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POSSIBLE TECHNIQUES FOR DECONTAMINATION
OF NATURAL GAS FROM GAS WELLS STIMULATED
BY A NUCLEAR EXPLOSION

John A. Wethington, Jr.

October 1, 1969

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POSSIBLE TECHNIQUES FOR DECONTAMINATION OF NATURAL GAS FROM GAS WELLS STIMULATED BY A NUCLEAR EXPLOSION

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ABSTRACT

Decontamination of the products from gas wells stimulated by nuclear explosions requires the removal of T, present as HT, CH₃T, C₂H₅T, etc., and ⁸⁵Kr from the production stream. Flaring of large volumes of gas from the Gasbuggy well led to the replacement of radioactive cavity gas with inactive formation gas, but this would not be a satisfactory production procedure because it releases T and ⁸⁵Kr into the atmosphere and wastes large amounts of product gas. Exchange reactions appear to offer promise for removing the tritium. For example, water or steam flowing countercurrent to tritiated gas in the presence of a suitable catalyst can participate in the exchange reactions

resulting in the transfer of T from gas into water. Other possibilities for utilizing exchange reactions include exchange of the gas with ethylene glycol used in the gas dryer, with silicate rocks introduced into the gas stream, or with a countercurrent stream of NH₃ or H₂S. As another approach, use of the contaminated gas for the manufacture of ammonia synthesis gas has potential for removal of both T and ⁸⁵Kr.

INTRODUCTION

Radiochemical data on gas obtained from the Gasbuggy well after nuclear stimulation have been compiled by Smith¹; these data show that the only significant radioactive contamination results from T and ⁸⁵Kr. The former is present mainly as HT and CH₃T with lesser amounts of C₂H₅T and C₃H₇T. Flaring of the well has produced significant decreases in the radioactivity level of the gases, but this procedure is undesirable on a production scale since it releases radioactivity into the biosphere, wastes large quantities of marketable gas, and interrupts the normal production in the distribution system. Better methods of decontaminating the gas are needed.

The quantities of gas involved and the economic structure of the industry seem to require that any chemical or physical process used for decontamination have a large throughput and employ inexpensive or reusable process materials. These requirements suggest using some combination of the isotope effect, exchange reactions, and/or gas-liquid extraction processes. This report examines some possible decontamination techniques and outlines a proposed program of studies aimed at developing a satisfactory production procedure.

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TRITIUM REMOVAL

The Isotope Effect

Equilibrium

Mass differences affect the energy of molecules, and for the hydrogen isotopes, these energy differences are large; consequently, the distribution of hydrogen isotopes among several molecular species at equilibrium is far from random. Isotopes of heavier elements, on the other hand, tend to be randomly distributed among the various possible molecular species. Representative values are shown in Table I.

Table I. Equilibrium distribution of selected isotopes, illustrating large departure from random distribution in isotopes of lighter elements.

Reaction	(K/K') ^a at 298.1°K
HT + H ₂ O ⇌ H ₂ + HTO	6.194
HD + H ₂ O ⇌ H ₂ + HDO	3.703
HCl + DI ⇌ DCl + HI	1.527
¹³ CO ₂ + ¹² CO ₃ ⁼ ⇌ ¹² CO ₂ + ¹³ CO ₃ ⁼	1.012
¹²⁷ I ¹²⁹ I + ¹²⁷ I O ₃ ⁻ ⇌ ¹²⁷ I ₂ + ¹²⁹ I O ₃ ⁻	1.002

^aK is the true equilibrium constant calculated from Urey's² summary of partition functions, and K' is the equilibrium constant from random distribution of isotopes.

Kinetics

Isotopic molecules also undergo chemical transformation at different rates, and Bigeleisen³ has estimated from statistical rate theory the maximum isotope effect on rate constants. These results, summarized in Table II, show clearly that separation of the hydrogen isotopes by differences in reaction rate is highly favored over such separation methods for heavier molecules; consequently a separation can be accomplished by using equilibrium values, kinetic effects, or a combination of the two.

Table II. Ratio of specific rate constants (k₁/k₂) at 25°C for selected isotope pairs (abstracted from Ref. 4).

