0.2% Ir</td>
<td>FIREBRICK</td>
<td>6</td>
<td>11</td>
<td>6</td>
<td>11.2</td>
<td>52.9</td>
<td>2.1</td>
</tr>
<tr>
<td>44</td>
<td>19.3</td>
<td>0.9% Ir</td>
<td>FIREBRICK</td>
<td>6</td>
<td>12</td>
<td>6</td>
<td>6.8</td>
<td>7.5</td>
<td>0.3</td>
</tr>
<tr>
<td>50</td>
<td>20</td>
<td>1%Ir</td>
<td>FIREBRICK</td>
<td>6</td>
<td>9</td>
<td>3</td>
<td>0.0</td>
<td>4.7</td>
<td>0.5</td>
</tr>
<tr>
<td>56</td>
<td>--</td>
<td>0.05%Ir</td>
<td>FIREBRICK</td>
<td>0</td>
<td>10</td>
<td>3</td>
<td>3.7</td>
<td>3.9</td>
<td>0.2</td>
</tr>
</tbody>
</table>

*Saska's Catalyst: Chlorocarbonylbis(Triphenylphosphine)Iridium

Feed gas was T₂ in Argon

45 ppm HT + 170 ppm H₂ remaining in gas phase

No HT or H₂ remaining in gas phase (activation with UV)

All tests were 48 hours duration

ND - No detectable tritium remaining in gas phase

NA - No analysis of remaining gases
Table II. Results for 1,4-Diphenylbutadiyne and 4-Phenyl-3-butyn-1-ol at 20°C and 1ATM of 10ppm T₂ in static dry air

<table>
<thead>
<tr>
<th>Exp. #</th>
<th>Organic Getter (w/w%)</th>
<th>Catalyst (w/w%)</th>
<th>Substrate</th>
<th>% T In Phase</th>
<th>Catalyst Source</th>
<th>Reducing Solvent</th>
<th>Wetting Agent</th>
<th>Test Duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>62T</td>
<td>20% DPBD</td>
<td>1% Pt</td>
<td>FIREBRICK</td>
<td>7.9</td>
<td>47.4</td>
<td>14.0</td>
<td>ND</td>
<td>MIM</td>
</tr>
<tr>
<td>65T</td>
<td>20% DPBD</td>
<td>1% Pt</td>
<td>FIREBRICK</td>
<td>10.5</td>
<td>42.9</td>
<td>22.7</td>
<td>ND</td>
<td>K₂PtCl₄</td>
</tr>
<tr>
<td>67T</td>
<td>20% DPBD</td>
<td>1% Pt</td>
<td>FIREBRICK</td>
<td>5.1</td>
<td>59.1</td>
<td>6.7</td>
<td>ND</td>
<td>K₂PtCl₄</td>
</tr>
<tr>
<td>68T</td>
<td>20% DPBD</td>
<td>1% Pt</td>
<td>FIREBRICK</td>
<td>10.2</td>
<td>67.4</td>
<td>11.8</td>
<td>ND</td>
<td>K₂PtCl₄</td>
</tr>
<tr>
<td>66T</td>
<td>20% DPBD</td>
<td>1% Pt</td>
<td>FIREBRICK</td>
<td>4.5</td>
<td>67.6</td>
<td>0.6</td>
<td>ND</td>
<td>PdCl₂</td>
</tr>
<tr>
<td>72T</td>
<td>20% DPBD</td>
<td>1% Pt</td>
<td>FIREBRICK</td>
<td>4.7</td>
<td>26.2</td>
<td>26.2</td>
<td>NA</td>
<td>PtCl₂</td>
</tr>
<tr>
<td>73T</td>
<td>20% DPBD</td>
<td>1% Pt</td>
<td>FIREBRICK</td>
<td>2.9</td>
<td>65.0</td>
<td>3.2</td>
<td>NA</td>
<td>PtCl₂</td>
</tr>
<tr>
<td>71T</td>
<td>20% DPBD</td>
<td>1% Pt</td>
<td>FIREBRICK</td>
<td>10.2</td>
<td>60.2</td>
<td>6.3</td>
<td>NA</td>
<td>PtCl₂</td>
</tr>
<tr>
<td>74T</td>
<td>20% DPBD</td>
<td>1% Pt</td>
<td>FIREBRICK</td>
<td>4.7</td>
<td>72.0</td>
<td>3.0</td>
<td>ND</td>
<td>PtCl₂</td>
</tr>
<tr>
<td>75T</td>
<td>20% DPBD</td>
<td>1% Pt</td>
<td>FIREBRICK</td>
<td>7.4</td>
<td>64.2</td>
<td>9.7</td>
<td>NA</td>
<td>PtCl₂</td>
</tr>
<tr>
<td>76T</td>
<td>20% DPBD</td>
<td>1% Pt</td>
<td>FIREBRICK</td>
<td>7.9</td>
<td>61.1</td>
<td>10.3</td>
<td>ND</td>
<td>PtCl₂</td>
</tr>
<tr>
<td>79S</td>
<td>20% DPBD</td>
<td>1% Pt</td>
<td>FIREBRICK</td>
<td>8.3</td>
<td>63.5</td>
<td>17.1</td>
<td>ND</td>
<td>PtCl₂</td>
</tr>
<tr>
<td>80S</td>
<td>20% DPBD</td>
<td>1% Pt</td>
<td>FIREBRICK</td>
<td>1.5</td>
<td>62.9</td>
<td>9.9</td>
<td>ND</td>
<td>PtCl₂</td>
</tr>
<tr>
<td>82S</td>
<td>20% DPBD</td>
<td>1% Pt</td>
<td>FIREBRICK</td>
<td>6.9</td>
<td>60.1</td>
<td>13.6</td>
<td>ND</td>
<td>PtCl₂</td>
</tr>
<tr>
<td>84S</td>
<td>20% DPBD</td>
<td>1% Pt</td>
<td>FIREBRICK</td>
<td>10.2</td>
<td>60.2</td>
<td>6.3</td>
<td>ND</td>
<td>PtCl₂</td>
</tr>
<tr>
<td>85S</td>
<td>20% DPBD</td>
<td>1% Pt</td>
<td>FIREBRICK</td>
<td>4.0</td>
<td>60.1</td>
<td>6.7</td>
<td>NA</td>
<td>PtCl₂</td>
</tr>
<tr>
<td>69T</td>
<td>20% PBol</td>
<td>1% Pt</td>
<td>FIREBRICK</td>
<td>17.9</td>
<td>60.1</td>
<td>6.7</td>
<td>NA</td>
<td>PtCl₂</td>
</tr>
<tr>
<td>70T</td>
<td>20% PBol</td>
<td>1% Pt</td>
<td>FIREBRICK</td>
<td>15.0</td>
<td>54.2</td>
<td>13.6</td>
<td>NA</td>
<td>PtCl₂</td>
</tr>
</tbody>
</table>

