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AN EVALUATION OF WATER PRODUCTION FROM THE GASBUGGY REENTRY WELL

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It is concluded that a decrease in the bottom hole pressure of GB-E resulted in Ojo Alamo water entering GB-E and either being produced or flowing down GB-E into the chimney. The water entry rate follows Darcy's Law in that it is proportional to the pressure gradient between the hydrostatic head and the chimney pressure. It is postulated that the water is flowing directly from the Ojo Alamo into GB-E and then flowing downward through the stemming material until it enters the inner casing through a break at 3796 feet, just 3 feet below the bottom of the production tubing.

A calculation of the water volume which could enter the chimney in this manner is less than could be detected by chimney volume measurement techniques presently available.

Hydrologic data shows that the hydrostatic level fluctuation of the Ojo Alamo correlates with chimney pressure and a sink is indicated at or near GB-ER.

Preliminary analyses from data obtained during the test period of October and November 1969 indicate that the leak in GB-ER has been sealed, water production during this period corresponds to the calculated vapor model, water levels have risen to near normal in the Ojo Alamo and tritium levels in produced water have increased to 0.5  $\mu$ Ci/ml.

#### INTRODUCTION

Gasbuggy was a 26-kiloton nuclear explosion which was detonated underground at a depth of 4240 feet. The event occurred on December 10, 1967 at a site 55 air miles east of Farmington, New Mexico. The purpose of the explosion was to create a chimney of broken rock and induce fractures in the rock beyond the chimney boundary in order to increase the rate of gas production in a gasbearing formation just above the detonation point.

It was anticipated that the gas produced from this chimney would contain water vapor and perhaps condensed water. The source of this water was expected to be the bound and the free water which existed preshot in the rock which was vaporized, melted, broken and fractured by the explosion.

Initially, the amount of water produced from the chimney through the reentry well was minor. During the November 1968 "blowdown," about 4 to 5 barrels of water per million standard cubic feet of gas was produced. As the program progressed, the water production rate increased. During the blowdown period in February and March of 1969 this rate of water production reached 40 to 50 barrels per million standard cubic feet of gas. Since this water contained tritium, it required special handling which in turn increased safety program and waste disposal costs.

Initially, (during the summer tests in 1968) the tritiated water was put into barrels and shipped to the Nevada Test Site for disposal. A vaporizing unit was fielded prior to November 1968 which could disperse the water vapor safely to the atmosphere.

The increase in water production rate was unexpected and a program was initiated to determine the source of the water and its relationship to the Gasbuggy chimney. A first step in understanding the situation was to develop an appropriate model which could calculate, reasonably well, the amount of water which should be produced under the observed conditions. In this we were fortunate in that the Production Department of El Paso Natural Gas Company had kept very good records of temperatures, pressures, flow rates and liquids production.

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#### MODEL OF WATER PRODUCTION

A schematic diagram of the chimney and reentry well (GB-ER) is shown in Figure 1. Bottom-hole temperature and pressure measurements were made by lowering an instrument package on a wire line through the 2 7/8" tubing to four feet below the packer which was set at 3786 feet. (Measurements at lower levels were not made even though the hole was open to a depth of 3916' because of the fear of not being able to retract the instrument package back into the 2 7/8" tubing.)

The model incorporates the assumption that sufficient water is present in the chimney to maintain a 100% humidity condition in the gas delivered from within the chimney to the bottom of the 2 7/8" tubing. This assumption results in a model which produces the greatest amount of water possible by condensation of vapor within the production tubing. Gas is transported from the cavity through a 7" OD casing to the lower end of a 2 7/8" OD tubing at the observed temperatures and pressures. The volume of gas and total water vapor entering the 2 7/8" OD tubing and the gas velocities in both the 7" casing and 2 7/8" tubing can be calculated as follows:

Gas volume transported per unit time (cubic feet per second) at bottom-hole conditions:

$$V_{B} = \frac{P_{A}}{T_{A}} \frac{P_{A}}{P_{A}} \frac{P_{A}}{P_{A}} \frac{P_{A}}{P_{A}} \frac{1}{8.64 \times 10^{4}}$$

where Q = Flow rate in standard cubic feet/day

 $T_{\rm p}$  = Measured bottom hole temperature (<sup>O</sup>R)

 $T_{O}$  = Standard temperature (520°R)

 $P_{R}$  = Bottom-hole partial gas pressure (psi)

 $Z_B = Gas$  compressibility (Ref. 1)

 $P_{O}$  = Standard pressure (14.7 psi)

It should be noted that  $P_B$  is a partial gas pressure and not the measured total pressure. The total pressure is the sum of the partial gas pressure and the vapor pressure of water at the bottomhole temperature.

The average gas velocity in a given diameter conduit is then given by  $v = V_{\rm R}/{\rm A}$ 

where A = inside cross section area of the pipe.

The amount of water vapor,  ${\rm W}_{\rm B}$  entering the 2 7/8" tubing is given by

 $\overset{W}{B} = \begin{array}{c} fV \\ B \end{array} \begin{array}{c} \rho \\ B \end{array} \begin{array}{c} dt \\ B \end{array} = \begin{array}{c} V \\ B \end{array} \begin{array}{c} \rho \\ B \end{array} \begin{array}{c} t \end{array}$ 

where t = time in seconds, and where  $\rho_R = density$  of water vapor at a given temperature.

Identical calculations can be made to calculate volume  $(V_T)$ , velocity  $(v_T)$ , and water vapor by weight  $(W_T)$ , at observed tophole conditions. If  $W_B$  is greater than  $W_T$ , the excess vapor will condense out of the vapor phase into a liquid. If the gas velocity is sufficiently great, this water, in the form of droplets, will be carried up the tubing and collected in the baffle separator at the surface.

