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INFRARED DIODE LASER ABSORPTION*

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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.[1]

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

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

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 x 10^{-11} g/cm^3 or 3 x 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.[8] 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.[8]

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.[8] 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 availale for $^{14}C^{16}O_2$ 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_2O, N_2O, 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 (± 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

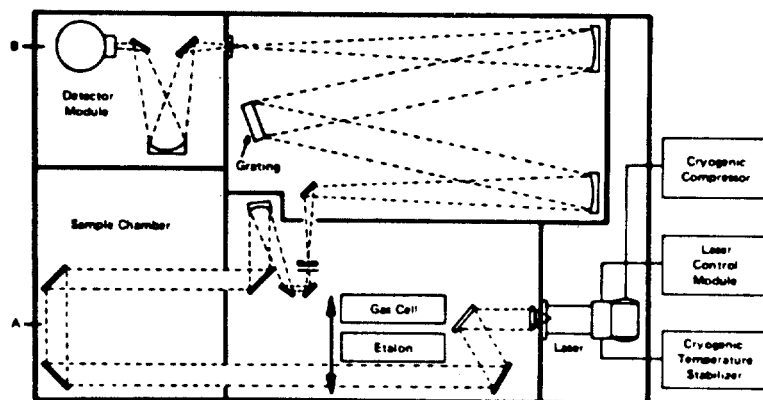The laser diode spectrometer is shown in Figure 1.

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 $^{14}CO_2$, can be tuned from 2200 cm^{-1} to 2250 cm^{-1} with a 1×10^{-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.
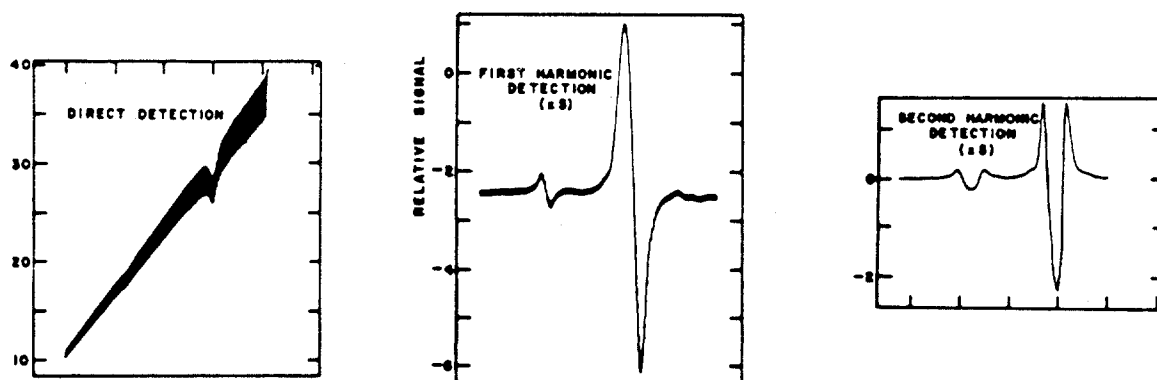

Figure 2. These plots demonstrate three detection schemes for scanning infrared laser diode absorption spectra. The three traces are taken under identical experimental conditions. The dramatic noise reduction in the spectra is apparent with the second harmonic detection scheme.

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

Molecule	Absorption Coefficient of Strong Lines $(m^{-1}ppb^{-1})$	Approximate Wavenumber of Lines (cm^{-1})	Sensitivity (ppb)
CH_4	3×10^{-6}	1300	0.03
SO_2	3.5×10^{-7}	1370	0.3
NO_2	5×10^{-6}	1600	0.02
NO	3×10^{-6}	1880	0.03
CO	10^{-5}	2120	0.01
CO_2	10^{-4}	2350	0.001

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.
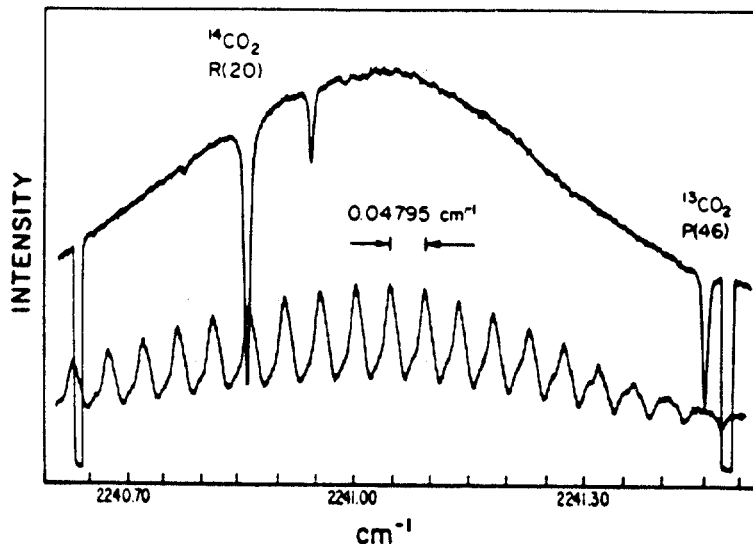

Figure 3. Spectral absorption scan near 2241 cm^{-1} showing the $^{14}CO_2$ R (20) and $^{13}CO_2$ P (46) lines. The un-labeled feature near the center of the scan is a $^{13}CO_2$ line at 2240. 95/cm^{-1}. The lower trace shows an etalon fringe scan. The etalon free spectral range is 0.04795 cm^{-1}. 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_2O. 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_2O features can be removed by first flowing the effluent through a 5% Pt:Pd catalyst at 350°C. The N_2O is oxidized to NO_2 quantitatively and no absorption features are then detectible which correspond to N_2O. 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.
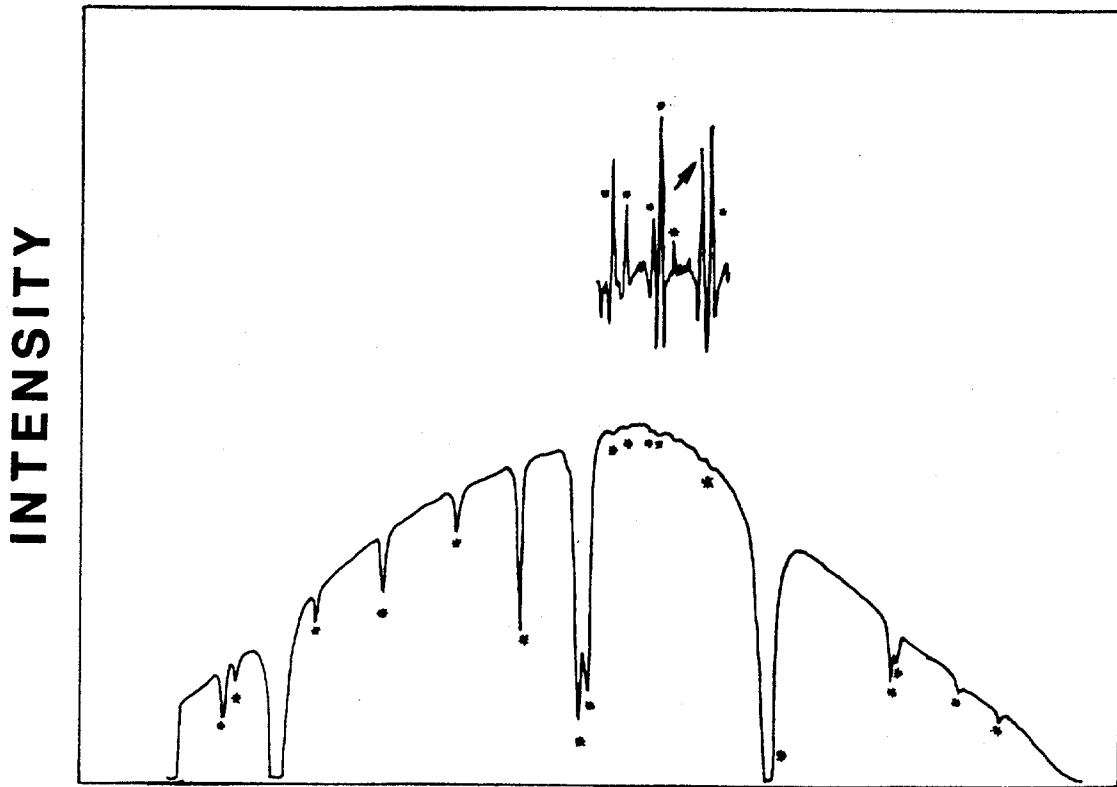
Figure 4.   Absorption spectrum of $^{14}CO_2$ at 80 ppb in a 80
            ppb in a synthetic effluent mixture. The mix-
            ture contains: "Air", 87.6%; CO_2, 3.66%; CO,
            0.78%; NO_2, 0.21%; N_2O, 0.10%; CH_4, 0.20%; C_2H_4,
            0.0095%; $^{14}CO_2$, 80 ppb. The $^{14}CO_2$ feature is
            indicated in the second derivative spectrum by
            an arrow.

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 fre-
quency with a current amplitude equal to exactly one of these fringe
spacings essentially washes out this pattern and results in an addi-
tional 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 mul-
tiple modulation techniques of Reid to routinely monitor concen-
trations in the few ppt range.

One of the more frustrating problems in the R&D involving scan-
ning diode laser spectrometers is acquiring the laser diodes them-
selves. 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 $H^{129}I$, TF, and TCl. Figure 5 gives an example of the absorption spectrum of 90% $H^{129}I$ and 10% $H^{127}I$ at a total pressure of 80 mtorr. The arrow corresponds to the predicted position of $H^{131}I$.
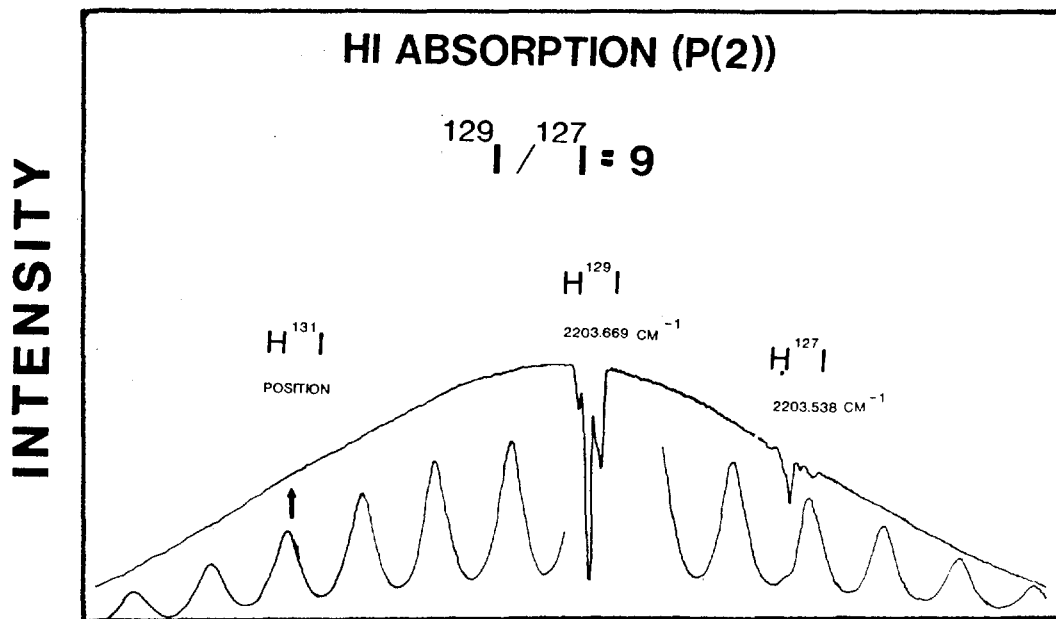

Figure 5. Absorption spectrum of 90% $H^{129}I$ and 10% $H^{127}I$. The expected position of $H^{131}I$ is labeled.

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 ^{129}I and ^{127}I. 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% $H^{129}I$ in $H^{127}I$. Even at this level of dilution, we have found no interference problems in monitoring $H^{129}I$.
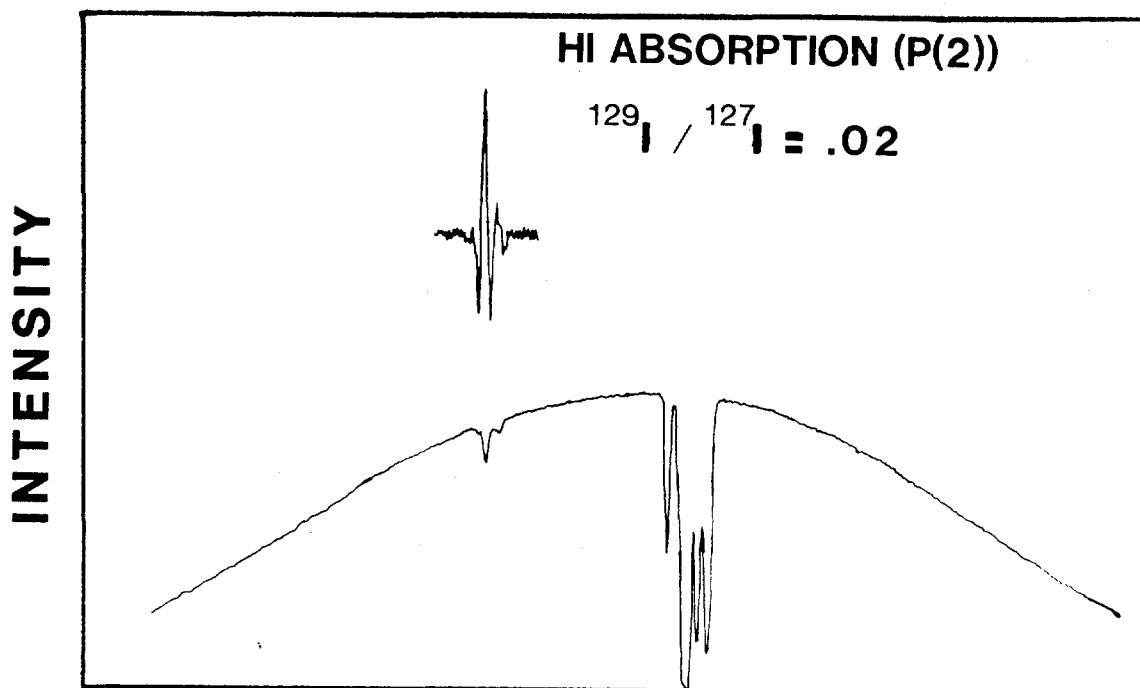
Figure 6. Absorption and second derivative spectra of 2% $H^{129}I$ in HI.