`a` Wetting agent put on substrate with the organic
`b` *Material was post heated to 100°C for 2 hours before test*
`c` Special test parameters: high pressure (1069 torr), low temperature (0°C)

ND - No detectable tritium remaining in gas phase
NA - No analysis of remaining gases

Wetting Test

<table>
<thead>
<tr>
<th>Wetting Agent</th>
<th>Duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerosol-OT</td>
<td>48 hrs</td>
</tr>
<tr>
<td>Aerosol-AV</td>
<td>24 hrs</td>
</tr>
<tr>
<td>DC Antifoam</td>
<td>24 hrs</td>
</tr>
<tr>
<td>Span 80</td>
<td>24 hrs</td>
</tr>
<tr>
<td>Aerosol-OT</td>
<td>6 hrs</td>
</tr>
<tr>
<td>Aerosol-AV</td>
<td>6 hrs</td>
</tr>
<tr>
<td>Aerosol-AV</td>
<td>6 hrs</td>
</tr>
<tr>
<td>Aerosol-AV</td>
<td>6 hrs</td>
</tr>
</tbody>
</table>

Table III. Dynamic air flow tests on 1,4-Diphenylbutadiyne and 4-Phenyl-3-butyn-1-ol at 20°C and 1ATM of 10ppm T₂ in dry air.

<table>
<thead>
<tr>
<th>Exp. #</th>
<th>Organic Getter (w/w%)</th>
<th>Catalyst (w/w%)</th>
<th>Substrate</th>
<th>% T In Phase</th>
<th>Catalyst Source</th>
<th>Reducing Solvent</th>
<th>Wetting Agent</th>
<th>Flow Rate, €pm</th>
</tr>
</thead>
<tbody>
<tr>
<td>77D</td>
<td>20% PBol</td>
<td>1% Pt</td>
<td>FIREBRICK</td>
<td>22.6</td>
<td>10.1</td>
<td>4.8</td>
<td>ND</td>
<td>MIM</td>
</tr>
<tr>
<td>83D</td>
<td>20% DPBD</td>
<td>1% Pt</td>
<td>FIREBRICK</td>
<td>8.0</td>
<td>76.7</td>
<td>10.3</td>
<td>ND</td>
<td>MIM</td>
</tr>
<tr>
<td>87D</td>
<td>20% PBol</td>
<td>1% Pt</td>
<td>FIREBRICK</td>
<td>24.8</td>
<td>67.9</td>
<td>7.5</td>
<td>ND</td>
<td>MIM</td>
</tr>
<tr>
<td>88D</td>
<td>20% PBol</td>
<td>1% Pt</td>
<td>FIREBRICK</td>
<td>22.1</td>
<td>66.7</td>
<td>7.0</td>
<td>ND</td>
<td>MIM</td>
</tr>
</tbody>
</table>

`a` Surfactant put on substrate with the organic
`b` All tests were 24 hours duration

ND - No detectable tritium remaining in gas phase
Table IV. The conversion of tritium to HTO in various gas mixtures