The critical gas velocity for a given droplet of water to be carried up the pipe can be determined by using Stokes' Law. Stokes' Law calculates the terminal velocity of a sphere moving in a gravitational field through a viscous media. The equation is

$$v_{s} = \frac{2 gr^{2} (\rho - \rho)}{\frac{1}{2}}$$

where g

= 980 cm/sec<sup>2</sup>

r = radius of sphere

 $\rho_1$  = density of sphere (gm/cm<sup>3</sup>)

 $\rho_2$  = density of viscous media (gm/cm<sup>3</sup>)

 $\eta$  = viscosity of viscous media (poises)

Stokes' velocity  $(v_s)$  is the relative velocity between the sphere and the viscous media. If the gas or viscous media is moving upward, the absolute velocity of the sphere will be the difference of the two velocities  $(v - v_s)$ . Thus, if the terminal velocity of a sphere of water is greater than the upward gas velocity, the water will fall back into the chimney. If the terminal velocity is less than the gas velocity, the water will be carried up the tubing and into the separator. Figure 2 shows a plot of terminal velocity versus droplet size. (Actually, n is dependent upon both temperature and pressure of the viscous media. For the range involved, however, the effect is small and has been neglected here.)

In actual practice small droplets spend enough time in the pipe to coalesce into bigger drops with resultant higher terminal velocities. As a result, there is a tendency for all or most of the condensed water to return downward to the chimney at low upward gas velocities. As the gas velocity is increased, water droplets and surface film collect in increasing amounts in the tubing causing an effective reduction in tubing diameter and a further increase in gas velocity. As gas velocities approach some critical value, the condensed water is produced to the surface, sometimes as intermittent slugs. At greater than critical velocities the water is produced at a more uniform rate.

The critical velocity used in the model was set at zero to simplify the calculations. The model, therefore, calculates the maximum water possible from condensed vapor sources and should give high values at low gas production rates. The total water is given by the equation

 $W_p = W_B - W_T$ 

,a

where  $W_P$  is the difference between the water vapor in the gas at the bottom and the top of the tubing.

#### COMPARISON OF MODEL WITH EXPERIMENTAL RESULTS

The period for this comparison extends from November 5, 1968 through May 7, 1969. This includes four rapid drawdowns, three thirty-day constant bottom-hole pressure runs and one long-term constant pressure run. (Some preliminary data from a rapid drawdown in October - November of 1969 are discussed briefly in a later section. However, it was too late to include this data in the main analysis.) This test program results in data points which form clusters at the high and low gas velocities. It is unfortunate that there is a paucity of data for intermediate flow rates.

Figure 3 shows the gas flow rate and cumulative gas production for this period. Figure 4 shows the top and bottom-hole temperatures and the corresponding partial gas pressures are shown in Figure 5. These quantities along with Z,  $T_0$  and  $P_0$  were used to calculate the water production which is compared to the measured water production in Figure 6.

It can be seen from Figure 6 that the model matches the data well at early times and at later times during periods of low flow rates. During periods of low flow rates the model predicts some water production whereas none was experienced. This is a result of using a zero value for Stokes' critical velocity in the model, as noted earlier.

It is obvious that during the last two high flow periods, considerably more water was produced than would be expected from the model. During these periods it is calculated that over 90% of the total water entering into the bottom of the tubing in vapor form condenses ( $W_p \ge 0.9 W_B$ ). Since the observed produced water is from three to over seven times the calculated water vapor during these periods, it must be concluded that quantities of additional water are entering the 2 7/8" tubing in droplet or liquid form.

In an effort to explain and locate this source of additional water, several correlations were performed.

#### EXCESS WATER CORRELATED WITH GAS PARAMETERS

Gas velocities in the well were calculated for several points

in the tubing and casing. The values calculated for the top and bottom of the 2 7/8" OD tubing are shown in Figure 7. (Velocities calculated for the 7" casing are not shown.) The model does not allow for frictional forces or a closure of the tubing due to the condensed liquid film adhering to the inner walls; hence, these calculated average velocities should not be greater than the actual gas velocities in the well bore. In fact, they are probably considerably less.

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In order to do a correlation on the available data, it was necessary to select time intervals of one day. This interval was necessary because water production records were kept only on a daily basis. Data points were selected such that each drawdown and long-term test was represented by at least two and no more than five data points except for the period of April to May. An attempt was made to limit data points to days when no changes in conditions or flow rates occurred. The data points selected for the correlation studies consisted of the 35 points shown as dots in Figure 3. The correlation study was performed using the graphical regression analysis described by Ezekiel (Ref. 3).

Since the water produced from GB-ER is apparently only partly due to water vapor in the gas, the first step in determining the other source or sources of water is to calculate the excess water. This residual or excess water can be easily obtained from Figure 6 since it is simply the difference between the calculated and the measured water. This method results in a negative excess water for some days as a result of the zero critical velocity in the model, which has already been discussed. This is not a serious problem since these negative values are never very large.

The residual or excess water is then correlated with the various parameters of temperature, pressure and velocity. In Figure 8, residual water is plotted as a function of the velocity at the lower end of the 2 7/8" OD tubing. This Figure indicates that there is a probable cut-off at about 40 ft/sec below which the gas has insufficient velocity to carry the excess water up the 2 7/8" tubing.

A good linear correlation was found between excess water and total bottom-hole pressure. This is shown in Figure 9. The concept of a critical velocity is very apparent in Figure 9 where the data points fall into two distinct groups, those which cluster about the abscissa and those which cluster about the line.

 $H_2O_{Res} = 126.5 - 0.1473 BHP_{Total}$ .

This linear relationship between excess water and pressure strongly suggests Darcy flow where the volumetric flow across a given surface is proportional to the pressure difference. If we were to assume the excess water were coming from a source of constant hydrostatic head, the available excess water would be proportional to bottom-hole pressure. This can be seen by the following form of Darcy's Law:

$$Q = \frac{k}{n} \nabla P = \frac{k}{n} (P_{H} - BHP)$$

If k (permeability),  $\eta$  (viscosity) and  $P_{\mbox{H}}$  (hydrostatic head) are constant, then

Q = A - B (BHP)

where A and B are constants.