Isotope 1	Isotope 2	k ₁ /k ₂
H	D	18
H	T	60
¹² C	¹³ C	1.25
¹⁶ O	¹⁸ O	1.19
¹²⁷ I	¹³¹ I	1.02

Exchange Reactions

Mechanism

Why do exchange reactions take place? The mechanism for many such reactions is not known, but in general, the rate-determining step is one of the following:

1. The reversible dissociation of one reactant to give a product that may exchange rapidly with the second reactant.

2. The decomposition of a transition state in which one or more electrons may be transferred from one reactant to the other.

3. The decomposition of a transition state in which one or more atoms may be transferred from one reactant to another.

This study is concerned with mechanism 3, illustrated by the exchange between halide ion and halogen, the trihalide ion presumably being the transition state as shown in the reaction

It should be clearly understood that this work is not concerned with the Wilzbach⁵ labeling which is commonly used to label organic compounds with T by means of the following radiation-induced reaction:

Certainly reaction (2) will take place in addition to the expected exchange reactions, but it will not be considered here.

Application to Tritium Removal

Clearly, an exchange reaction, if it will proceed at a reasonable rate, can remove T from the gas produced from a nuclearly stimulated gas well. Data from the Gasbuggy Experiment¹ showed that, during the initial shut-in period, two of the main gaseous components were CH₄ (30-40%) and H₂ (10-20%). The corresponding radioactive species, CH₃T and HT, accounted for the majority of the T contamination. Consequently, subsequent discussions are concerned with these two gases, with the main emphasis placed on CH₃T.

Exchange reactions (3)-(7) below, which involve only common chemicals, are worth considering for gas decontamination. Analogous reactions (except for reaction (7)), where HT replaces CH₃T should also be considered for decontamination. Both sets of reactions must be considered in a thorough decontamination study.

Glycol dryers,⁶ as used in natural gas processing, might be used in decontamination procedures by employing the ethylene glycol as a reactant:

Reactions of a similar nature where the gas stream is passed through a bed of silicate rocks or through rocks containing metal hydroxides might also be employed. These reactions will not be considered further in this paper.

Flow Requirements for Separation

If an exchange reaction proceeds at a reasonable rate, then separation can be accomplished by contacting the flowing gas with a stream of the other component moving in the opposite direction. Consider reaction (3); what water flow would be required?

Let

$A = \mu\text{Ci of CH}_3\text{T per ml of produced gas,}$

$G = \text{gas flow rate, ft}^3/\text{day,}$

$W = \text{water flow rate, ft}^3/\text{day,}$

$(\text{RPG})_g = \text{amount of T in gas, } \mu\text{Ci/cc,}$

$(\text{RPG})_w = \text{amount of T in water, } \mu\text{Ci/cc,}$

where (RPG) denotes Radiation Protection Guide.* Conservation of radio-activity shows that

$$W = \frac{[A - (\text{RPG})_g]G}{(\text{RPG})_w}. \quad (9)$$

The order of magnitude of CH_3T in the gas during the shut-in period was $\sim 15 \mu\text{Ci/ft}^3$ or $\sim 5.3 \times 10^{-4} \mu\text{Ci/cc}$. The required water flow is, of course, a function of the values taken for $(\text{RPG})_g$ and $(\text{RPG})_w$. Since no values have been tabulated for natural gas, $(\text{RPG})_g$ was taken as $(\text{RPG})_a$, the value for air, with T as HTO and no dilution with uncontaminated gas or combustion products. No dilution of the waste water was considered. Results are tabulated in Table III.

Table III. Water flow required for production of 1 million cubic feet gas per day.

Condition of exposure	$(\text{RPG})_g$, $\mu\text{Ci/cc}$	$(\text{RPG})_w$, $\mu\text{Ci/cc}$	Water flow, ft^3/day
168-hr week, general population, gas as HTO	7×10^{-8}	1×10^{-3}	5.3×10^5
40-hr week, occupational, gas as HTO	5×10^{-6}	1×10^{-1}	5.3×10^5

Number of Stages Required

Clearly, the gas can be decontaminated by countercurrent equilibrium between the gas and water, and a logical question is how many stages might be required for extraction of T into H_2O ?