Since ^{129}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 characoal 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}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_2O 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.
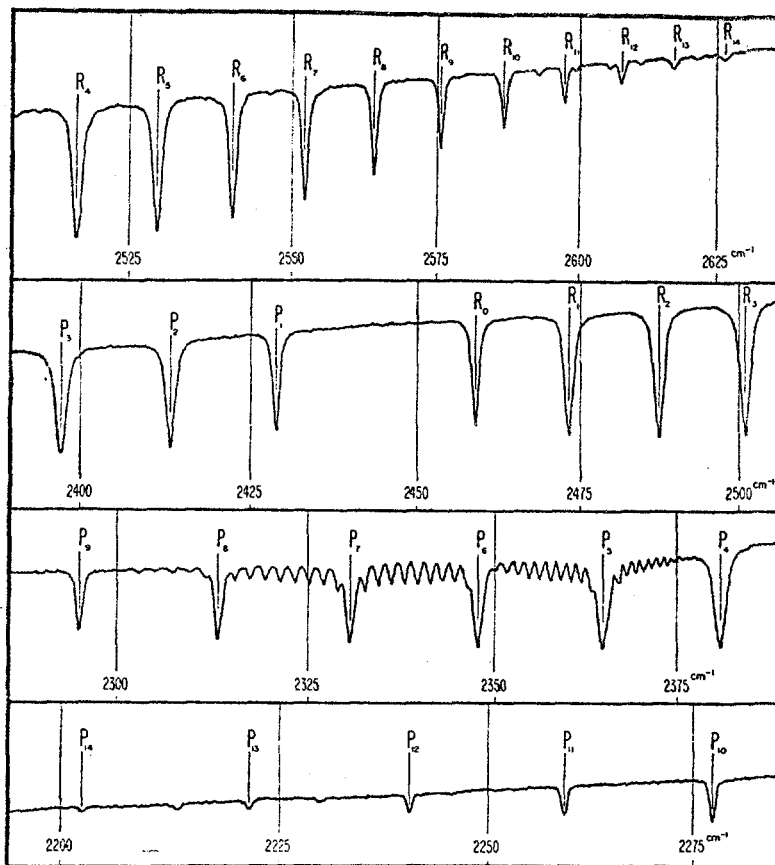
Figure 7. Conventional infrared absorption spectrum of 240 torr of TF with a 10 cm path length at room temperature.

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. $H^{127}I$ lines can be used to calibrate $H^{129}I$ and $H^{131}I$ 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 consumming modifications to the instrument.

Further developmental 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.

References

1. "Removal of ^{14}C-contaminated CO_2 from simulated
    LWR Full Reprocessing Off-gas by Utilizing the Reaction
    Between CO_2 and Alkaline Hydroxides in Either Slurry
    or Solid Form"
    D. W. Holladay and G. L. Haag
    15th DoE Nuclear Air Cleaning Conference, Boston, MA., Aug. 1978.

2. "C-14 Gaseous Effluents from Pressurized Water Reactors"
    C. Kunz, W. E. Mahoney, and T. W. Miller
    Health Physics Society, Symposium on Population Expenses,
    Knoxville, TN, October 1974.

3. "C-14 Gaseous Effluents from Boiling Water Reactors"
    C. Kunz, W. E. Mahoney, and T. W. Miller
    Annual Meeting of the American Nuclear Society,
    New Orleans, LA June 1975.

4. C. O. Kunz, W. E. Mahoney and T. W. Miller
    Trans. Am. Nucl. Soc. 21, 91 (1975).

5. "Process Behavior of and Environmental Assessments of ^{14}C
    Releases from an HTGR Fuel Reprocessing Facility"
    J. W. Snider and S. V. Kaye
    Controlling Airborne Effluents from Fuel Cycle Plants,
    ANS-AeChE Meeting, Sun Valley, ID, August 1976.

6. "Nuclear Energy: Health Impact of Carbon-14"
    R. O. Pohl
    Rad. And Environm. Biophys. 13, 315 (1976).

7. "Production and Emission of Carong-14 from Nuclear Power
    Stations and Reprocessing Plants and its Radiological
    Significance"
    H. Bonka, K. Brusserman, G. Schwartz and V. Wollrodt
    4th International Congress of the IRPA, Paris, April 1977.

8. "Monitoring and Removal of Gaseous Carbon-14 Species"
    M. J. Kabot
    15th DoE Nuclear Air Cleaning Conference, Boston, MA, August 1978.

9. "The Predicted Radiation Exposure of the Population of the
    European Community Resulting from Discharfges of Krypton-85,
    Tritium, Carbon-14, and Iodine-129 from the Nuclear Power
    Industry in the Year 2000."
    J. N. Kelly, J. A. Jones, P. M. Bryant and F. Morley
    V/2676/75 Commission of the European Communities, Luxemburg,
    September 1975.

10. "Public Health Considerations of Carbon-14 Discharges from
    Light Water-Cooled Nuclear Power Reactor Industry"
    T. W. Fowler, R. L. Clark, J. M. Gruheke and J. L. Russell
    OPR/Tad-76-3, U.S.E.P.A., July 1976.

11. J. Reid, J. Schewchun, B. K. Garside, and E. A. Ballik
    App. Opt. 17, 300 (1978).

12. E. D. Hinkley
    Laser Monitoring of the Atmosphere
    (Springe-Verlag, New York, 1976), Chapter 6.

13. S. Fernandez, Private Communication

14. J. Reid, Private Communication

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.

CARBON-14 IMMOBILIZATION VIA THE CO_2–Ba(OH)$_2$ HYDRATE GAS–SOLID REACTION*

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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 CO_2–Ba(OH)$_2$ hydrate gas–solid reaction to directly remove and immobilize ^{14}C. The reaction product, $BaCO_3$, 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 CO_2) gas streams.

Experimental studies have been conducted on fixed and fluidized beds of Ba(OH)$_2$ hydrates. For these studies, commercial-grade Ba(OH)$_2$·H$_2$O, Ba(OH)$_2$·5H$_2$O, and Ba(OH)$_2$·8H$_2$O and analytical-grade Ba(OH)$_2$·8H$_2$O have been examined. Studies at ambient conditions have indicated Ba(OH)$_2$·8H$_2$O to be the active species. Therefore, process operating conditions will likely be required which favor the formation of Ba(OH)$_2$·8H$_2$O. The dissociation water vapor pressure for Ba(OH)$_2$·8H$_2$O at 25°C is 1.10 kPa (8.26 mm Hg). Although both commercial- and analytical-grade Ba(OH)$_2$·8H$_2$O have been found to be reactive toward CO_2, they are considerably less reactive than either Ba(OH)$_2$·H$_2$O or Ba(OH)$_2$·5H$_2$O which have been hydrated to Ba(OH)$_2$·8H$_2$O. We have observed that during the fixed-bed treatments of humidifed-air gas streams, the two reactants undergo a conditioning period during which the 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 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 Ba(OH)$_2$·8H$_2$O flakes possess acceptable 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 CO_2 or low-molecular-weight hydrocarbons with the most probable method of treatment being the oxidation of the hydrocarbons to CO_2 and subsequent fixation of the CO_2. Likely CO_2 gas concentrations would range from 10 to 330 ppm with gas flow rates of up to 20 m^3/min (700 ft^3/min) anticipated. Expected release rates from various nuclear facilities are presented in Table I.

Table I. Approximate production and release rates of ^{14}C in the Nuclear Fuel Cycle[2]

Nuclear Reactors	Ci/Gw(e)yr
LWR	8-10
CANDU	500
Reprocessing Plant	
LMFBR	6
LWR	18
HTGR	200

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/man-rem.

II. Suggested Technologies for $^{14}CO_2$ Control

Suggested technologies for ^{14}C control have generally followed commercially available technology for CO_2 control. The processes range from CO_2 absorption in amine-bearing solutions to physical adsorption on molecular sieves to chemical reaction with a NaOH solution and carbonate interchange with $Ca(OH)_2$, the double alkali process.[15] However physical absorption, adsorption, and reaction with NaOH solution share a common trait in that they are CO_2 removal processes, but they do not chemically fix the CO_2 for final disposal, a requisite for the disposal of nuclear waste. Therefore, suggested technologies for the treatment of dilute CO_2-bearing gases have generally employed a removal or an enrichment step to increase the CO_2 gas concentration, followed by a final fixation step whereby the

CO_2 is reacted with $Ca(OH)_2$ slurry.[15-20] The product, $CaCO_3$, 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-CO_2-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 CO_2-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 CO_2 sorbents such as ascarite (NaOH on asbestos) and $LiOH \cdot H_2O$, which has been used extensively for CO_2 control in life support systems, lack sufficient carbonate stability for final waste disposal. Studies in CO_2 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 Na_2CO_3 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 CO_2 partial pressures [21,22]

|	Molal solubility		Decomposition temperature (°C)
	25°C	100°C	
Group 1 carbonates			
Li_2CO_3	0.18	0.10	1310
Na_2CO_3	2.80	4.26	—
K_2CO_3	8.10	4.41	—
Rb_2CO_3	19.48	—	740
Cs_2CO_3	8.00	—	610
Group 2 carbonates			
$MgCO_3$	0.00126[a]	—	350
$CaCO_3$	0.00013	0.000375	825
$SrCO_3$	0.000075	0.00044	1340
$BaCO_3$	0.000124	0.000332	1450

[a]Cold water.

It has been suggested in the literature, and confirmed experimentally at ambient conditions in our lab, that a $CaCO_3$ coating forms about the $Ca(OH)_2$ reactant thereby resulting in severe diffusional limitations.[29] 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.[30] 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.[5]

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.[31] 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 $LiOH_2 \cdot H_2O$, $Sr(OH)_2 \cdot 8H_2O$, $Ba(OH)_2 \cdot H_2O$, and $Ba(OH)_2 \cdot 8H_2O$ would be efficient CO_2 absorbents if the chemical reactions were kinetically favored. One might also predict $Ba(OH)_2 \cdot 8H_2O$ to be more efficient than $Ba(OH)_2 \cdot H_2O$ for CO_2 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[32] and the Naval Research Laboratory[33] have indicated $LiOH \cdot H_2O$, Pilling-Bedworth ratio of 0.64, to be the reactive species in CO_2 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[29] as being reactive toward CO_2 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

$$Ba(OH)_2 \cdot xH_2O(s) + CO_2(g) \rightarrow BaCO_3(s) + (x+1)H_2O(g) , \qquad (1)$$
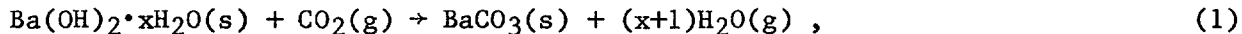
where x is the initial degree of hydration.

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, Kovtunenko, and Bundel.[34] The results were published in 1964. In this study, the water vapor pressure of $Ba(OH)_2 \cdot xH_2O$ 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
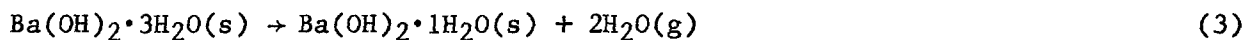
Table III. Molar volume relationships among some possible
carbon dioxide absorbents

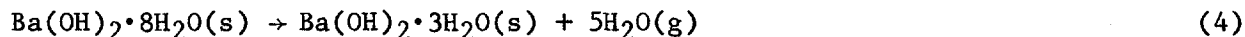| Substance	Formula weight	Density (g/cm^3)	Molar volume $(cm^3/g\text{-mole})$	Pilling-Bedworth ratio
LiOH	23.95	1.43	16.75	1.07
$LiOH \cdot H_2O$	41.96	1.51	27.79	0.64
Li_2CO_3	73.89	2.07	35.70	
NaOH	40.01	2.13	18.78	$1.47\text{-}Na_2CO_3 \cdot H_2O$
				$1.13\text{-}Na_2CO_3$
Na_2CO_3	106.00	2.51	42.25	
$Na_2CO_3 \cdot H_2O$	124.02	2.25	55.12	
$Mg(OH)_2$	58.34	2.39	24.41	1.14
$MgCO_3$	84.33	3.04	27.77	
$Ca(OH)_2$	74.10	2.34	31.63	1.18
$CaCO_3$	100.09	2.71	36.92	
$Sr(OH)_2 \cdot 8H_2O$	265.76	1.90	139.87	0.29
$SrCO_3$	147.63	3.70	39.90	
$Ba(OH)_2 \cdot 8H_2O$	315.48	2.10	150.23	0.30
$Ba(OH)_2 \cdot 1H_2O$	189.48	3.65	51.8	0.86
$BaCO_3$	197.35	4.43	44.47	

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 $Ba(OH)_2 \cdot H_2O$,
$Ba(OH)_2 \cdot 3H_2O$, and $Ba(OH)_2 \cdot 8H_2O$ 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:

$$Ba(OH)_2 \cdot 1H_2O(s) \rightarrow Ba(OH)_2(s) + H_2O(g) \tag{2}$$

$$\log P = -\frac{61353}{19.155T} + 12.421 ,$$

$$Ba(OH)_2 \cdot 3H_2O(s) \rightarrow Ba(OH)_2 \cdot 1H_2O(s) + 2H_2O(g) \tag{3}$$

$$\log P = \frac{-62618}{19.155T} + 13.823 ,$$

$$Ba(OH)_2 \cdot 8H_2O(s) \rightarrow Ba(OH)_2 \cdot 3H_2O(s) + 5H_2O(g) \tag{4}$$

$$\log P = \frac{-58230}{19.155T} + 13.238 ,$$

where

P = vapor pressure, Pa or $nt \cdot m^{-2}$,

T = temperature, K.