The residual or excess water is also shown as a function of top-hole pressure in Figure 10. Clearly this does not result in a linear relationship. Similar plots using the pressure at various depths within the well bore would yield a family of curves ranging between those shown in Figures 9 and 10. Because of the excellent correlation between the data and a linear relationship to bottomhole pressure, it is most likely that the excess water is entering the well bore near the bottom of the 2 7/8" tubing. This is consistent with what was found during drill-back through the 7" OD casing when it was noted that the cement in the emplacement hole was wet below a depth of 3029 feet and casing breaks were detected at 3796 feet and lower in the 7" casing (Ref. 4). ייאטיין גיינעי

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The most probable source of water is the aquifer in the Ojo Alamo Formation. However, since production is through the 2 7/8" tubing and a packer is set at 3786 feet, the water would have to be entering the gas stream either through the joints in the 2 7/8" tubing or through the bottom opening of the tubing which extends through the packer to 3793 feet. The measurements which put the bottom of the tubing at 3793 feet and the casing break at 3796 feet are close enough (considering the degree of accuracy involved) to suggest that the excess water is probably entering at this point.

Borehole photographs of the well bore (Ref. 4, Figure 5) indicate that just after drill back, considerable water was present in droplets and adhering to the side of the 7" casing in a uniform manner at a depth of 3828 feet. It is possible that water is being sprayed through the casing break and into the 7" casing just below the packer where it is either caught directly into the gas stream entering the 2 7/8" tubing or it is collecting on the surface of the 2 7/8" tubing and running down to the lip where it is then drawn into the production tubing.

Assuming that all hole surveys are accurate to within one foot, it appears most reasonable that water is entering the 7" casing just below the 2 7/8" tubing in such a manner that at that point the water is in the form of a fine mist. If this mist were close enough to the bottom of the tubing, the critical Stokes' velocity that would apply would be the 40 ft/sec threshold value from Figure 8. This would mean that all or most of the droplets must be less than .01" in radius. If we use the velocity in the 7" casing (6 ft/sec), we must conclude that the droplets are less than .004" in radius. The conclusion that six feet per second is the critical velocity is supported by the fact that when the gas velocity in the 2 7/8" tubing drops to less than ten feet per second, no water is produced at all and even condensed water vapor returns to the chimney.

If we assume that water is seeping into GB-ER and is either being produced or, at low flow rates, is entering the chimney, we can use Figures 5 and 9 to calculate the total influx of water into GB-ER. This is shown in Figure 11. Between November 4, 1968 and October 25, 1969, about 25,000 barrels of water are estimated to

have entered GB-ER. After subtracting the water which was produced at the surface, we find that about 125,000 cubic feet of water has entered the chimney. This volume change is just at the level of detectibility using the present volumetric measurement methods available to us. No volume change greater than this limit of accuracy has been observed and it can be concluded that no more than about 125,000 cubic feet of water has entered the chimney during this time. Thus, it is unlikely that water is entering the chimney through any other path.

#### WATER RADIOACTIVITY

Radioactivity in the produced water further indicates a dilution of the chimney water. Liquid samples containing water from the cavity gas have been extracted by dehydration and particulate removal at the wellhead complex. These samples have been analyzed for both chemical composition and tritium radioactivity (HTO) since the inception of the first flow tests in late June 1968. Figure 12 presents the radioactivity concentration in the produced water. Liquid scintillation measurements were made by LRL (Ref. 5) and Eberline Instruments (Ref. 6). The concentration of early tritium radioactivity appears relatively constant slightly above 1.0  $\mu$ Ci/ml through December 1968. During the drawdown for the second thirty-day test in mid-January 1969, a sharp decline in the water radioactivity occurred. From February 1969 until October 1969 the concentrations remained consistently below about .2  $\mu$ Ci/ml, declining gradually to a level of about .05  $\mu$ Ci/ml. This sudden and large change in radioactivity at all flow rates seems to indicate a dilution in either or both the chimney vapor and produced water.

A very interesting sidelight is the fact that it is difficult to account for the total tritium. If one were to assume uniform mixing in the cavity water, then the initial radioactivity concentration of about 1.2  $\mu$ Ci/ml combined with the assumption that about 90% of the initial four gms. of tritium went into the water (only about 10% can be accounted for in the gas) would require that the chimney contain something like 800,000 cubic feet of water. This is roughly one-third of the calculated void volume of the Gasbuggy cavity! In order to get a concentration of < .1  $\mu$ Ci/ml, many times the cavity void volume of water would be required.

Two questions are emphasized by the foregoing considerations:

- 1) What happened to the tritium?
- 2) Why the order of magnitude decrease in water radioactivity during January of 1969?

It is possible (a) a considerable fraction of the tritium was trapped at early time in the melt; (b) a considerable fraction of tritium exists in a form which is bound chemically with rocks in the cavity; or (c) an isolated tritium-rich water pool exists somewhere in the cavity. It may be possible for tritium in these forms to exchange with circulating gas or free liquids containing hydrogen. No indication that such an exchange establishes a base level tritium concentration for the gas has been observed to date. The decrease in radioactive concentration since January could have resulted from dilution by water from outside the cavity environment. Two possible sources of water suggest themselves:

- 1) water from Ojo Alamo, and
- 2) water from Pictured Cliffs.

#### CHEMICAL COMPOSITION

The top of the Gasbuggy chimney occurs at 3906 feet. This is very near to the boundary between the Pictured Cliffs sandstone and the Fruitland coal. The Ojo Alamo sandstone aquifer occurs some 200-250 feet above the top of the chimney. Chemical composition analyses of water samples taken from the Ojo Alamo Formation and the Pictured Cliffs Formation are depicted in Table I. This table shows the characterization of water by formation association in a rather straightforward way by sulfate or chloride content. One can characterize Pictured Cliffs water as having high chloride content and relatively low sulfate content, contrasted with the Ojo Alamo water which has high sulfate and relatively low chloride.