Exchange processes can be considered in terms of the single-stage separation factor, α , defined as the abundance ratio (atoms desired isotope/atoms undesired isotope) in the heads (product) stream divided by the isotope abundance ratio in the tails (waste) stream. The separation factor can be related to the equilibrium constant, K_{eq} , as shown below. If one considers reaction (3), defines T as the "desired" isotope, and replaces activities by molar concentrations, he finds that

$$\alpha(3) = \frac{[\text{HTO}]}{2[\text{H}_2\text{O}]} \bigg/ \frac{[\text{CH}_3\text{T}]}{4[\text{CH}_4]} = 2 K_{\text{eq}}. \quad (10)$$

On the other hand, replacement of CH_3T by HT in reaction (4) gives reaction (4'):

* (RPG) values taken from Standards for Protection Against Radiation, Code of Federal Regulations, Title 10, Chapter 1, Part 20 (U.S. Govt. Printing Office, Washington, D.C.) (Revised Jan. 1, 1969).

and

$$\alpha(4') = K_{eq} . \quad (11)$$

Alpha is then related to but not necessarily equal to K_{eq} .

Values of α for many T-containing compounds have been published,⁷ and some appropriate values are listed in Table IV.

Table IV. Single-stage separation factors (α) for selected reactions involving tritium compounds (abstracted from Ref. 7).

Reaction	α
$\text{CH}_3\text{T} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_4 + \text{HTO}$	1.14
$\text{CH}_3\text{T} + \text{NH}_3 \rightleftharpoons \text{CH}_4 + \text{NH}_2\text{T}$	1
$\text{CH}_3\text{T} + \text{H}_2\text{S} \rightleftharpoons \text{CH}_4 + \text{HTS}$	1
$\text{CH}_3\text{T} + \text{H}_2 \rightleftharpoons \text{CH}_4 + \text{HT}$	0.17

Consider the liquid-gas extraction unit shown in Fig. 1 and the cases listed in Table III. It can be shown that m of Fig. 1 and α are related by the formula

$$m = \frac{1.6 \times 10^{-3}}{\alpha} \quad (12)$$

G = volume of CH_4 flowing upward
(cu ft per day per unit area),

y = concentration of desired component
in gas stream at any stage (μCi of
 CH_3T per cu ft),

W = volume of H_2O flowing downward
(cu ft per day per unit area),

x = concentration of desired component in
liquid stream (μCi of HTO per cu ft).

Fig. 1. Symbols and parameters used in column design. (Treatment based on Sherwood and Pigford.⁸)

for this particular reaction and system of units. Substitution of these data into equation (13) shows that only three or four plates are required in the cases considered.

Referring to Fig. 1, one sees that a material balance applied below plate c requires that

$$W(x_1 - x_c) = G(y_1 - y_d),$$

and a linear equilibrium relationship states that at any stage

$$y_n = mx_n.$$

The solution for the required number of plates, N_p , can be expressed as:

$$N_p = \frac{\ln \left[\left(1 - \frac{mG}{W} \right) \left(\frac{y_1 - mx_2}{y_2 - mx_2} \right) + \frac{mG}{W} \right]}{\ln (W/mG)}. \quad (13)$$

Similar considerations apply to HT, C₂H₅T, etc., but these reactions were not studied because of lack of time.

Reaction Rates

These results show that if the previously discussed exchange reactions proceed at an acceptable rate, tritium decontamination is possible; however, the real question is whether or not the reactions proceed at a reasonable rate. A literature search showed no evidence for the homogeneous gas-phase exchange of either D or T between H₂O and CH₄. Recent data⁹ have verified that this homogeneous exchange does not occur in a mixture standing for 24 hours at 450°C. These results are not surprising when the possible rate-determining steps mentioned earlier are considered.

The exchange should occur by atomic interchange in the transition complex, and this behavior requires that the reaction take place either in aqueous solution with a homogeneous catalyst or in the gas phase with a heterogeneous catalyst.