<table>
<thead>
<tr>
<th>Mixture</th>
<th>T₂ Concentration (Ci liter⁻¹)</th>
<th>Conversion rate dHTO/dt (Ci liter⁻¹ sec⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>T₂ + H₂ + O₂</td>
<td>95-328</td>
<td>1.98 x 10⁻⁶ T₂</td>
<td>a</td>
</tr>
<tr>
<td>T₂ + O₂ + Ar</td>
<td>0.09-90</td>
<td>1.7 x 10⁻⁸ T₂ ⁵⁄₃</td>
<td>b</td>
</tr>
<tr>
<td>T₂ + O₂ + N₂</td>
<td>0.018-1</td>
<td>3.30 x 10⁻⁷ T₂ ²</td>
<td>c</td>
</tr>
<tr>
<td>T₂ + O₂ + H₂O</td>
<td>&lt; 1</td>
<td>1.20 x 10⁻⁶ T₂ ²</td>
<td>c</td>
</tr>
<tr>
<td>T₂ + Dry Air</td>
<td>0.015-0.8</td>
<td>1.7 x 10⁻⁷ T₂ ²</td>
<td>c</td>
</tr>
<tr>
<td>T₂ + H₂O + He, N₂, Ar, Kr</td>
<td>0.05-0.7</td>
<td>4.2 x 10⁻⁷ T₂ ²</td>
<td>d</td>
</tr>
<tr>
<td>T₂ + H₂O + Dry Air</td>
<td>6 x 10⁻⁴-600</td>
<td>1.7 x 10⁻⁸ T₂ ⁵⁄₃</td>
<td>b</td>
</tr>
</tbody>
</table>

HERRMANN: Do you have any idea of the costs of this substance, the diphenylbutadiene?

MILLER: It is a very inexpensive organic material. I cannot quote figures because we have not approached that particular stage of our development yet. However, the fire brick substrate is a very cheap material which is basically just a diatomaceous earth composite. The skeletal structures of diatoms are pressed into a diatomaceous earth and are used in chromatographic supports and also other filtration systems. All of the materials are very cheap, except for the catalyst itself. The catalyst is used in approximately 1% concentration. We still have some work in evaluating whether or not that could be brought to minimum. We have some idea that we could reduce that by a factor of ten. In looking at the economic ramifications, I think that only the platinum catalyst, itself, will be the expensive part of it.

LAMBERGER: Do you have data that show that the tritium is really tied up in that organic molecule? And have you monitored the tritium release from that compound over time to see what the radiation dose does to the compound?

MILLER: Yes, we have measured that the tritium has reacted with the organic. As I said, it is not enough just to say that we are going to remove the tritium from air 100%. It is important to realize that the same catalyst that reacts the acetylene bond goes to make water. Therefore, we have analyzed our phases very carefully to evaluate the percents, and the percents that were shown here are those that went into the organic. The rest, for total closure of 100%, is the amount that went to form water. Now, the second part of your question which was, have we measured the outgassing instability of the material? No, that is something that will come later and is on our future list as something that is definitely planned.

LAMBERGER: Do you have an expectation that after five years, or ten years, that most of the tritium would still be in that compound? You say you have picked the compound on purpose because it has certain inherent expected stability.

MILLER: I cannot say, other than the fact that it is a relatively nonvolatile organic and it does have the phenyl groups that are present to give radiation stability. That is yet to be measured.

PATEL: Has any other work been done on capturing airborne tritium in the containment?

MILLER: Did I understand your question as, has anyone else done work on this?

PATEL: Yes. And in the future, will you develop some kind of routine system to capture airborne tritium? Have you got a system for containment systems and reprocessing streams?
MILLER: There are a number of attractive engineering applications. As far as I know, there is no one currently working on gathering tritium from air. Many people feel that they have an effective technology right now by deliberately oxidizing tritium to make water and adsorbing it on zeolite. But with the current political situation, and the need to sell fusion energy as a clean technology, I think that they may have to address the fact that it would be more favorable not to increase the radiotoxicity of tritium by a factor of 25,000 for the purpose of waste disposal. Addressing your question about reprocessing streams, there are people at Savannah River who have approached me with great interest in the ramifications of the work and its application to processing streams for removing very low level tritium concentrations from equipment or gas streams. The water problem is a problem in many reprocessing steps. We have proposed a better system for use in static air for $T_2$ concentrations of 100-500 ppm in air which is approximately 75% efficient, i.e., 75% of the input $T_2$ reacts with the organic compound, the other 25% makes water.

STONE: Would you say a word about the safety aspects of these compounds?

MILLER: As far as the toxicity of the material is concerned, all I can say at this point is that it is a hydrophobic material and is relatively nonvolatile. By comparison, the toxicity has to be far less than water (tritiated), but I cannot give you a number. We have been doing this work for a year now, and although we have covered a lot of territory, there is still a lot of territory to cover. From the fact that tritiated water is the most easily assimilated form of tritium, in that it is 100% absorbed by the body, it seems that any of the nonvolatile organics would be an improvement.

STONE: Do they offer any fire or explosion hazards?

MILLER: No fire or explosion hazards. We are not using organic compounds that could form peroxides or other explosive groups. We have avoided those intentionally by looking for stable compounds.