#### Table I

#### Water Chemical Composition

Ojo Alamo Formation

Location	1 Sample	D	ate	C1 ppm.	<u>SO4</u> ppm.
3450'	GB	Nov.	2, 1967	140	3580
3539	GB	Nov.	2, 1967	120	3700
3650'	GB	Nov.	2, 1967	130	3340
3636'	GB-1	Mar.	1, 1967	170	5470
3696	GB-1	Mar.	1, 1967	170	5470
3505'	GB-ER	Jan.	12, 1968	280	4330

#### Pictured Cliffs Formation

3920		GB-2	May	1,	1967	5320	480
Indian	E-1	Well	May	5,	1967	3700	0
Feasel	#2	Well	Feb.	8,	1968	12,100	0

With the exception of the reentry sample from GB-ER and Feasel #2, all samples shown in Table I were taken preshot from their respective formations. Feasel #2 is the only well listed which is not in the immediate area of the GB-E well; i.e., within a three-mile radius. It does not appear that water chemical composition changes will occur in samples taken from the same formation at this distance (three miles) in the absence of a geologic anomaly.

Table II shows the results of chemical analyses on water produced from GB-ER. Analyses of the data in Table II strongly indicate the presence of Ojo Alamo water in the produced gas postshot. Samples taken on November 7, 1968 and between December 14, 1968 and December 30, 1968 are strongly indicative of distilled water. During the high flow rate periods and continuously after January 11, 1969, the water produced from GB-ER shows chemical composition very similar to the Ojo Alamo water. The concentration of ions during these periods is so high as to indicate this water has not passed through the vapor state since it left the aquifer. At no time has water been detected postshot in the produced water which has characteristic Pictured Cliffs chemical composition. This, of course, does not preclude the possibility that Pictured Cliffs water is entering the chimney at lower depths where gas velocities are insufficient to carry the liquids into the production tubing.

Date	Cl ppm	SO <sub>4</sub> ppm	Date	Cl ppm	SO <sub>4</sub> ppm
11/ 7/68	20	82	1/17/69	216	3500
11/10	190	1620	1/23	10	583
11/12	140	2095	1/25	14	208
11/14	185	2135	1/29	16	208
11/16	170	2180	2/18	160	2945
11/18	144	2220	2/19	220	3200
11/20	135	2160	2/20	240	4033
11/24	310	550	2/21	220	3993
11/26	200	2160	2/22	240	3934
11/29	135	2180	2/24	280	3380
12/1	140	2200	2/25	248	3875
12/ 3	80	2240	2/26	232	3855
12/7	32	158	2/27	252	3555
12/ 8	28	267	2/28	248	3695
12/10	8	178	3/ 1	248	3890
12/11	40	257	3/2	256	3500
12/12	40	247	3/3	264	3830
12/14	16	0	3/4	264	4360
12/16	20	0	3/5	276	4690
12/18	4	59	3/6	285	4690
12/20	16	0	3/7	268	4550
12/22	20	0	3/8	275	4740
12/24	20	0	3/10	264	4600
12/26	48	0	3/12	84	3260
12/28	20	0	3/13	264	4640
12/30	6	0	3/15	285	4520
1 /11/69	148	2372	3/17	255	4395
1 /12	168	2866	3/19	285	3980
1 /13	140	3222	3/21	48	1150
1 /14	184	3360	3/24	225	3090
1 /15	208	3560	3/27	28	820
1 /16	212	3140	4/2	320	3260
			4/24	225	3090

Table II

#### HYDROSTATIC LEVEL OBSERVATIONS

If water from the Ojo Alamo Formation were entering GB-ER, the hydrostatic level in this aquifer should reflect this by showing an appropriate fluctuation. Good level measurements were obtained during the entire program in the nearby well designated as San Juan 29-4 Unit Well #10, which is about 420 feet from GB-ER. In addition, several observations were made in the 7" casing in GB-ER beginning in March of 1969 and a single data point was taken in GB-3 in September 1969 (Ref. 7). GB-3 is located about 200 feet from GB-ER at the Ojo Alamo Formation depth of 3550 feet.

Figure 13 shows the hydrostatic level history in all three locations. The level in 29-4 #10 well shows a distinct response to the decreases in chimney pressure and suggests a "sink" somewhere in the vicinity. It was not until March of 1969 that a measurement was accomplished in the GB-ER annulus which verified the existence of a sink. The observation in GB-3 appears to indicate (when combined with other observations) that GB-ER is at or near the center of the sink.

#### LATER RESULTS

On October 28, 1969 a drawdown was started to lower the chimney pressure to about 125 psig. This was completed on November 14, 1969 and GB-ER was then shut in for pressure buildup studies. Because of the time limitation in getting this paper to the publisher, it was impossible to include data from this late period in the graphs and figures. However, we can report the following preliminary results.

- Chimney volume measurements during the October 28 to November 14 period show no decrease in chimney volume greater than the uncertainty in the calculations (10<sup>5</sup> cubic feet).
- Water production during this period corresponds to that which would result from condensed vapor alone; i.e., no excess water was observed. This in spite of the fact that calculated gas velocities were greater than critical.
- 3) Tritium in water increased from 0.1  $\mu$ Ci/ml to roughly 0.5  $\mu$ Ci/ml during the first few days of production and remained at that level for the rest of the period. (Ref. 8)
- 4) During this seventeen-day period, the water level in 29-4 #10 rose from 1021' to 976'. Correspondingly, the water level in GB-ER was at 1225' on October 28 and rose to about 1010' or 1020'.

All of this indicates that the leak has been sealed during this last test period. An examination of the history of 29-4 #10 shows that a partial sealing of the leak may have occurred in mid-April 1969.

#### CONCLUSIONS

The production of water during the period of November 1968 to May of 1969 from GB-ER exceeded that which could be expected from condensed vapor entrained in the gas flow. Radioactivity levels of the produced water indicated a high dilution from an extraneous source. Chemical analyses of this water and hydrostatic level observations support the proposition that the source of the extraneous water is the Ojo Alamo Aquifer. The hydrostatic level and chimney volume measurements support the thesis that the "sink" is at or near GB-ER. In view of the difficulties encountered during cementing operations on the lower portion of GB-E, it is not surprising that there was a leak into the chimney area through the stemming materials in this hole. It now appears that the leak has been plugged by some obscure process although the permanency of this plug is not assured.