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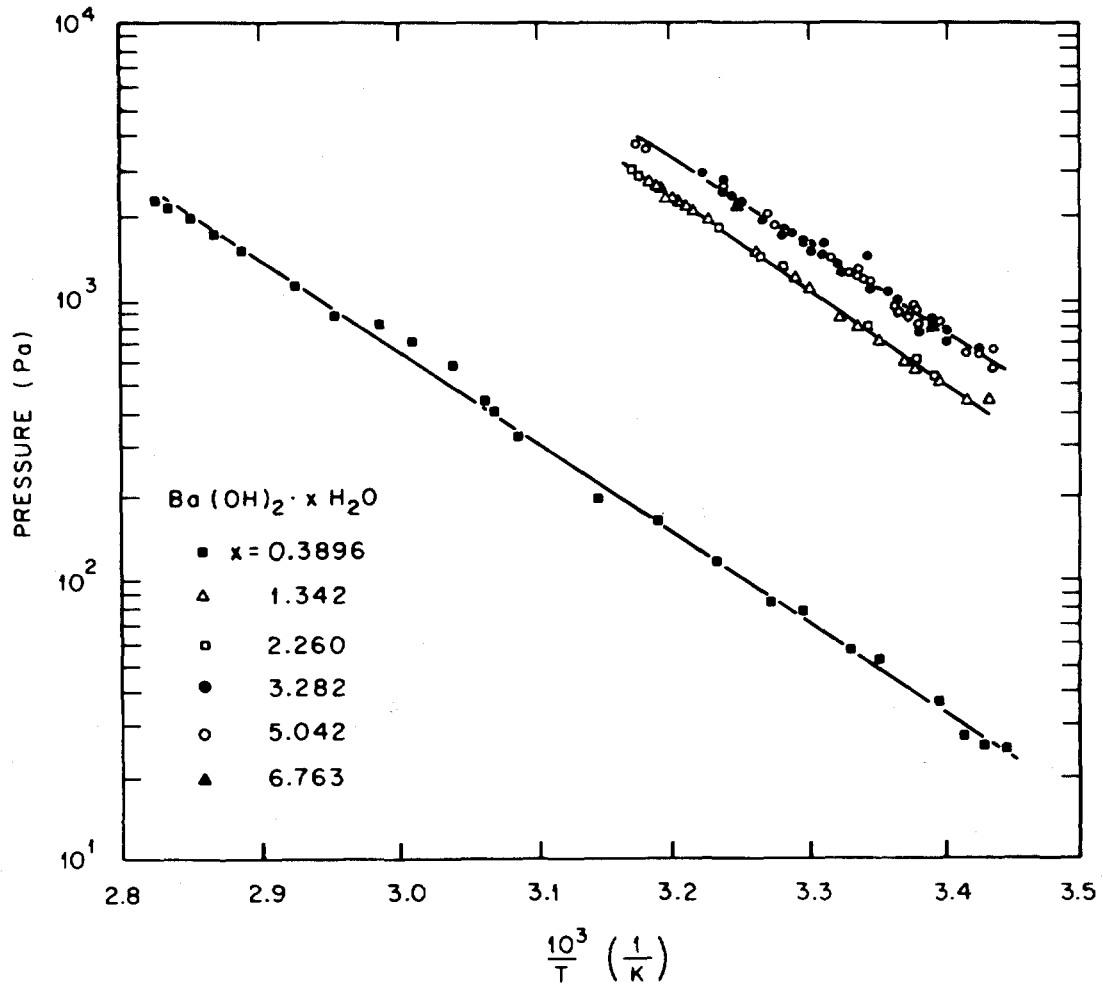Fig. 1. Dissociation vapor pressures for Ba(OH)$_2$ hydrates.

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 $Ba(OH)_2 \cdot 2H_2O$ and amorphous compounds to exist.

With the exception of $Ba(OH)_2 \cdot 2H_2O$, 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:
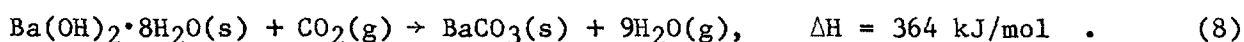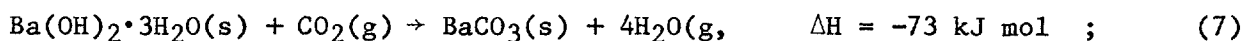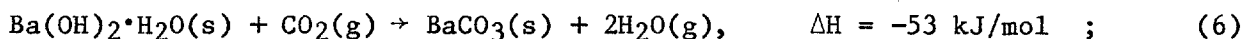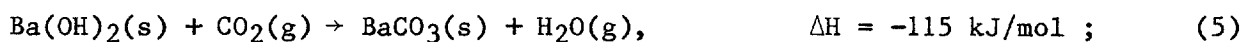
$$Ba(OH)_2(s) + CO_2(g) \rightarrow BaCO_3(s) + H_2O(g), \qquad \Delta H = -115 \text{ kJ/mol} ; \qquad (5)$$

$$Ba(OH)_2 \cdot H_2O(s) + CO_2(g) \rightarrow BaCO_3(s) + 2H_2O(g), \qquad \Delta H = -53 \text{ kJ/mol} ; \qquad (6)$$

$$Ba(OH)_2 \cdot 3H_2O(s) + CO_2(g) \rightarrow BaCO_3(s) + 4H_2O(g, \qquad \Delta H = -73 \text{ kJ mol} ; \qquad (7)$$

$$Ba(OH)_2 \cdot 8H_2O(s) + CO_2(g) \rightarrow BaCO_3(s) + 9H_2O(g), \qquad \Delta H = 364 \text{ kJ/mol} . \qquad (8)$$

Table IV. Thermodynamic properties of the CO_2-$Ba(OH)_2$ hydrate gas-solid reaction at 298.15 K[32-37]

| Reaction	ΔG kJ·mol^{-1}	ΔH kJ·mol^{-1}	ΔS J·mol^{-1}· K^{-1}	K_{eq}
5	-85.7	-114.6	-37.2	$1.05 \cdot 10^{15}$
6	-66.5	-53.0	104.6	$4.52 \cdot 10^{11}$
7	-41.6	-72.6	442.3	$1.94 \cdot 10^{7}$
8	15.9	364.4	1230.0	0.00187
9	-61.9	-31.8	161.3	$6.84 \cdot 10^{10}$

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 ∿1. 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
CO_2—$Ba(OH)_2$ hydrate gas-solid reaction

Reaction	K_{eq}	Reactant hydration	P_{CO_2}	
			Pa	mm Hg
5	$1.0 \cdot 10^{15}$	0	$3.1 \cdot 10^{-12}$	$2.4 \cdot 10^{-14}$
6	$4.52 \cdot 10^{11}$	1	$2.2 \cdot 10^{-10}$	$1.7 \cdot 10^{-12}$
7	$1.94 \cdot 10^{7}$	3	$5.0 \cdot 10^{-9}$	$3.7 \cdot 10^{-11}$
8	$1.87 \cdot 10^{-3}$	8	$1.5 \cdot 10^{-6}$	$1.1 \cdot 10^{-8}$
9	$6.84 \cdot 10^{10}$	8	$1.5 \cdot 10^{-6}$	$1.1 \cdot 10^{-8}$

Based upon a dissociation pressure for $Ba(OH)_2 \cdot 8H_2O$ 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 $Ba(OH)_2 \cdot 8H_2O$. 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 CO_2 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:

$$Ba(OH) \cdot 8H_2O(s) + CO_2(g) \rightarrow BaCO_3(s) + 9H_2O(l) \quad H = -32 \text{ kJ/mol} . \qquad (9)$$
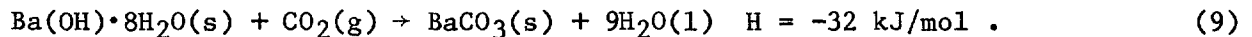
Again, the reactions will be equilibrium controlled only for very low CO_2 partial pressures.

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 CO_2, 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 CO_2 — $Ba(OH)_2$ hydrate gas-solid reaction and to develop a process capable of treating a high-volumetric, low-CO_2-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 $Ba(OH)_2 \cdot 8H_2O$ and commercially available $Ba(OH)_2 \cdot H_2O$, $Ba(OH)_2 \cdot 5H_2O$, and $Ba(OH)_2 \cdot 8H_2O$. 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 $Ba(OH)_2 \cdot 8H_2O$ flakes. Reactant analyses were conducted on two 200-lb drums of the commercial $Ba(OH)_2 \cdot 8H_2O$. These results are presented in Table VII.

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

Sample	Observed line intensities
$Ba(OH)_2 \cdot H_2O$	$Ba(OH)_2 \cdot H_2O$ – strongest
	$Ba(OH)_2 \cdot 3H_2O$
$Ba(OH)_2 \cdot 5H_2O$	$Ba(OH)_2 \cdot H_2O$ ⎤
	$\cdot 3H_2O$ ⎟ – same intensity
	$\cdot 8H_2O$ ⎦
$Ba(OH)_2 \cdot 8H_2O$ – commercial	Unidentified
$Ba(OH)_2 \cdot 8H_2O$ – analytical	$Ba(OH)_2 \cdot 8H_2O$

Table VII. Reactant analyses on commercial $Ba(OH)_2 \cdot 8H_2O$

Drum No.	Average composition	Standard deviation	Number of samples
1	$Ba(OH)_2 \cdot 7.54H_2O$	0.0966	12
2	$Ba(OH)_2 \cdot 7.47H_2O$	0.0830	20

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 $Ba(OH)_2 \cdot 8H_2O$.
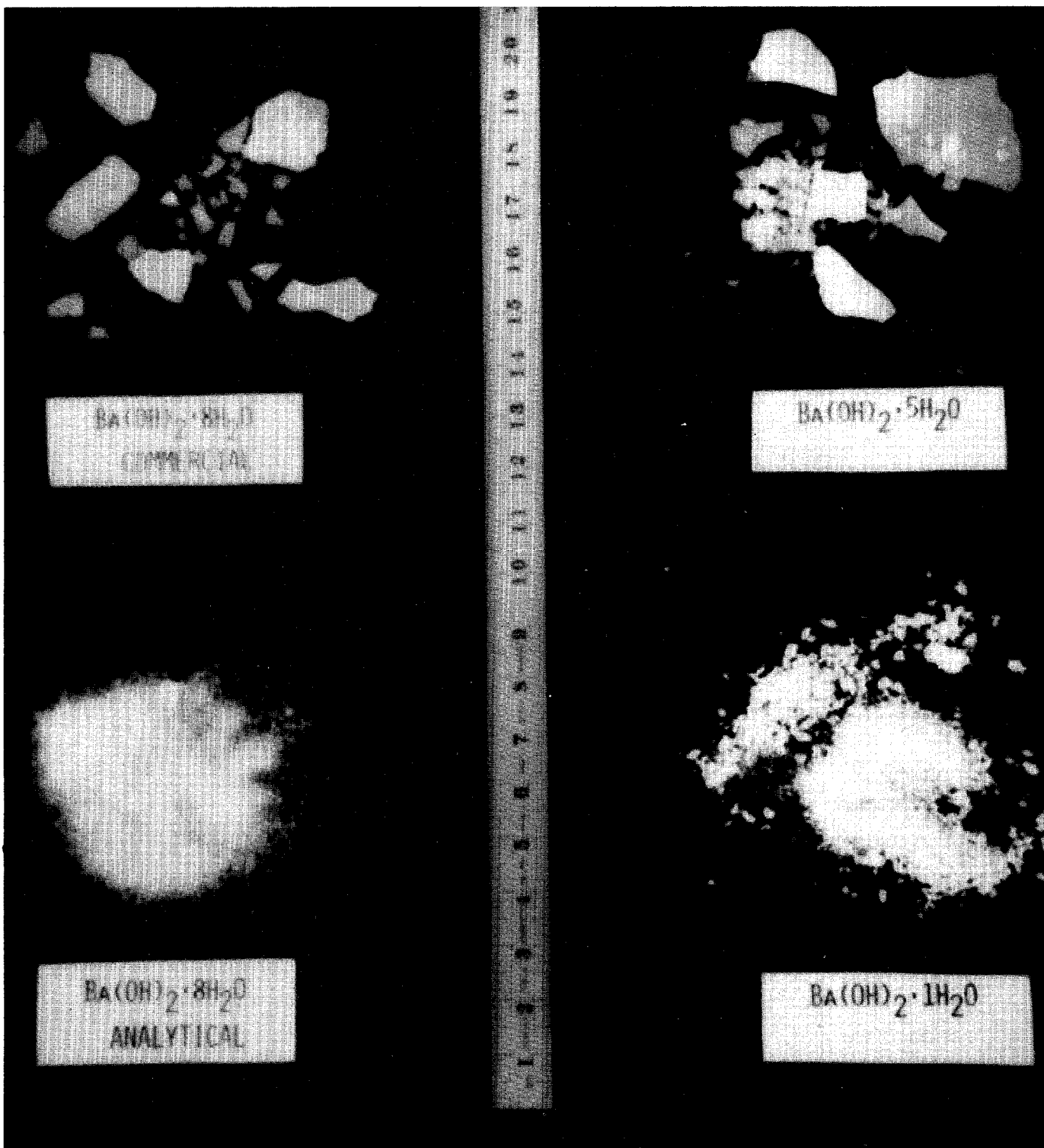
Fig. 2. Commercial and analytical Ba(OH)$_2$ hydrates.

Therefore, the deviation about the mean which was observed for the two drums of commercial-grade $Ba(OH)_2 \cdot 8H_2O$ may be attributed to the analytical technique and not the sample position in the drum. Vendor specifications for the commercial-grade $Ba(OH)_2 \cdot 8H_2O$ indicate the reactant composition to be between $Ba(OH)_2 \cdot 7.13H_2O$ and $Ba(OH)_2 \cdot 7.86H_2O$. The mean of these values is $Ba(OH)_2 \cdot 7.50H_2O$, which agrees well with the analyses reported above. It is interesting to note that Michaud reported a $Ba(OH)_2 \cdot 3H_2O$ — $Ba(OH)_2 \cdot 8H_2O$ eutectic to exist during solubility studies on the $Ba(OH)_2$ hydrate—water system.[41,42] The stoichiometric composition of the eutectic corresponds to $Ba(OH)_2 \cdot 7.12H_2O$, which agrees with the lower specification cited by the vendor. This eutectic consists of 18 mole % $Ba(OH)_2 \cdot 3H_2O$. Therefore, the samples of commercial $Ba(OH)_2 \cdot 8H_2O$ used in our studies appear to consist of 47 mole % eutectic and 53 mole % $Ba(OH)_2 \cdot 8H_2O$. The total amount of $Ba(OH)_2 \cdot 3H_2O$ 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 ($\sim$.3 mm thick) on a conveyer 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 $Ba(OH)_2 \cdot 8H_2O$.[43] This material preferentially crystalizes next to the cool surface at the conveyor belt and then extends in a dendritical manner up through the flake. The eutectic then precipitates out and fills in the voids. The stoichiometric composition of the commercial $Ba(OH)_2 \cdot 8H_2O$ is 47% eutectic, 53% $Ba(OH)_2 \cdot 8H_2O$.