Horiuti and Polanyi,¹⁰ using Pt black or active Ni catalysts, found that the reaction

reached equilibrium in 24 hours at 80°C. The reaction

reached equilibrium after 2 hours at 200°C, and the exchange between C₆H₆ and H₂O was found to be 10⁵ times slower than C₆H₆ and H₂ when both reactions were carried out over a Ni catalyst.

Extensive exchange studies with CH₄ were conducted by Morikawa et al.¹¹⁻¹⁴ who reported that CH₄ exchanged with D₂, CD₄, and D₂O at 140°C and higher over an active Ni catalyst. The rates were in the order CD₄ > D₂ > D₂O. Clearly, H₂O vapor and CH₄ gas undergo catalytically induced H atom exchange.

The preparation of deuterated or tritiated organic compounds by direct exchange of the compound with H₂O was pioneered by Garnett.¹⁵ Platinum (II) oxide was employed as a catalyst; the procedure was most successful with aromatic compounds, but exchange occurred between T₂O and a wide variety of alicyclic, aromatic, and aliphatic compounds. Rapid exchange was

attributed to interaction between π -bonds of the aromatic molecules and d-orbitals of the Pt^{+2} . Aliphatic hydrocarbons, containing only σ -bonds, underwent much slower exchange on the platinum surface. This procedure has now been extended to homogeneous systems¹⁶ using Na_2PtCl_4 as a homogeneous catalyst, and compounds which are difficult to label in the heterogeneous system (e.g., nitrobenzene, bromobenzene, naphthalene, and acetophenone) have been labeled by the homogeneous method. A review of these methods has been published.¹⁷

KRYPTON REMOVAL

Possible methods for ^{85}Kr removal include (1) solution of ^{85}Kr in H_2O , (2) chemical synthesis of a clathrate or a fluorine compound, and (3) use of the contaminated gas as feed material for ammonia synthesis.

The first of these is ruled out because the solubility¹⁸ of Kr in water is too small for effective removal during the exchange process. The second appears unpromising for the following reasons: Although the placing of large amounts of a fluorine-containing compound around the nuclear explosive used for gas well stimulation might have some potential for forming krypton fluorides, the compounds KrF_2 and KrF_4 lack stability.¹⁹ Clathrate compounds of Kr with phenol²⁰ and with β -hydroquinone^{21,22} have been described, but in general these compounds have been made under high Kr pressures. Nothing is known about the stability of possible Kr compounds in the postshot environment.

The third method, use of the contaminated gas for ammonia synthesis, seems to have real potential. The normal process²³ for manufacturing ammonia synthesis gas starts with the partial oxidation of a hydrocarbon to a mixture of CO and H_2 . An iron catalyst then converts steam and CO to H_2 and CO_2 ; the gas is subsequently washed with water to remove CO_2 . Tritium can be removed from the H_2 in this step by the reaction

The gas is then passed through a tower countercurrent to liquid N_2 which condenses Ar, CO, and residual CH_4 and adds the required amount of N_2 to the process stream. The ^{85}Kr will be removed from the process stream at this point; however, it may be necessary to add inert Kr as a carrier.

RECOMMENDATIONS

The use of exchange reactions seems to have potential for decontamination of product gas, but this potential needs verification. A program to confirm the usefulness of this technique should include the following:

1. Equilibrium constants should be calculated for reactions (3) through (8), and their H_2 counterparts, which offer potential means of removing the tritium.
2. Equilibrium data plus reasonable flow data should be employed in preparing a preliminary reference design for such a possible separation plant. A cost estimate should be made.
3. Use of the gas for ammonia synthesis should be examined carefully, since this appears to be a promising way to remove the ^{85}Kr .
4. Experimental work on the rates of these reactions should be started. Can the reaction be made to go with liquid water? Is a catalyst necessary? Is the catalyst poisoned by liquid water, thereby requiring that the reactions be run in the vapor phase?
5. An effort should be made to set some standards for radioactivity in natural gas. This is a difficult question, but without standards it is impossible to do practical planning for nuclear stimulation of gas wells.

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