It is important to realize that the device explosion did not alter the region such that the chimney region was flooded by massive quantities of water from the overlying aquifer and the leak in GB-ER should be regarded as an exception due to the difficulties which were encountered in cementing the emplacement hole at the depth of the Ojo Alamo Formation

#### ACKNOWLEDGEMENT

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FIGURE 1. Schematic drawing of the Gasbuggy reentry well showing its relationship to the chimney region and geologic formations.



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### FIGURE 2. A plot of terminal velocity in methane for spherical water droplets as a function of droplet radius according to Stokes' Law.



FIGURE 3. Gas production history and cumulative total gas for the Gasbuggy reentry well. The circles indicate those days which were used to perform the correlation study.



FIGURE 4. Temperature history in GB-ER at 2 points: top hole (surface) and bottom hole (in the 2 7/8" tubing at a depth of 3790 feet).



FIGURE 5. Gas partical pressure history for GB-ER at two points: top hole (surface) and bottom hole (in the 2 7/8" tubing at a depth of 3790 feet).



FIGURE 6. Observed and calculated water production for GB-ER.



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FIGURE 7. Calculated average gas velocities at two points in the 2 7/8" tubing in GB-ER: Top hole (surface) and bottom hole (at a depth of 3790 feet).



FIGURE 8. Correlation of excess water from GB-ER with bottom hole gas velocity. It appears that little or no excess water is produced below a velocity of 40'/sec.



FIGURE 9. Correlation of excess water produced from GB-ER with chimney (bottom hole) gas partial pressure. The squares are data points for which gas velocities exceeded 40'/sec with the 3 following exceptions: The two squares at the extreme right are at velocities of about 28'/sec and are the only points which exist between 15'/sec and 40'/sec (the exclusion of these points does not change the slope of the line) and datum point marked by a (?) at the top center of the Figure. The validity of this point is questionable since it occurs at the start of a "blowdown" and may reflect some peculiarity in the data collection and analysis.



FIGURE 10. Correlation of excess water production with top-hole pressure. The only points shown are those for which gas velocity exceeded 15'/sec. The relationship is nonlinear and hence it is doubtful that a positive correlation can be deduced.



FIGURE 11. Rate of water influx into GB-ER with the chimney and cumulative water history. Net influx would be the amount shown less the excess water produced from GB-ER.



FIGURE 12. Tritium radioactivity in water and gas produced from GB-ER.



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### Studies of Chemical and Radiochemical Composition of Natural Gas from the Cavity Produced by the Project Gasbuggy Nuclear Shot'

#### Charles F. Smith and Floyd F. Momyer<sup>2</sup>

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Data relating to the chemical and radiochemical results from Project Gasbuggy chimney-gas samples obtained prior to 210 days after detonation (December 10, 1967) are presented for significant non-radioactive components of the gas and for tritium and krypton-85. A discussion of changes in composition occurring during the flaring of  $5 \times 10^7$  ft<sup>2</sup> gas in the late spring of 1968 is included. Some interpretation of the observed changen is advanced but with the data now available, no definitive conclusions seem warranted. This is a status report of the continuing effort to define and understand the chemical and radiochemical aspects of project Gasbuggy.

Major constituents of the Gasbuggy gas during the period from 34 days to 200 days following the detonation were methane (increasing from 37 to 44 percent), ethane (increasing from 4 to 5 percent), propane (constant at  $\sim$ 1 percent), carbon dioxide (constant at  $\sim$ 36 percent), hydrogen (decreasing from 17 to 12 percent) and carbon monoxide (decreasing from 4 to less than 2 percent). Much more significant changes were observed during the first month. The major reactions used to explain these trends are:

 $CO + H_1O \rightarrow CO_1 + H_2$  and  $4H_2 + CO_1 \rightarrow CH_4 + 2H_2O$ 

Krypton-85 concentration (2.8  $\mu$ Ci/ft<sup>3</sup>) NTP (normal temperature and pressure) remained essentially constant over the entire sampling period implying mixing with a constant volume (1.2  $\times$  10<sup>6</sup> ft<sup>3</sup> NTP) of noncondensable gas during this time.

Tritium was observed primarily as hydrogen gas soon after detonations. A rapid decrease in HT came within the first month converting most of the HT to HTO but producing some CH<sub>2</sub>T and C<sub>2</sub>H<sub>2</sub>T. The predominant tritium-containing species, except at very early time, is CH<sub>3</sub>T, at a concentration of 12 to  $14 \, \mu$ Ci/ft<sup>2</sup> NTP. Both CH<sub>3</sub>T and C<sub>2</sub>H<sub>3</sub>T concentrations increase slightly over the first

200 days, that of HT continues to decrease. The ratios  $\frac{CH_{*}T_{*}}{CH_{*}}$  and  $\frac{C_{*}H_{*}T}{C_{*}H_{*}}$  are

essentially constant over the period from 20 to 200 days implying that the exchange equilibrium was attained rapidly. The ratio  $HT/H_s$  continues to decrease over the same period implying a continuing influx of non-tritiated water into the chimney and a reasonably rapid exchange reaction between HT and H<sub>4</sub>O.

Changes in concentrations of cavity gas components as a function of flow rate indicate that removal of 80 percent of the original chimney gas was accomplished by flaring  $5 \times 10^7$  ft<sup>3</sup> at a rate of  $5 \times 10^4$  ft<sup>4</sup>/day. This result is encouraging but the test was too short to provide verification of this process as a reasonable method of reducing contamination levels.

Among the more important problems related to the application of nuclear explosives to stimulation of natural gas fields is that of radioactive contamination of the gas in the chimney formed by the detonation. One of the primary objectives of Project Casbuggy is to determine the gas quality with regard to contamination by radioactivity and to evaluate various techniques suggested for reducing this contamination.