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 ($\frac{1}{4}$ 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 1A infrared 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
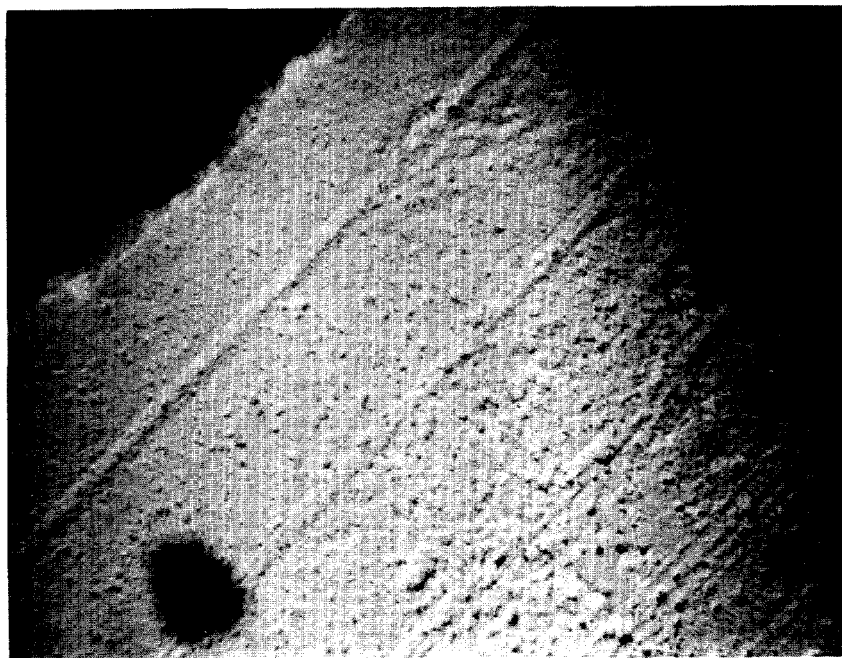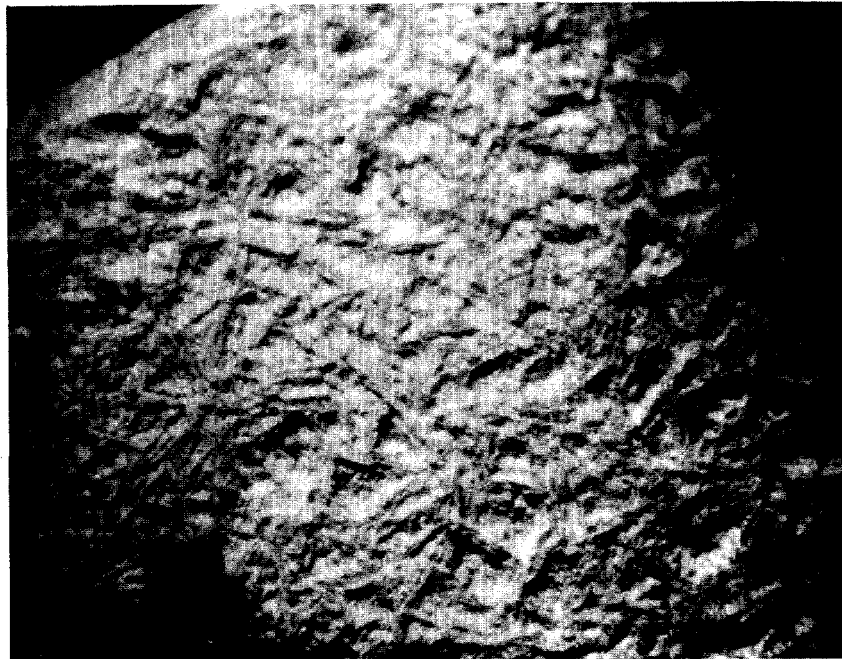
Fig. 3.   Top and bottom views of commercial $Ba(OH)_2 \cdot 8H_2O$ flakes; 2.85 by 3.75 in. original photograph, magnification — 12.75X.

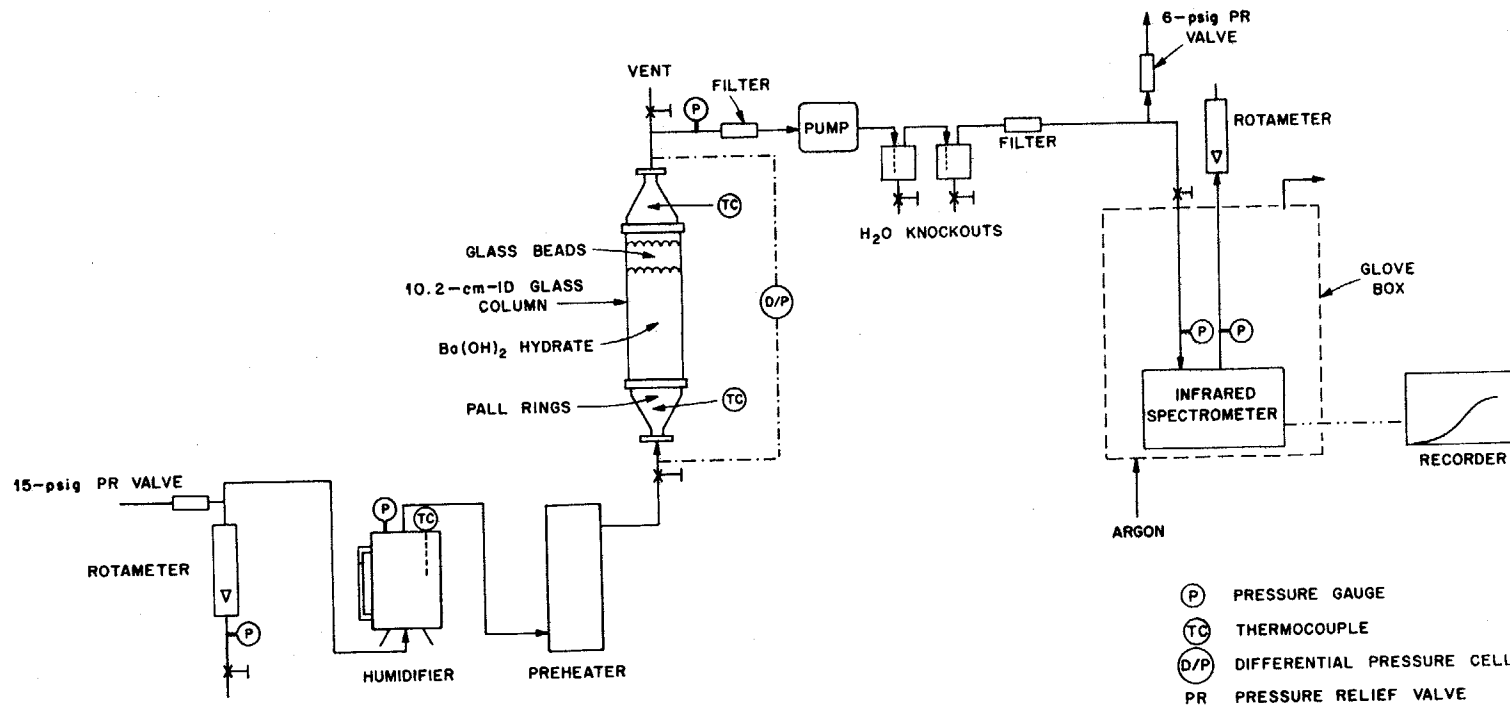Fig. 4. Ba(OH)$_3$·8H$_2$O flake; 2.85 by 3.75 in. original photograph, magnification — 12.75X.

Fig. 5. Schematic of the experimental equipment for CO_2 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 CO_2 concentrations. The instrument has been calibrated over the concentration range of 100 ppb to 330 ppm CO_2, 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 CO_2). 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.

$Ba(OH)_2 \cdot H_2O$ 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 $Ba(OH)_2 \cdot H_2O$ were superior to either beds of $Ba(OH)_2 \cdot 8H_2O$ or $Ba(OH)_2 \cdot 5H_2O$ for the treatment of a humidified 4.8% CO_2 gas stream. Therefore, initial experimental emphasis was placed upon the use of $Ba(OH)_2 \cdot H_2O$ for CO_2 removal and fixation. The results of these studies indicated CO_2 removal from air (330 ppm CO_2) 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 $Ba(OH)_2 \cdot H_2O$ 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 $Ba(OH)_2 \cdot 8H_2O$ (Fig. 8 or Fig. 7), the reaction proceeded quite rapidly. The formation of $Ba(OH)_2 \cdot 8H_2O$ was confirmed by x-ray diffraction analysis. As shown in Run 10 (Fig. 8), a packed bed of $Ba(OH)_2 \cdot H_2O$ undergoes a conditioning period when contacted with a humid CO_2-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 $Ba(OH)_2 \cdot 8H_2O$ which is gradually depleted. In time, moisture from the air converts the rest of the bed to active $Ba(OH)_2 \cdot 8H_2O$. 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 $Ba(OH)_2 \cdot 8H_2O$ 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 $Ba(OH)_2 \cdot 1H_2O$ over that of either $Ba(OH)_2 \cdot 5H_2O$ or $Ba(OH)_2 \cdot 8H_2O$ is now attributed to the existence of a more active (greater surface area) form of $Ba(OH)_2 \cdot 8H_2O$. Similar results were obtained on fluidized-bed studies with humidified air (330 ppm) CO_2 as a feed gas and $Ba(OH)_2 \cdot H_2O$ 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 CO_2) gas stream, initial studies on packed beds of commercially designated $Ba(OH)_2 \cdot 5H_2O$ flakes were discontinued as the material degraded upon conversion to octahydrate. This degradation resulted in severe pressure drop problems. Attempts to press either $Ba(OH)_2 \cdot H_2O$ or
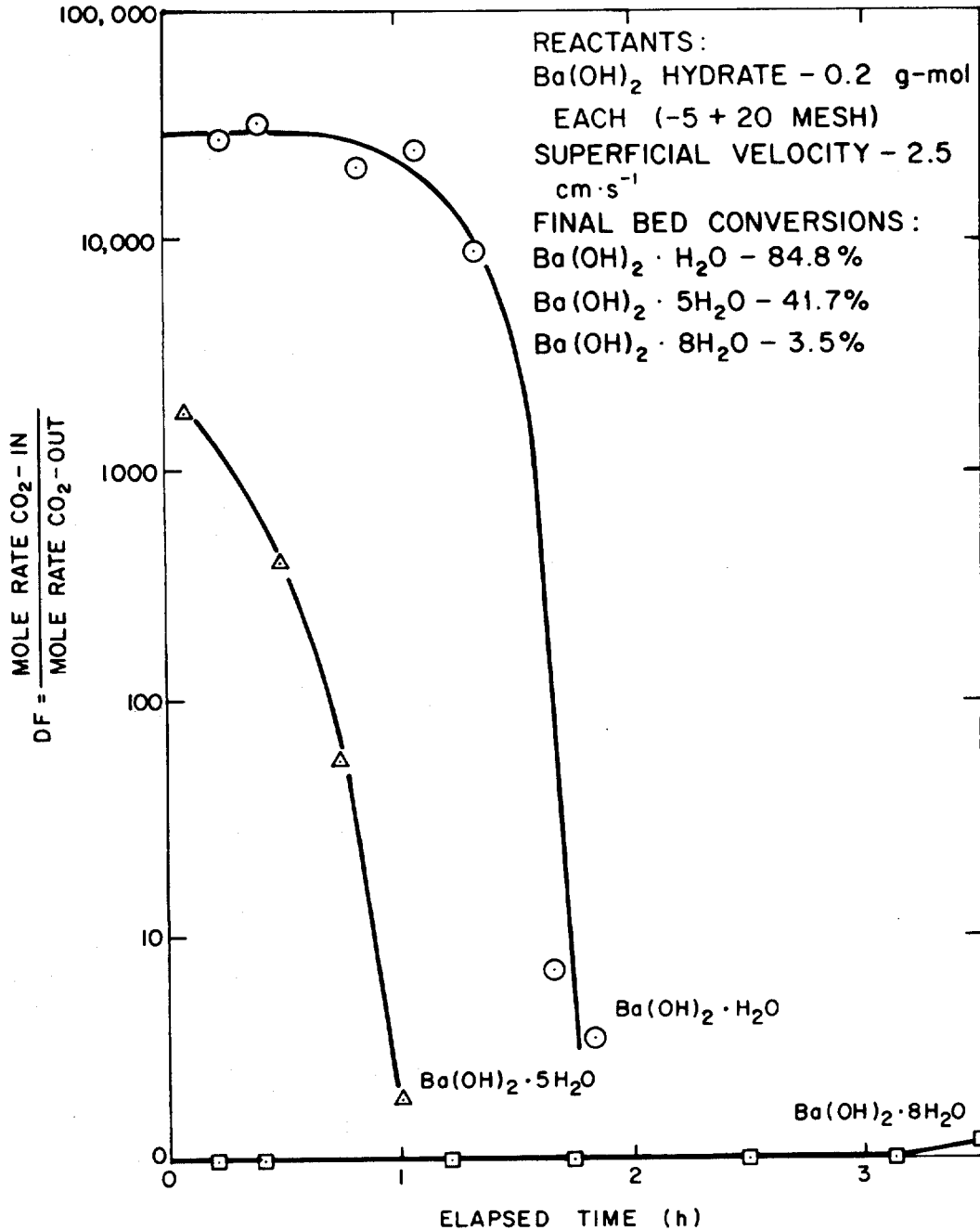
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Fig. 6. Comparison of Ba(OH) hydrates in packed beds with a humidified 4.8% CO_2 feed gas.

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REACTANTS:
$Ba(OH)_2 \cdot H_2O : SAND$ (1:1 vol) — .17 g-mol
330 ppm_v CO_2 — 6 ℓ · min^{-1}
SUPERFICIAL VELOCITY — 20 cm · sec^{-1}
BED DEPTH — 15.2 cm
COLUMN TEMPERATURE — 20°C

DF = $\dfrac{\text{MOLE RATE } CO_2 - \text{IN}}{\text{MOLE RATE } CO_2 - \text{OUT}}$

DRY FEED GAS

WATER SATURATION BEGAN

TIME (h)
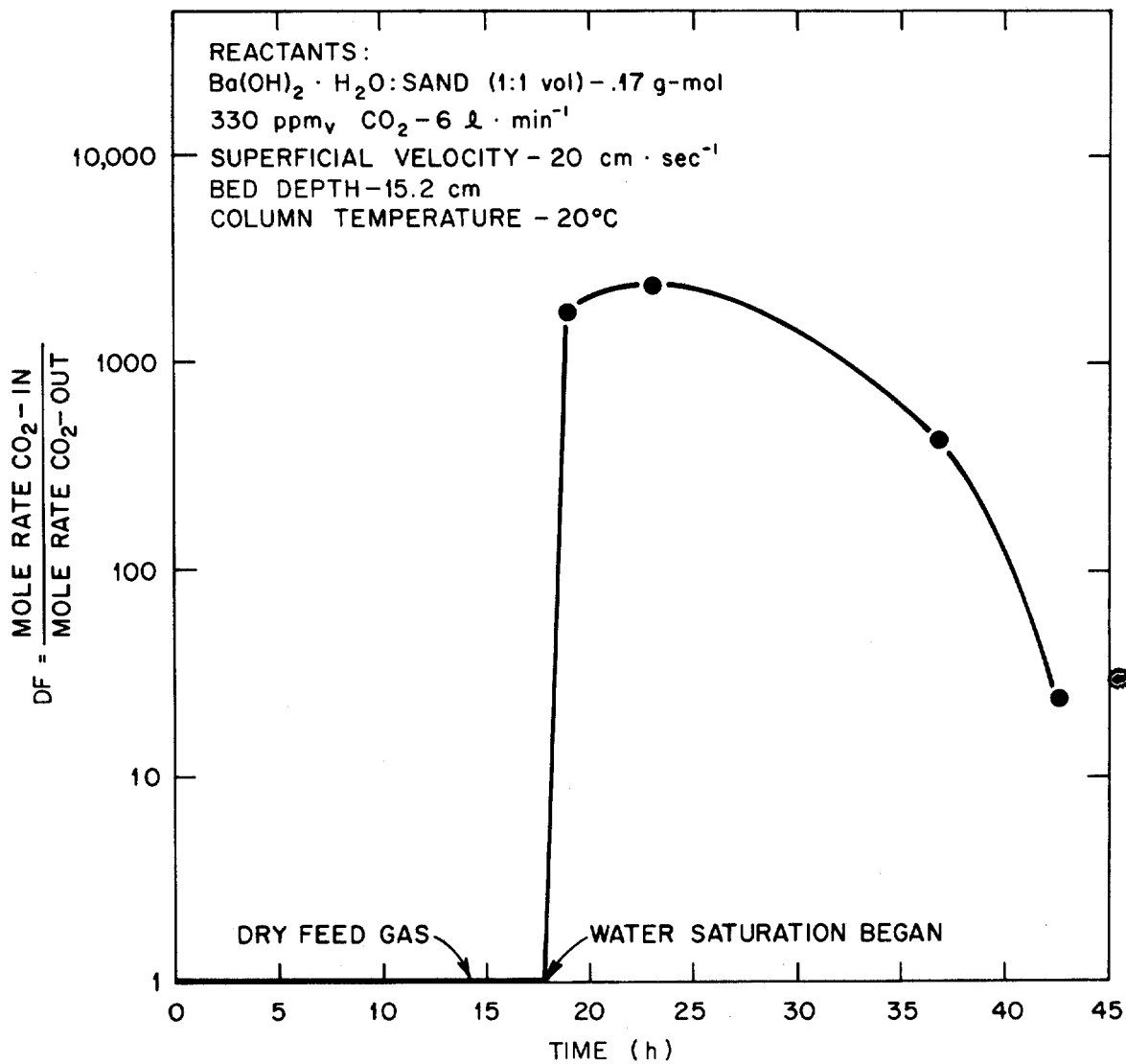
Fig. 7. The effect of water vapor pressure on the reactivity of $Ba(OH)_2 \cdot H_2O$ beds.
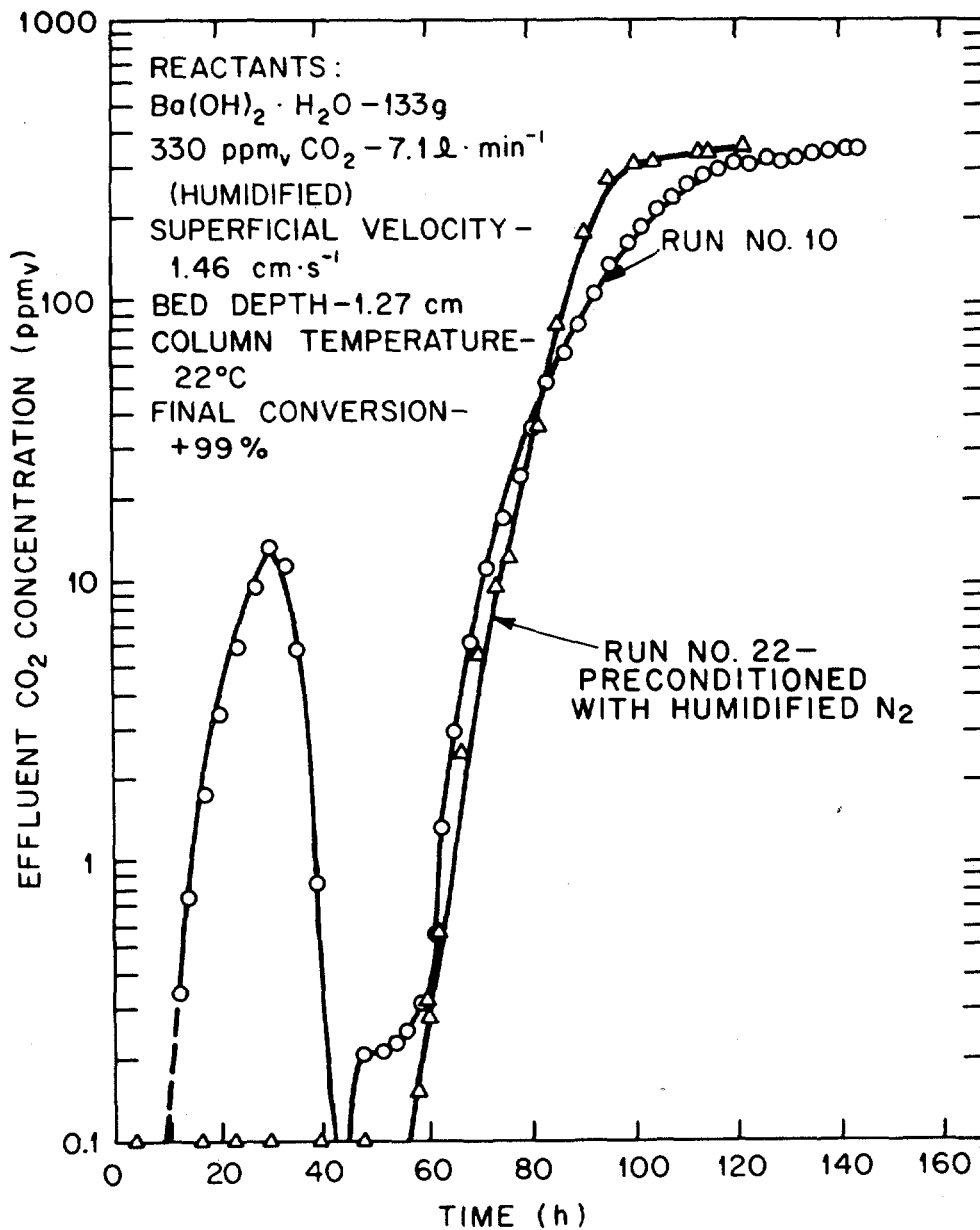
Fig. 8. The effects of bed preconditioning on Ba(OH)$_2$·H$_2$O with humidifed nitrogen.

$Ba(OH)_2 \cdot 5H_2O$ 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 $Ba(OH)_2 \cdot 8H_2O$ species which, when placed in a packed bed, resulted in acceptable operational characteristics, particularly with respect to pressure drop.

Commercial $Ba(OH)_2 \cdot 8H_2O$ Flake

Present efforts are directed toward the use of the flakes of commercial $Ba(OH)_2 \cdot 8H_2O$ in packed-bed reactors. Although these flakes possess considerably less reactivity than hydrated $Ba(OH)_2 \cdot H_2O$, 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 (.04 lb·in.$^{-2}$ft^{-1}) and gradually increased to 3.64 kPa/m (.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 preceeding 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 $Ba(OH)_2 \cdot 8H_2O$ 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 $Ba(OH)_2 \cdot 8H_2O$ have resulted in bed deactivation and early CO_2 breakthrough, indicating $Ba(OH) \cdot 3H_2O$ to be considerably less reactive than $Ba(OH)_2 \cdot 8H_2O$. This deactivation step appears to be kinetically controlled. Studies are presently under way to develop a better understanding of the deactivation phenomenom. Although prolonged operation at vapor pressures below the dissociation vapor pressure of $Ba(OH)_2 \cdot 8H_2O$ 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 $Ba(OH)_2 \cdot 8H_2O$ are composed of 53 mole % $Ba(OH)_2 \cdot 8H_2O$ and 47 mole % $Ba(OH)_2 \cdot 8H_2O - Ba(OH)_2 \cdot 3H_2O$ 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 $Ba(OH)_2 \cdot 3H_2O$ to $Ba(OH)_2 \cdot 8H_2O$ and capillary condensation of H_2O 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
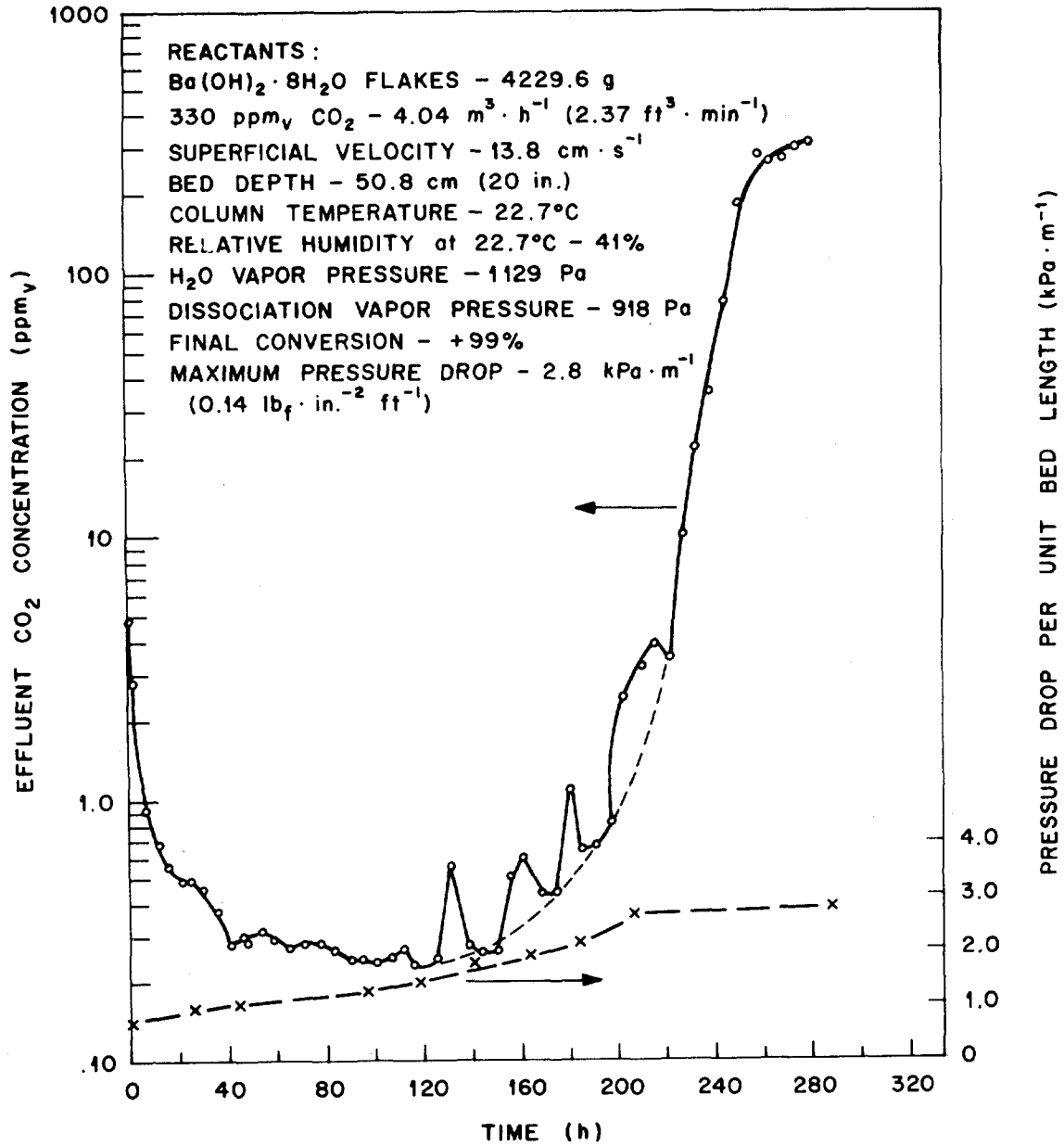
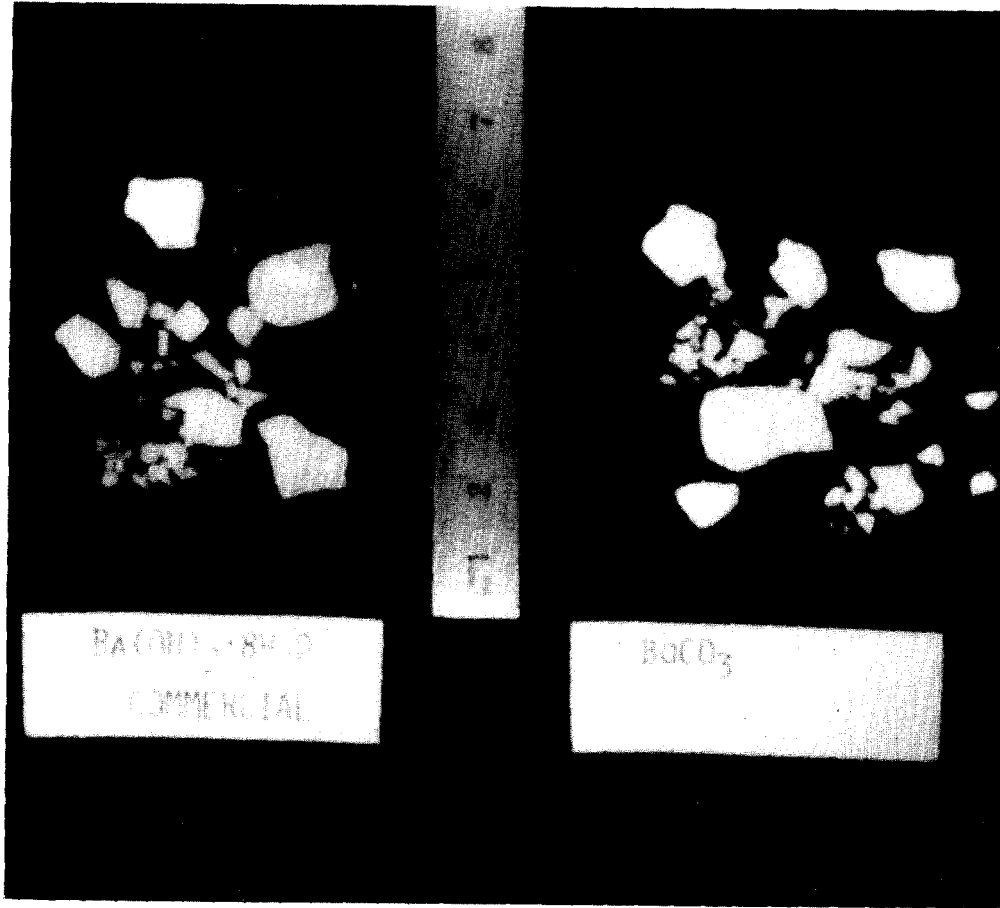Fig. 9. Near optimal conditions for CO_2 removal from air (330 ppm_v) with $Ba(OH)_2 \cdot 8H_2O$ flake bed.