A large quantity of data has been collected from analysis of the Gasbuggy chimney gas, and some systematic trends have been observed. Although some of the chemical and radiochemical analyses are not yet complete, that portion relating to the most important nuclides, tritium and krypton-85, can be presented, along with the mass spectrometric analyses for the major components of the gas.

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<sup>&#</sup>x27;Work performed under the auspices of the U.S. Atomic Energy Commission. This paper was presented at the Society of Petroleum Engineers Meeting in Houston. Tex. on September 20, 1963.

<sup>&</sup>lt;sup>4</sup> Dr. Smith and Dr. Momyer are associated with the Lawrence Radiation Laboratory, University of California, Livermore, Calif.

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Figure 1. Chromatographic gas columns in the Radiochemistry Laboratory at the Lawrence Radiation Laboratory

Only a tentative assessment of the incomplete results is intended by this presentation. More information must be assembled before detailed interpretations of the chemistry can be made. Indeed, the lack of samples at early times when major changes were occurring may cause ambiguous interpretation of the processes involved as far as this particular experiment is concerned.

#### Analytical procedures

It might be of some interest to describe briefly the process by which the data are obtained. The sample is introduced to the separation system and condensed on a large activated charcoal column (figure 1). These separation systems are, in reality, large-scale gas chromatographs. Samples of Gasbuggy gas as large as  $\frac{1}{2}$  ft<sup>2</sup> can be easily separated, however, the objical sample size is 1 liter.



Figure 2. Chart recorder and ionization counter apparatus at has react Radiation haboratory

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Helium is passed through the column as the temperature is progressively raised stepwise. The gases pass through the column in inverse order of their degree of adsorption. For a complete separation, both charcoal and a molecular sieve are employed at temperatures ranging from liquid nitrogen  $(-240^{\circ}\text{F})$  to  $+600^{\circ}\text{F}$ .

During the course of an elution, the procedure is monitored using a thermal conductivity detector and an ionization chamber. These are read out on the chart recorder (figure 2). The purified gas is recovered for transfer to a radiation counter.

Two types of counters are used. The "gas-cell," thin-window proportional counter is employed for krypton 85 radioassay. The krypton is contained in small cells that are loaded on a sample changer (figure 3). Each cell, in turn, is rotated underneath the lead chield of the counter, where it is raised to the counting position. Gases containing tritium are placed in internal proportional counting tubes and become a part of the fill gas in the active volume of the tube (figure 4). These tubes are counted inside a shielded cave.



Figure 3. Gas cells containing radioactive krypton=85 separated from Gasbuggy chimney gas samples, being loaded on an automatic sample changer

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Figure 4. Internal proportional counter containing tritium contaminated gas separated from Gasbuggy chimney gas samples, being placed in a shielded arrangement

Systematic errors which may be present in these determinations are not estimated. The calibration factors for the two counting methods are known to within a few percent and were determined by counting gases of known radioactivity. A conservative estimate of the uncertainty in the absolute value of these measurements is, therefore, less than ±10 percent of the value given. Precision of these determinations is improved by our standard practice of counting replicates. Results of duplicate counts are averaged to obtain the final result and an estimate of its reliability. The numbers to be presented here have individual standard deviations of less than 3 percent. Precision within a group of samples includes this uncertainty but is primarily determ ned by real variations in sample composition between samples. As will be seen, this variation is significant for hydrogen but much less so for the other gases of interest. In the data which follow, the precision of the measurements is indicated by inclusion of  $\pm 1$  sigma (standard deviation of the mean) as the indicated uncertainty. FROM LLNL NOD

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In the plotted data, error bars are used to indionte precision, standard deviation of the mean included. Where no such bars are shown, the error bars lie within the plotted point system. All data are related to cavity gas after air (based on  $O_2$ ) was removed from the sample.

Analytical errors vary according to the percent composition, but are generally less than 1 or 2 percent for the species of interest here. Small variations between samples within a group have been observed and are the primary source of the errors attached to the data.

#### Sampling

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At the present time, data are available from 16 samples grouped in five sampling periods. Except for the production testing which occurred last June and July, no significant variation was observed within a sampling period. Therefore samples within a period have been averaged. Only these averages are presented. These averages are identified according to the mid-point of their saming time following the detonation (December 10, 1967) as follows:

1st day samples: Four samples were obtained as a result of leakage through the cable conduits to the sealed annulus of the emplacement hole. While these samples were gathered about 1 day after the detonation, the actual time of their separation from the body of chimney gas is most certainly much shorter. They probably represent the chimney gas composition shortly after chimney collapse. Two were suitable for radiochemical analysis. However, these were 85 percent air. Therefore, the errors of the chemical analyses are magnified for the 15 percent of the sample deemed "cavity gas". In spite of this, the results do seem to provide useful information and to fit well with the main body of information obtained from the other groups of samples.

34th day samples: Seven samples were taken between 32 and 36 days after detonation when communication with the chimney by GB-ER<sup>3</sup> had been established. Five of these have been analyzed —two downhole samples and a surface sample taken before  $3 \times 10^3$  ft<sup>2</sup> of gas was flared and one downhole and one surface sample after flaring. No significant differences in the results reported were seen between surface and downhole samples, or between samples prior to and following the flaring. The air correction of sample composition to obtain cavity gas composition was a few percent for these samples.

79th day samples: Of the four samples taken, results from one surface and one downhole sample following flaring of  $4 \times 10^{\circ}$  ft<sup>3</sup> of gas are reported. As was the case of 34 days, no significant difference between samples was observed. Downhole sampling has therefore been eliminated. The air correction was only 1 percent for these samples.

134th day samples: Results of the two surface samples taken after  $4 \times 10^3$  ft<sup>3</sup> of gas were flared are included in this report. No air correction was required.