Fig. 10. Commercial $Ba(OH)_2 \cdot 8H_2O$ reactant and $BaCO_3$ product flakes.
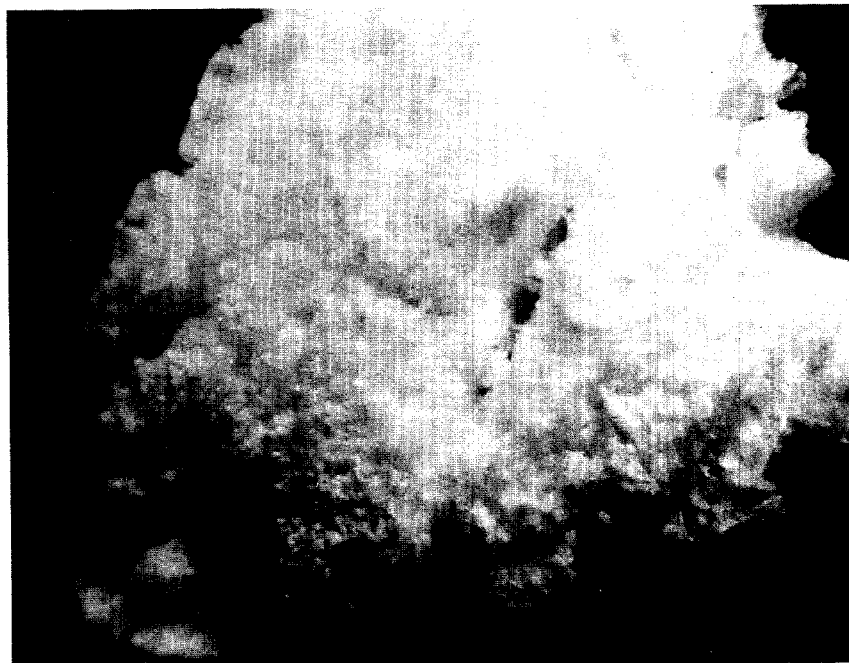
Fig. 11. Top and bottom views of commercial Ba(OH)$_2 \cdot$8H$_2$O subjected to high humidity; 2.85 by 3.75 in. original photograph, magnification — 16.5 and 13X, respectively.

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 $Ba(OH)_2 \cdot 8H_2O$ 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 $Ba(OH)_2 \cdot 8H_2O$, 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 $Ba(OH)_2 \cdot 8H_2O$ to $BaCO_3$ and not from the hydration of the commercial $Ba(OH)_2 \cdot 8H_2O$ (i.e., $Ba(OH)_2 \cdot 7.50H_2O$) to $Ba(OH)_2 \cdot 8H_2O$.

VI. REFERENCES

1. H. Bonka et al., "Contamination of the Environment by Carbon-14 Produced in High Temperature Reactors," Kernetechnik 15(7), 297 (1973).

2. W. Davis, Jr., Carbon-14 Production in Nuclear Reactors, ORNL/NUREG/TM-12 (February 1977).

3. C. O. Kunz, W. E. Mahoney, and T. W. Miller, "Carbon-14 Gaseous Effluents from Boiling Water Reactors," Trans. Am. Nucl. Soc. 21, 91 (1975).

4. C. O. Kunz, W. E. Mahoney, and T. W. Miller, "C-14 Gaseous Effluent from Pressurized Water Reactors," pp. 229-234 in Proceedings of the Health Physics Society 8th Midyear Symposium, Knoxville, Tenn., 1974, CONF-741018.

5. M. J. Kabat, "Monitoring and Removal of Gaseous Carbon-14 Species," Proceedings of the 15th DOE Nuclear Air Cleaning Conference, Boston, Mass., Aug. 7-10, 1978.

6. H. Schuttelkopf, Releases of $^{14}CO_2$ from Nuclear Facilities with Gaseous Effluents, Kernsforschungszentrum Karlsruhe KFK 2421, June, 1977 (translated from German) ORNL-tr-4527.

7. National Strategy Document for Airborne Wastes Management-Draft, Idaho National Engineering Lab - Allied Chemical Corporation (February 1979).

8. P. J. Magno, C. B. Nelson, and W. H. Ellett, "A Consideration of the Significance of Carbon-14 Discharges from the Nuclear Power Industry," p. 1047 in Proceedings of the Thirteenth AEC Air Cleaning Conference, San Francisco, Calif., Aug. 12-15, 1974, CONF-740807.

9. G. G. Killough et al., Progress Report on Evaluation of Potential Impact of ^{14}C Releases from an HTGR Reprocessing Facility, ORNL/TM-5284 (July 1976).

10. L. Machta, "Prediction of CO_2 in the Atmosphere," Carbon and the Biosphere, G. M. Woodwell and E. V. Pecan, eds., Technical Information Center, Office of Information Services, U.S. Atomic Energy Commission (August 1973).

11. G. G. Killough, A Diffusion-Type Model of the Global Carbon Cycle for the Estimation of Dose to the World Population from Releases of Carbon-14 to the Atmosphere, ORNL/TM-5269 (1977).

12. J. W. Snider and S. V. Kaye, "Process Behavior and Environmental Assessment of [14]C Releases from an HTGR Fuel Reprocessing Facility," Proceedings of the ANS-AIChE Topical Meeting, Sun Valley, Idaho, Aug. 5-6, 1976.

13. L. Pauling, "Genetic and Somatic Effects of Carbon-14," Science 128, 1183 (1958).

14. J. Schwibach, H. Riedel, and J. Bretschneider, Studies on the Emission of Carbon-14 from Nuclear Facilities (Nuclear Power Plants and Reprocessing Plants): Its Measurement and the Radiation Exposure Resulting from Emissions, Series of the Institute for Radiation Hygiene of the Federal Health Office, No. 20, 1979 (translated from German) OLS-80-233.

15. A. G. Croff, An Evaluation of Options Relative to the Fixation and Disposal of 14C-Contaminated CO_2 as $CaCO_3$, ORNL/TM-5171 (April 1976).

16. D. W. Holladay, Experiments with a Lime Slurry in a Stirred Tank for the Fixation of Carbon-14 Contaminated CO_2 from Simulated HTGR Fuel Reprocessing Off-Gas, ORNL/TM-5757 (1978).

17. D. W. Holladay, An Experimental Investigation of the Distribution of Krypton from Simulated HTGR Fuel Reprocessing Off-Gas During the Removal and Fixation of CO_2 by the CO_2-$Ca(OH)_2$ Slurry Reaction, ORNL/TM-6539 (in preparation).

18. D. W. Holladay and G. L. Haag, "Removal of ^{14}C-Contaminated CO_2 from Simulated LWR Fuel Reprocessing Off-Gas by Utilizing the Reaction Between CO_2 and Alkaline Hydroxides in Either Slurry or Solid Form," pp. 547-569 in Proceedings of the 15th DOE Nuclear Air Cleaning Conference, Boston, Mass., Aug. 7-10, 1978.

19. D. W. Holladay and G. L. Haag, "Methods for Removing Carbon-14 from Effluent Gases Produced in Nuclear Fuel Reprocessing Plants," to be submitted to Nucl. Tech. (in preparation).

20. K. J. Notz, D. W. Holladay, C. W. Forsberg, and G. L. Haag, "Processes for the Control of [14]CO_2 During Reprocessing," paper presented at the International Symposium on Management of Gaseous Wastes from Nuclear Facilities, Vienna, Austria, Feb. 18-22, 1980.

21. Handbook of Chemistry and Physics, 52nd ed., The Chemical Rubber Co., Cleveland, Ohio, 1972, pp. 13-70.

22. W. F. Linke and A. Seidell, Solubilities of Inorganic and Metal Organic Compounds, Fourth Edition, American Chemical Society, Washington, D.C. , 1958.

23. R. B. Cook, Temperature and Pressure Effects on Sodasorb and Baralyme, U.S. Naval Academy - TSPR No. 25 (1972).

24. L. J. Nuhn, "Acid-Gas Absorbent," U.S. Patent 2,997,445, Aug. 22, 1961.

25. T. C. Wang, "Temperature Effects on Baralyme, Sodasorb, and Lithium Hydroxide," Ind. Eng. Chem. Process. Dev., 14(2), 191 (1975).

26. J. G. Smith, "Low Temperature Performance of CO_2 Scrubber Systems," 1973 Diver's Gas Purity Symposium (November 1973).

27. J. Adriani and D. H. Bolten, "The Efficiency of Mixtures of Barium and Calcium Hydroxides in the Absorption of Carbon Dioxide In Rebreathing Appliances," Anesthesiology, 3(1), 1 (1942).

28. D. H. Batten and J. Andriani, "Clinical and Experimental Studies of Barium and Calcium Hydroxide Mixtures (Baralyme) for Carbon Dioxide Absorption in Anethesic," Anesth. and Analg., May-June, 151 (1942).

29. J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry," vol. III. Longman, Green and Co., N.Y., 1923, p. 817.

30. R. Engel, B. Decken, Claus (Brown Boveri) Krupp Reaktorvbau G.m.b.H.), "Removing Carbon Dioxide and Water from a Gas Stream," U.S. 3, 519, 384, Ger. Appl. 8/19/65. CA73:68063k.

31. M. M. Markowitz, Foote Prints, 34,9 (1965).

32. D. A. Boryta and H. J. Maas, "Factors Influencing Rate of Carbon Dioxide Reaction with Lithium Hydroxide," Ind. Eng. Chem. Process Des. Develop. 10(4), 489 (1971).

33. D. D. Williams and R. R. Miller, The Effect of Water Vapor on the $LiOH-CO_2$ Reaction, Part 1 - Dynamic Isothermal System, NRL Report 6937 (October 1969).

34. B. A. Kondakov, P. V. Kovtunenko, and A. A. Bundel, "Equilibria Between Gaseous and Condensed Phases in the Barium Oxide - Water System," Russ. J. Phys. Chem. 38(1), 99-102 (1964).

35. JANAF Thermochemical Data, calculated and compiled by the Dow Chemical Company, Thermal Laboratory, Midland, Mich. (updated November 1979).

36. F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, Selected Values of Chemical Thermodynamic Properties — Circular 500," U.S. Dept. of Commerce (February 1952).

37. D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, Selected Values of Chemical Thermodynamic Properties - Tables for the First 34 Elements in the Standard Order of Arrangement, U.S. Dept. of Commerce/NBS Technical Note 270-3 (January 1968).

38. V. B. Parker, D. D. Wagman, and W. H. Evans, Selected Values of Chemical Thermodynamic Properties - Tables for the AlkaLine Earth Elements, U.S. Dept. of Commerce/NBS Technical Note 270-6 (November 1971).

39. O. Kubaschewski and E. L. Evans, Metallurgical Thermochemistry, Pergamon, London, 1958.

40. P. I. Barin and O. Knacke, Thermochemical Properties of Inorganic Substances, Springer-Verlag, New York, 1973.

41. M. Michaud, "Contribution to the Study of the Hydroxides of Potassium and Barium," Revue de Chimie Minerale, t.5, 89 (1968). Translated from French by ORNL Translations Department.

42. M. Michaud, "Inorganic Chemistry – Study of the Binary Water–Barium Hydroxide System," C. r. hepd. Se'anc. Acad. Sci. Paris 262.C, 1143 (1966).

43. M. C. Flemings, Solidification Processing, McGraw-Hill, Inc., N.Y., 1974.

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 gettered 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 10^4 separating the relative radiotoxicity of HT to HTO, adding an additional factor of 10^2 for protective clothing,[7] a system which operates at an oxide removal efficiency less than 10^5 to 10^6 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.

The first organic getter was studied at Sandia, Albuquerque.[8-10] 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.[8] The compound reacted incompletely with pure tritium then outgassed due to possible radiation damage.[10]

We initially selected 1,4-diphenylbutadiyne,[11] $C_{16}H_{10}$, m.p. 87°C, which is a hydrocarbon of the structure $C_6H_5-C\equiv C-C\equiv C_6H_5$. 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.[12]

In addition to the butadiyne compound, we have collected data on the acetylene based alcohol 4-phenyl-3-butyn-1-ol $C_{10}H_{10}O$, m.p. < 20°C of the structure $C_6H_5-C\equiv C-CH_2CH_2OH$. 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-1-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).

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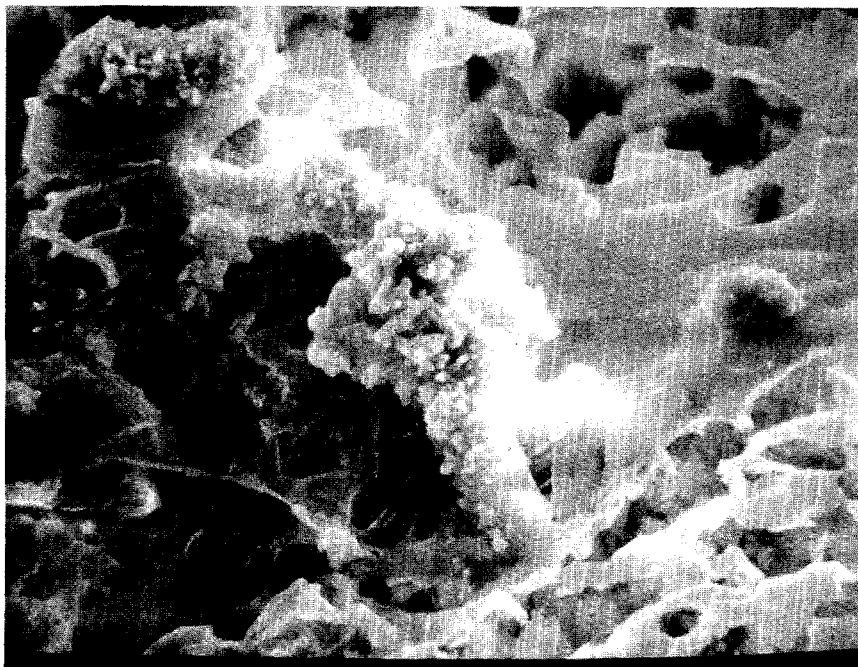
Fig. 1.   95% DPBD/Pd-CaCO$_3$ X 3,500.

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.

Fig. 2.   20% DPBD-1%Pd   X 3,500.