203rd day samples: Data points at 203 days are taken from the first good sample obtained during the extended flow test. Approximately  $5 \times 10^6$  ft<sup>2</sup> of gas had been flared prior to sampling. Samples were taken at intervals of  $5 \times 10^6$  ft<sup>3</sup> or daily. Analytical results from six of these will be reported. No air correction was required for these samples.

#### Gasbuggy analytical results

For convenience and presentation the samples have been divided into two time periods. The first group is composed of those samples taken during the shut-in pariod prior to flow testing. Samples obtained during the flow testing comprise the second group. Somewhat arbitrary curves have been drawn through the data points.

Figure 5 (table 1) presents the observed electric in chemical composition of the cavity gas as a function of time. The effect of temperature equilibrium is clearly evident. Light gases predominate at early times, moving towards more complex gases as the chemical equilibrium shifts. Plottect across the lower portion of the graph is the total volume of gas with which the krypton-85 is mixed. Its constancy within analytical uncertainty is remarkable. Evidently equilibration of the cavity with formation pressure occurred quite rapidly and has been maintained throughout the shut-in period.

The total gas volume was obtained by dividing the total krypton-85 by the krypton-85/ft<sup>2</sup> NTP (normal temperature and pressure) determined

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<sup>&</sup>lt;sup>3</sup> GB-ER, Gasbuggy-Emplacement re-entry hole, a postdetonation hole drilled directly through the original emplacement hole.

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Figure 5. Chemical composition of cavity gas as a function of time after detonation

from radiochemical analysis of the samples. Total krypton-85 is estimated at 350 curies according to the anticipated performance of the nuclear explosive (1).

The rapid increase in  $CO_2$  and the corresponding decrease in CO suggests that the water-gas reaction:

 $CO + H_2O \rightarrow CO_2 + H_3 \tag{1}$ 

reaches equilibrium at early times.

The gradual decrease in  $H_2$  concentration appears to be due to the reaction:

$$4H_2 + CO_2 \rightarrow CH_4 + 2II_2O \tag{2}$$

which is observed to proceed development of equilibrium throughout the sampling period. In addition, natural gas from the formation has entered the cavity to maintain constant pressure. Adding reactions (1) and (2) produces:

$$3H_{z} + CO \rightarrow CH_{z} + H_{z}O$$
 (3)

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Note that CO<sub>2</sub> does not enter and is indeed constant over the major sampling period. H<sub>2</sub> and CO are: being used up while methane is increasing. The observed increase in ethane concentration may be due to a reaction such as:

$$CH_4 + CO + 2H_2 \rightarrow C_2H_6 + H_2O \qquad (4)$$

The observed decrease in propane may or may not be significant. Variation such as that seen can be attributed to fractionation of the sample during the later sampling periods.

Another way to view the coemical data is in terms of totals of elements in the gas (figure 6). The total gas volume is plotted across the bottom of the figure to provide a base line. Above it, in the center of the figure are the concentrations of the elements of interest. Because of the constancy of the total gas volume, these curves represent totals equally well. The curves at the top of the figure are chemical composition in terms of atom percent.

This figure illustrates the tiend toward more complex molecules by the chemical reaction processes coupled with the influx of formation gases



Figure 6. Elemental composition of cavity gas in a function of time after detonation

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Table 1. Chemical composition of Gasbuggy cavity gases

The second states	Mole percent						
(ilays after deconation)	it <sub>2</sub>	CH4	CrHe	Calle	<u>CU</u>	COa	
1	$ \begin{array}{r} 18.1 \pm 0.6 \\ 16.8 \pm .4 \\ 15.2 \pm 1.0 \\ 13.2 \pm .1 \\ 12.0 \pm .2 \end{array} $	$\begin{array}{c} 34.0 \pm 0.5 \\ 55.9 \pm .8 \\ 40.1 \pm 2.0 \\ 43.2 \pm .7 \\ 44.2 \pm .7 \end{array}$	$\begin{array}{c} 1.37 \pm 0.02 \\ 3.60 \pm .06 \\ 4.1 \pm .2 \\ 4.5 \pm .1 \\ 4.7 \pm .2 \end{array}$	$\begin{array}{c} - \\ 1.3 \pm 0.1 \\ 1.19 \pm .04 \\ 1.02 \pm .05 \\ .97 \pm .03 \end{array}$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	7.8 曲 0.2 35.8 士 5 75.8 士 1.6 35.3 士 7 35.3 士 7 36.2 士 7	

to maintain a constant volume of gas within the chimney. Note that the fraction of hydrogen decreases even though the total number of hydrogen atoms increases early.

The increase in oxygen at early time is due to the production of  $CO_2$  by the water-gas reaction (1). The decrease at late time can be accounted for by invoking reaction (3).

The radiochemical results for tritium in hydrogen, methane, and ethane, are plotted on figure 7 (table 2). Again, total gas volume is plotted along the base line for reference. The observed gas volume of  $1.2 \times 10^{\circ}$  ft<sup>3</sup> NTP can be contained in  $2.1 \pm 0.1 \times 10^{\circ}$  ft<sup>3</sup> void at 150°F and 950 psig<sup>4</sup> (the observed conditions on January 23). Such a void was estimated from data obtained during the production testing, implying that the total krypton-85 estimate is reasonable.

The actual krypton-85 data seem to be moving toward lower concentrations but because of analytical errors associated with the data no conclusion can be reached as to the significance of this trend. The best fit to the data within these uncertainties is probably the line shown.

At early times a large fraction of the gaseous tritium existed in the form of hydrogen gas. The data point for gaseous trituim at 1 day corresponds to some 30 percent of the total of 4 grams of



<sup>4</sup> psig-pounds per square inch gauge.