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
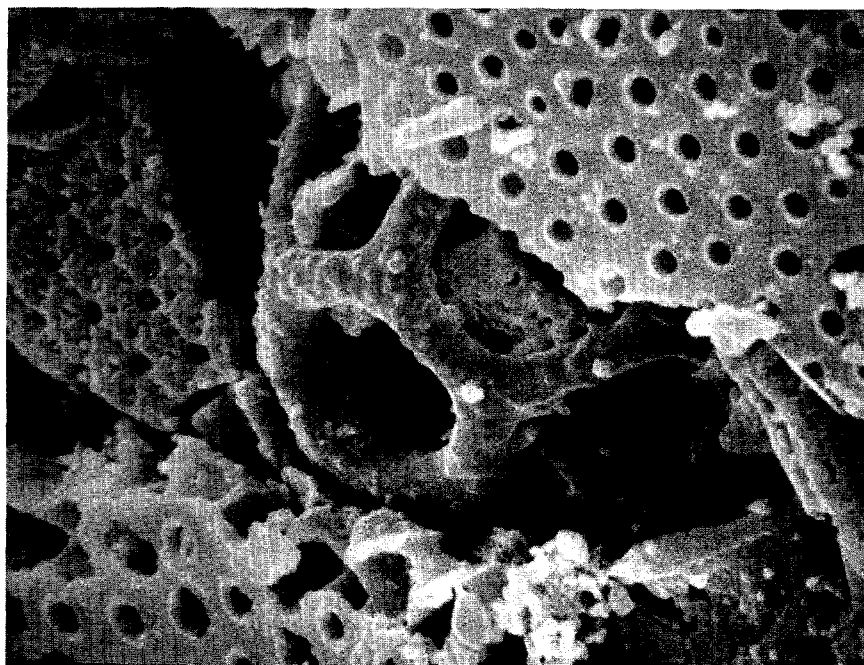the firebrick. No T_2 remained in the gas phase. Our best results
at 300ppm T_2 in static dry air were obtained using 20% DPBD/1% Pt
on firebrick. Among the experiments using material of this composi-
tion, experiments 42, 54 and 55 show extreme differences in perform-
ance. Effects produced by changing the solvent in which the catalyst
was reduced, plus the addition of a wetting agent, Aerosol-OT, re-
sulted 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 K_2PtCl_4 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/sub-
strate 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 K_2PtCl_4
was performed in MlM (ethylene glycol monomethyl ether) instead of
methanol. We measured 75% of the input T_2 in the organic for this
sample. The remaining T_2 formed HTO; no T_2 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 cata-
lysts 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 $IrCl(CO)(PPh_3)_2$, 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 activiation, (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 activiation, 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 activiation 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(O) of the structure:
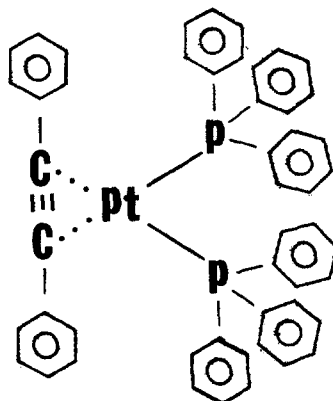
and bis(phenylacetylene)bis(triphenyl-phosphine)platinum(II)
of the structure:
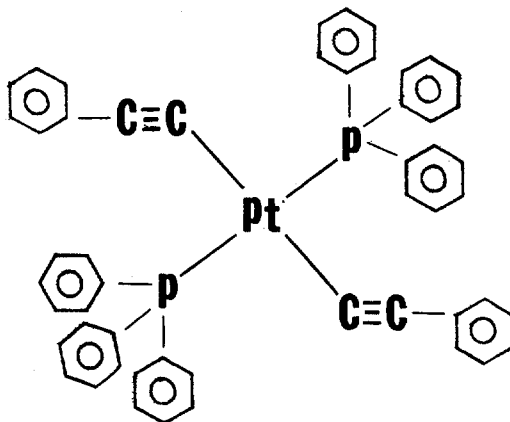
After 17 hours these compounds still showed no reactivity to hydrogen.

Scavenging T_2 at concentrations 30 times more dilute has
proven more difficult. Using 10ppm T_2 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 T_2 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 T_2 in static air for 6 hours. 7.9% of the input
T_2 reacted with the organic (Exp. 75) showing the same organic
reaction efficiency obtained for a 48 hour test on the same mate-
rial. A new wetting agent, Aerosol AY, was added with catalyst in
the formulation of the material, then exposed to 10ppm T_2 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 T_2 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 T_2. 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 T_2 under dynamic airflow.
The system shown in Fig. 3 has a total volume of 1.1 liters.
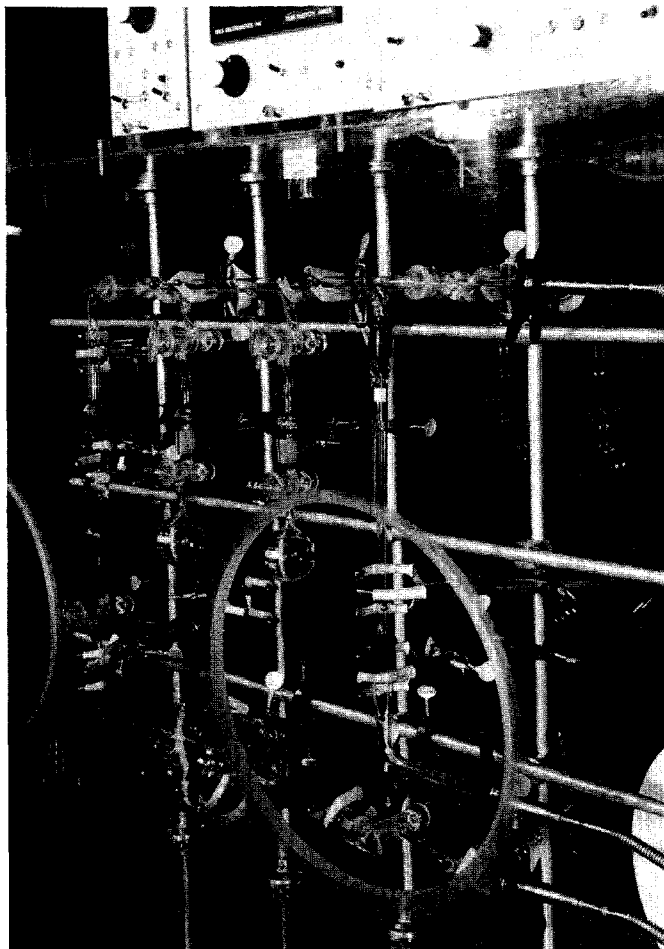
Fig. 3.   Dynamic air-flow system.

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-diphenylbuta-diyne 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 reac-tion 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 con-centration, 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).[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.[22]
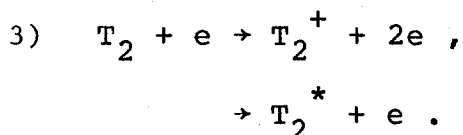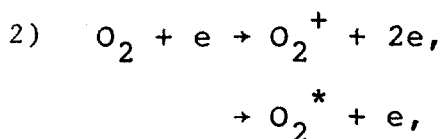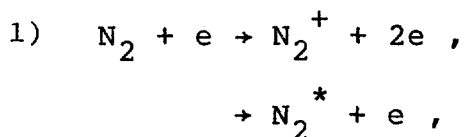
We know that tritium molecules in a mixture decay by emitting beta particles (electrons) with an average energy of 5.7 KeV. These beta particles lose energy through collisions with the mixture molecules and disappear by recombination with positive ions or by attachment to neutral molecule. These molecules undergo ionization or excitation depending on the energy of the primary electrons.[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.[24] The positive ions collide with neutral molecules and undergo charge transfer or initiate ion-molecule reactions.[25] These processes result in the formation of free radicals (T, OT) which are responsible for the formation of the final products.

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

1) $N_2 + e \rightarrow N_2^+ + 2e$,

$\rightarrow N_2^* + e$,

2) $O_2 + e \rightarrow O_2^+ + 2e$,

$\rightarrow O_2^* + e$,

3) $T_2 + e \rightarrow T_2^+ + 2e$,

$\rightarrow T_2^* + e$.

Since N_2 is the major component in air, N_2^+ ions are the main positive ions in the mixture. They probably undergo the reactions:[33-34]

$$N_2^+ + O_2 \xrightarrow{K_1} O_2^+ + N_2 \ , \qquad K_1 = 5 \times 10^{-11} \ cm^3 \ molecule^{-1} \ sec^{-1} \qquad (1)$$

$$N_2^+ + T_2 \xrightarrow{K_2} N_2T^+ + T \ , \qquad K_2 = 2 \times 10^{-9} \ cm^3 \ molecule^{-1} \ sec^{-1} \qquad (2)$$
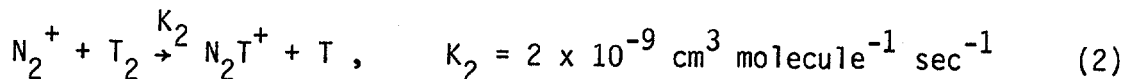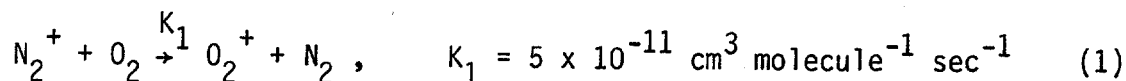
The tritium atoms produced in reaction (2) initiate a number of free radical reactions,[35] the most important of which are:

$$T + O_2 + T_2 \to T_2O + T_2 \ , \qquad K_3 = 4.0 \times 10^{-32} \ cm^6 \ molecule^{-2} \ sec^{-1}; \quad (3)$$

$$T + TO_2 \to T_2 + O_2 \ , \qquad K_4 = 1.3 \times 10^{-11} \ cm^3 \ molecule^{-1} \ sec^{-1}; \quad (4)$$

$$\to OT + OT \ , \qquad K_5 = 1.7 \times 10^{-11} \ cm^3 \ molecule^{-1} \ sec^{-1}; \quad (5)$$

$$\to T_2O + O \ , \qquad K_6 = 1.6 \times 10^{-11} \ cm^3 \ molecule^{-1} \ sec^{-1}; \quad (6)$$

$$OT + T_2 \to T_2O + T \ , \qquad K_7 = 6.4 \times 10^{-15} \ cm^3 \ molecule^{-1} \ sec^{-1}; \quad (7)$$

$$OT + TO_2 \to OT + O_2 \ , \qquad K_8 = 1 \times 10^{-11} \ cm^3 \ molecule^{-1} \ sec^{-1}; \quad (8)$$
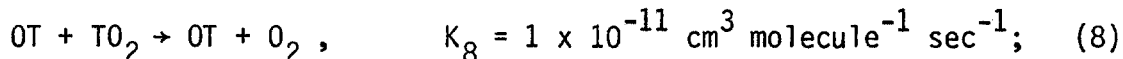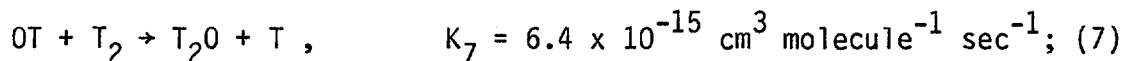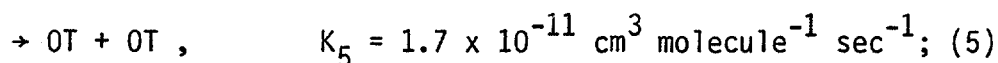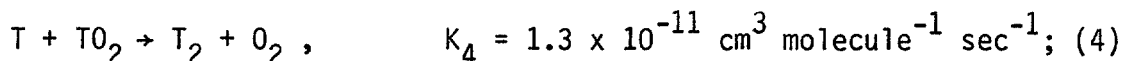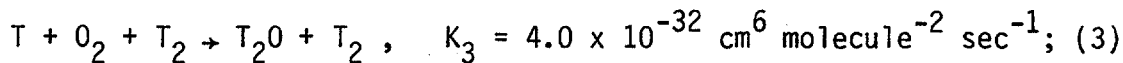
A small number of tritium atoms are removed through the reaction:

$$T + T + N_2 \to T_2 + N_2 \qquad (9)$$

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:[36]

$$\frac{d[T_2O]}{dt} = 1.5 \times 10^{-8} \ [T_2] \ sec^{-1} \qquad (10)$$

This reaction rate constant of $1.5 \times 10^{-8} \ sec^{-1}$ is in good agreement with the experimental found value of $5.2 \times 10^{-8} \ sec^{-1}$ by Caseletto et al.,[18] 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:

$$300\text{ppm } T_2 \text{ (static)} \quad - \quad 2.0 \times 10^{-5} \text{ moles liter}^{-1}$$
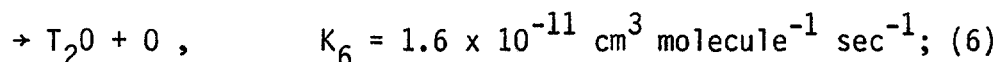
$$\frac{d[T_2O]}{dt} = 3.0 \times 10^{-13} \text{ molecules cm}^{-1}$$

$$10\text{ppm } T_2 \text{ (static)} \quad - \quad 4.6 \times 10^{-7} \text{ moles liter}^{-1}$$

$$\frac{d[T_2O]}{dt} = 6.9 \times 10^{-15} \text{ molecules cm}^{-1} \text{ sec}^{-1}$$

$$10\text{ppm } T_2 \text{ (dynamic)} \quad - \quad 4.0 \times 10^{-10} \text{ moles liter}^{-1}$$

$$\frac{d[T_2O]}{dt} = 5.9 \times 10^{-18} \text{ molecules cm}^{-1} \text{ sec}^{-1}$$

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 $298°K$ with an equilibrium constant of $K_{eq} = 10^{42}$. The hydrogenation of aliphatic alkynes has a heat of reaction of about -140kJ/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:

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

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

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

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

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

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

$$H + C_6H_{12} \rightarrow C_6H_{13}, \qquad k = 1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}; \quad (17)$$

$$H + C_6H_6 \rightarrow C_6H_7 \,, \qquad k = 9.5 \times 10^{-14} \ cm^3 \ molecule^{-1} \ sec^{-1}; \quad (18)$$

$$H + C_2H_5 \rightarrow 2CH_3 \,, \qquad k = 6.0 \times 10^{-11} \ cm^3 \ molecule^{-1} \ sec^{-1} . \quad (19)$$

Ethene is known to be used as an inhibitor of the water forming reaction by reaction (12) above.[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_2 and O_2 until dissociation occurs. The dissociation energies of H_2 and O_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_2 away from the catalyst surface. To this end the organic should completely surround the catalyst particle. The lighter mass T_2 will permeate the organic up to an order of magnitude faster than O_2; the principle used in membrane gas separation.[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-diphenyl-butadiyne and 4-phenyl-3-butyn-1-ol with 1% platinum on firebrick plus wetting agent were subjected to analysis using electron microprobe 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 1×10^{-6} layer of organic.

Future Work

Our future work with organic getter systems will include further investigation of heterogenous catalysis using organic/Pt getters and optimizing their performance for 1-10ppm T_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 activiation. 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 baritron 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_2O or 2M HCl to elute the tritium in the aqueous phase. An aliquot of this solution is taken and counted. Because water is slightly soluable 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

References

1. International Commission on Radiological Protection, "Limits for Intakes of Radiometals by Workers", ICRD Publication 30, Part 1, (1979).

2. K. B. Lee and R. Madey, "Transport of a Fluid Through a Packed Bed", Trans. Faraday Soc. 67, 329, (1971).

3. R. G. Aune, H. P. Cantelow and R. L. Boltin, "Practical Control of Tritiated Water Vapor by Silical Gel and of Tritium Gas by the Use of a Purging Device", in Tritium ed. by A. A. Moghissi and M. W. Carter, Messenger Graphics, Phoenix (1973).

4. T. M. Flanagan, M. L. Rogersand, R. W. Wilkes, "Experiment with a Tritium Emergency Containment System", Proc. Third Topical Meeting on the Technology of Controlled Nuclear Fusion, CONF-780508, Vol 2, p. 729, Santa Fe (1978).

5. A. E. Sherwood, B. G. Monahan, R. A. McWilliams, F. S. Uribe and C. M. Griffith, "Catalytic Oxidation of Tritium in Air at Ambient Temperature", UCRL-52811, (1979).

6. P. D. Gildeu and W. R. Wall, "Results of Tritium Tests Performed on Sandia Laboratories Decontamination System", Proc. Third Topical Meeting on the Technology of Controlled Nuclear Fusion, CONF-780508, Vol 2, p. 245, Santa Fe, (1978).

7. C. E. Easterly and J. E. Phillips, "Tritium Conversion and Its Influence in Personnel Protection at a Fusion Reactor", Proc. Tritium Technology in Fission, Fusion and Isotopic Applications, Dayton, (1980).

8. R. L. Courtney and L. A. Harrah, J. Mat. Sci, 12, 175 (1977).

9. R. E. Trujillo and R. L. Courtney, J. Mat. Sci, 12, 937 (1977).

10. C. W. Schoenfelder and L. A. West, "Tritium Removal: A Preliminary Evaluation of Several Getters, "Proc. Int. Conf. Radiation Effects and Tritium Technology for Fusion Reactors, Gatlinburg, TN, October 1-3, 1975, CONF-750989, J. S. Watson and F. W. Wiffen, Eds. (National Technical Information Service, Springfield, VA, 22161, 1976), III, 482.

11. From Frachan Chemical Co., Willoughby, OH 44094.

12. Mike Smith, Bendix Corporation, Kansas City, Missouri 64141, private communication, October 5, 1979.

13. S. Weller and W. A. Steiner, Chem. Eng. Progr. 46, 585 (1950).

14. P. B. Chock and J. Halpern, J. Amer. Chem. Soc. 88, 3511 (1966).

15. J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, J. Chem. Soc. A. 1966, 1711.

16. J. Vaska, J. W. DiLvzio, J. Amer. Chem. Soc. 84, 679 (1962).

17. L. Vaska, R. E. Rhodes, J. Amer. Chem. Soc. 87, 4970 (1965).

18. G. J. Casaletto, L. H. Gevantman, J. B. Nash, The Self-Radiation Oxidation of Tritium in Air, NRDL - TR - 565, 1962.

19. G. J. Casaletto, L. H. Gevantman and J. B. Nash, "The Self-Radiation Oxidation of Tritium in Oxygen and Air", USNRDL - TR - 565, Naval Radiological Defense Lab., San Francisco, (1962).

20. L. M. Dorfman and B. A, Hemmer, "Ion Pair Yield of the Tritium-Oxygen Reaction", J. Ch. Phys. 22, 1555 (1954).

21. J. Y. Yang and L. H. Gevantman, "Tritium β-Radiation Induced Isotopic Exchange with Water Vapor", J. Phys. Chem. 68, 3115, (1964).

22. L. F. Belovodskii, V. K. Gaevoi, V. I. Grishmanovskii and N. V. Nefedov, "Oxidation of Tritium in Air Under the Action of Intrinsic Radiation", At. Energ. 38, 379, (1975).

23. J. H. Futreel and T. O. Turnan, Fundamental Processes in Radiation Chemistry, p. 171, ed. by P. Ausloos, Interscience, New York, 1968.

24. R. L. Platzman, Int. J. Appl. Radiat. Isot. 10, 116 (1961).

25. A. R. Anderson, Fundamental Processes in Radiation Chemistry, p. 281, ed. by P. Ausloos, Interscience, New York, (1968).

26. CRC Handbook of Chemistry and Physics, 57th ed., R. C. Wrast, ed. (CRC Press), Cleveland, (1976), pp. D-71, D-82-83.

27. K. Schofield, Int. J. Chem. Kinetics 4, 255 (1972).

28. L. G. Anderson, Rev. Geophys. Space. Sci. 14, 151 (1976).

29. W. A. Payne and L. J. Stief, J. Chem. Phys. 64, 1150 (1976).

30. D. A. Whytock, W. A. Payne, and L. J. Stief, J. Chem. Phys. 65, 191 (1976).

31. J. H. Lee, J. V. Michael, W. A. Payne, and L. J. Stief, J. Chem. Phys. 68, 1817 (1978).

32. R. R. Baldurn, R. F. Simmons, and R. W. Walker, Trans Faraday Soc. 62, 2476 (1966).

33. (a) E. E. Ferguson, At. Data Nucl. Data Tables. <u>12</u>, 159 (1973).

    (b) M. J. McEwan and L. F. Phillips, Chemistry of the Atmosphere, p. 170, J. Wiley and Sons, Inc., New York, (1975).

34. W. Lindinger, F. C. Fehsenfeld, A. L. Schmeltekof and E. E. Ferguson, J. Geophys. Res. <u>79</u>, 4753 (1974).

35. L. G. Anderson, Rev. Geophys. Spac. Phys. <u>14</u>, 151 (1976).

36. P. J. Papagiannakopoulos and C. E. Easterly, Conversion of Tritium Gas to Tritiated Water, ORNL/TM-6699, (1979).

Table I. Results for 1,4-Diphenylbutadiyne at 20°C and 1ATM OF 300-500ppm T_2 in static dry air

Exp. #	DPBD (w/w%)	Catalyst (w/w%)	Substrate	Initial Moles Organic e-3	T_2 e-7	O_2 e-4	% T In Phase Organic	Water	Substrate	Gas	PPM T_2	Catalyst Source	Reducing Solvent	Wetting Agent
29	60	5% Pd	$CaCO_3$	3	7	5	10.5	61.9	--	ND	303	Strem Chemical Co.		
35	60	5% Pd	$CaCO_3$	3	9	a	10.6	22.4	--	NA	389	Strem Chemical Co.		
34	20	1% Pd	Fluoropak 80	8	12	5	0.7	10.4	--	ND	493	$PdCl_2$	--	--
33	20	1% PD	Chromosorb W	8	12	5	6.5	36.7	13.0	ND	493	$PdCl_2$	MeOH	--
36	20	1% PD	Chromosorb W	8	9	a	21.9	42.1	4.5	NA	389	$PdCL_2$	MeOH	--
46	20	~5%	Carbon	7	12	5	5.3	43.6	--	ND	493	Bendix Material		
30	20	1% Pd	FIREBRICK	5	6	5	32.6	64.3	--	NA	303	$PdCl_2$	MeOH	--
32	20	0.1% Pd	FIREBRICK	3	11	5	6.1	62.1	14.0	ND	493	$PdCl_2$	MeOH	--
40	20	1% Pd	FIREBRICK	6	10	5	39.4	42.3	8.1	ND	493	$PdCl_2$	MeOH	--
43	20	1% Pd	FIREBRICK	6	12	4	19.5	45.6	3.0	ND	493	K_2PdCl_4	MeOH	--
42	20	1% Pt	FIREBRICK	4	11	5	46.6	48.4	5.0	ND	493	K_2PtCl_4	MeOH	--
55	20	1% Pt	FIREBRICK	6	9	2	0.6	59.5	23.4	ND	385	K_2PtCl_4	MeOH	Aerosol-OT
54	20	1% Pt	FIREBRICK	6	9	3	74.8	4.8	184	ND	385	K_2PtCl_4	M1M	Aerosol-OT
60	20	1% Pt	FIREBRICK	6	9	3	33.1	55.4	4.0	ND	385	K_2PtCl_4	M1M	--
61	20	1% Pt	FIREBRICK	6	10	3	30.4	52.2	5.0	ND	385	K_2PtCl_4	M1M	--
41	20	1% Ni	FIREBRICK	5	11	5	3.7	20.1	0.2	86.2	493	$NiCl_2 6H_2O$	MeOH	--
47	20	1%Au	FIREBRICK	4	11	3	2.4	11.4	0.4	59.3	493	$HAuCl_4 3H_2O$	MeOH	--
48	20	.5%Au/ .5%Pd	FIREBRICK	3	13	3	9.6	51.5	2.7	ND	493	$HAuCl_4 3H_2O$ K_2PdCl_4	MeOH	--
38	20	0.2%Ir	FIREBRICK	6	11	6	11.2	52.9	2.1	5.7[b]	493	VASKA'S*	--	--
44	19.3	0.9Ir	FIREBRICK	6	12	6	6.8	7.5	0.3	59.4[c]	493	VASKA'S	--	--
58	20	1%Ir	FIREBRICK	6	9	3	0.0	4.7	0.5	95.0	385	$Na_3IrCl_6 2H_2O$	MeOH	--
56	--	0.9%Ir*	FIREBRICK	0	10	3	3.7	3.9	0.2	13.9	385	VASKA'S	--	--

*Vaska's Catalyst: Chlorocarbonylbis(Triphenylphosphine)Iridium

[a]Feed Gas was T_2 in Argon

[b]45ppm HT + 170ppm H_2 remaining in gas phase

[c]No HT or H_2 remaining in gas phase (activation with UV)

[d]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 T$_2$ in static dry air

Exp. #	Organic Getter (w/w%)	Catalyst (w/w%)	Substrate	% T In Phase Organic	Water	Substrate	Gas	Catalyst Source	Reducing Solvent	Wetting Agent	Test Duration
62T	20% DPBD	1% Pt	FIREBRICK	7.9	47.4	14.0	ND	K$_2$PtCl$_4$	M1M	Aerosol-OT	48 hrs
65T	20% DPBD	1% Pt	FIREBRICK	10.5	42.9	22.7	.6	K$_2$PtCl$_4$	MeOH	Aerosol-AY	48 hrs
67T	20% DPBD	1% Pt	FIREBRICK	5.1	59.1	6.7	0.2	K$_2$PtCl$_4$	MeOH	Aerosol-AY	24 hrs
68T	20% DPBD	1% Pt	FIREBRICK	10.2	67.4	11.8	0.2	K$_2$PtCl$_4$	M1M	Aerosol-OT	24 hrs
66T	20% DPBD	1% Pt	FIREBRICK	4.5	67.6	0.6	0.2	PdCl$_2$	MeOH	--	48 hrs
72T	20% DPBD	1% Pt	FIREBRICK	4.7	26.2	26.2	NA	PtCl$_2$	MeOH	--	24 hrs
73T	20% DPBD	1% Pt	FIREBRICK	2.9	65.0	3.2	NA	PtCl$_4$	MeOH	--	24 hrs
71T	20% DPBD	1% Pt	FIREBRICK	10.2	60.2	6.3	NA	K$_2$PtCl$_4$	M1M	Aerosol-AY	6 hrs
74T	20% DPBD	1% Pt	FIREBRICK	4.7	72.0	3.0	NA	K$_2$PtCl$_4$	MeOH	--	6 hrs
75T	20% DPBD[a]	1% Pt	FIREBRICK	7.4	64.2	9.7	NA	K$_2$PtCl$_4$	M1M	Aerosol-AY	6 hrs
76T	20% DPBD[b]	1% Pt	FIREBRICK	7.9	61.1	10.3	NA	K$_2$PtCl$_4$	M1M	--	6 hrs
79S	20% DPBD	1% Pt	FIREBRICK	8.3	63.5	17.1	ND	K$_2$PtCl$_4$	M1M	DC AntifoamB	24 hrs
80S	20% DPBD[b]	1% Pt	FIREBRICK	1.5	62.9	9.9	ND	PtCl$_4$	MeOH	--	24 hrs
82S	20% DPBD[c]	1% Pt	FIREBRICK	6.9	88.1	3.4	ND	K$_2$PtCl$_4$	M1M	Aerosol-OT	24 hrs
84S	20% DPBD	1% Pt	FIREBRICK	3.4	81.8	13.6	ND	K$_2$PtCl$_4$	M1M	Span 80	24 hrs
85S	20% DPBD	1% Pt	FIREBRICK	4.0	76.3	13.3	ND	K$_2$PtCl$_4$	MeOH	Span 80	24 hrs
69T	20% PBol[a]	1% Pt	FIREBRICK	17.9	60.1	6.7	NA	K$_2$PtCl$_4$	M1M	Aerosol-OT	6 hrs
70T	20% PBol	1% Pt	FIREBRICK	15.0	54.2	13.6	NA	K$_2$PtCl$_4$	M1M	--	6 hrs

[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

Table III. Dynamic air flow tests on 1,4-Diphenylbutadiyne and 4-Phenyl-3-butyn-1-ol at 20°C and 1ATM of 10ppm T$_2$ in dry air.

Exp. #	Organic Getter (w/w%)	Catalyst (w/w%)	Substrate	% T In Phase Organic	Water	Substrate	Gas	Catalyst Source	Reducing Solvent	Wetting Agent	Flow Rate, ℓpm
77D	20% PBol	1% Pt	FIREBRICK	22.6	10.1	4.8	ND	K$_2$PtCl$_4$	M1M	Aerosol-OT	10
83D	20% DPDB	1% Pt	FIREBRICK	8.0	76.7	10.3	ND	K$_2$PtCl$_4$	M1M	Aerosol-OT	3
87D	20% PBol[a]	1% Pt	FIREBRICK	24.8	67.9	7.5	ND	K$_2$PtCl$_4$	M1M	Aerosol-OT	3
88D	20% PBol[a]	1% Pt	FIREBRICK	22.1	66.7	7.0	ND	K$_2$PtCl$_4$	M1M	Aerosol-OT	1

[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

Mixture	T_2 Concentration (Ci liter^{-1})	Conversion rate $dHTO/dt$ (Ci liter^{-1} sec^{-1})	Reference
$T_2 + H_2 + O_2$	95–328	$1.98 \times 10^{-6}\ T_2$	a
$T_2 + O_2 + Ar$	0.09–90	$1.7 \times 10^{-8}\ T_2^{5/3}$	b
$T_2 + O_2 + N_2$	0.018–1	$3.30 \times 10^{-7}\ T_2^{2}$	c
$T_2 + O_2 + H_2O$	< 1	$1.20 \times 10^{-6}\ T_2^{2}$	c
$T_2 + Dry\ Air$	0.015–0.8	$1.7 \times 10^{-7}\ T_2^{2}$	c
$T_2 + H_2O + He,$ N_2, Ar, Kr	0.05–0.7	$4.2 \times 10^{-7}\ T_2^{2}$	d
$T_2 + H_2O + Dry\ Air$	6×10^{-4}–600	$1.7 \times 10^{-8}\ T_2^{5/3}$	b

[a]L. M. Dorfman and B. A. Hemmer, _J. Chem. Phys._, _22_, 1555 (1954).

[b]L. F. Belovodskii, V. K. Gaevoi, V. I. Grishmanovskii, and N. V. Nefedov, _At. Energ._, _38_ (1975).

[c]G. J. Casaletto, L. H. Gevantman, and J. B. Nash, "The Self-Radiation Oxidation of Tritium in Oxygen and Air," USNRDL-TR-565, Naval Radiol. Def. Lab., San Francisco, California, 1962.

[d]J. Yang and L. H. Gevantman, _J. Phys. Chem._, _68_, 3115 (1964).

DISCUSSION

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 outgasing 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.