Figure 7. Radionuclide concentrations in cavity gas as a function of time after detonation

Sampling time (days after detonation)	Total yas "olumo (10" (t' NTF)	Radionuclide concentration* ("Ci/ft" of cavity gas)					
		Krypton-85	нт	CHIT	CiHit	Total tritium	
1	$\begin{array}{c} 1.25 \pm 0.05 \\ 1.17 \pm .07 \\ 1.20 \pm .08 \\ 1.24 \pm .06 \\ 1.28 \pm .07 \end{array}$	$\begin{array}{c} 2.8 \pm 0.2 \\ 3.0 \pm .2 \\ 2.9 \pm .2 \\ 2.8 \pm .1 \\ 2.7 \pm .1 \end{array}$	$\begin{array}{c} 91  \pm 1 \\ 4.4  \pm 1.1 \\ 3.1  \pm .5 \\ 2.3  \pm .1 \\ 1.6  \pm .1 \end{array}$	$\begin{array}{c} 8.9 \pm 0.1 \\ 11.7 \pm .1 \\ 12.0 \pm .7 \\ 13.8 \pm .7 \\ 13.9 \pm .7 \end{array}$	$\begin{array}{c} 0.45 \pm 0.01 \\ 2.06 \pm .03 \\ 2.15 \pm .60 \\ 2.3 \pm .1 \\ 2.4 \pm .1 \end{array}$	$ \begin{array}{c} 100 \pm i \\ 15 \pm 1 \\ 17 \approx 1 \\ i8.\pm 1 \\ 18 \pm 1 \\ 18 \pm 1 \end{array} $	
Average	1.23 ± 0.04	$2.8 \pm 0.1$				► (18 ± 0.8)	

Table 2. Radionuclide concentration in Gasbuggy cavity gases

\* Errors quoted are 1-standard deviation of the mean of averaged measurements.

\* Average does not include the I day sample result

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tritium assumed present in the post-shot chimney. During the first month the HT level dropped auite rapidly and continued to decline at a secwer rate. Prior to the time re-entry of the chimney well was accomplished, tritiated methane became the principle contaminant of the chimney gas. About 5 percent of the total tritium remains gaseous at late times. Presumably the other 95 percent is in the form of water. No meaningful tritiated water results can be reported. Obtaining a representative sample of water in the chimney gas is extremely difficult. The actual numbers range from about a microcurie per cubic foot of cavity gas to 0.001 of that value, the variation being due primarily to dilution of the tritiated water in the sample by tritium-free water within the cavity and re-entry well casing coming from the overlying aquifers.

Iodine-131, a potential problem radionuclide at early times, was not seen in any of the samples. An upper limit of  $10^{-3} \,\mu\text{Ci/ft}$  (NTP) of this radionuclide existing as a gas within the chinney appears conservative. No other radionuclides have been detected which would cause a problem at times longer than a few months. Argon-37 produced by neutron activation of the calcium in the rock is the only other radionuclide now prominent in the gas. Its initial concentration was about 120  $\mu\text{Ci/ft}^2$  NTP. Due to its half-life (35.4 days) the argon-37 concentration is now less than that of krypton-85.

Analysis of a sample obtained from  $GB-2R^2$  is not yet complete, but does indicate the presence of a small quantity of cavity gas in the formation out to at least 300 feet.

Changes in the concentrations of the tritiated species appear to follow the trends observed for chemical compositions, with the exception that the decrease of tritiated hydrogen is more marked than the corresponding decrease in hydrogen gas. Equilibrium reaction such as the water-gas reaction (1) provide a path whereby tritium can exchange with hydrogen in water, reducing the tritium concentration. The overall effect is that the ratio of tritium to hydrogen tends to equalize in all hydrogen containing species participating in the exchange. The degree to which this is observed depends on the exchange rate.

The rapid initial decrease in HT concentration

can therefore be explained using the water-gas reaction:

$$\mathrm{HT} \neq \mathrm{CO}_2 \rightarrow \mathrm{HTO} \neq \mathrm{CO} \qquad (5)$$

and reactions such as (2) and (4) can be used to explain the observed increases in tritiated methane and ethane.

In figure 8, specific activities are compared for the tritiated species. These curves demonstrate the trend toward a uniform tritium to protium ratio. The  $HT/H_2$  ratio is seen to drop quite rapidly as the water-gas reaction approaches equilibrium and to change slope as the slower chemical reactions begin to dominate. The rapid decrease observed indicates that the T/H in cavity water was quite low, and is consistent with the production of CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> by reactions such as (2) or (4).

The fact that both the  $CH_3T$  and  $C_2H_3T$  curves appear to be flat over the entire sampling period is not contradictory. They are being produced by



SAMPLING TIME (days after detonation)

Figure 8. Specific activities of tritinted species as a function of time

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Second Gasbuggy re-entry hole drilled about 300 feet from GB-ER.

hydrogen of nearly comparable specific activity. In fact, the samples at 134 days show very nearly the classical 11210 ratio for the three curves. Presumably the eventual downward trend should appear when the HT is further reduced by exchange with water. The fact that exchange equilibrium existed at 134 days and that the HT/H<sub>2</sub> ratio is still decreasing may imply entry of non-tritiated water into the chimney.

Isotopic effects are not considered here but would also tend to reduce the tritium as elemental hydrogen in favor of water at low temperatures.

Changes in chemical composition of the gas during the 11-day flow test which occurred during June-July 1968 are plotted on figure 9. Logarithmic increases with flow for con ponents of natural gas are complimented by corresponding decreases for gases solely of cavity origin. Results plotted cover the flaring period at  $5 \times 10^{6}$  f<sup>\*a</sup> per day nominal flow.

The produced gas is nearly according gas in composition. About one this is the original cavity gas was removed by discoping two fifths of a cavity volume of gas. On the average only 17 percent of the produced gas came from outside the chimney. At this rate a factor of 10 reduction in contamination of the chimney gas can be achieved by flaring about two chimney volumes  $(2.5 \times 10^8 \text{ ft}^3 \text{ NTP})$ . Further experiments are needed to define the long-term behavior of the cavity flushing and to establish a consistent model for estimating the fraction of cavity gas removed as a function of flow rate.

Radiochemical analysis of these samples are not yet complete. Preliminary assessment of changes in concentration that have been observed, do, however, seem to generally fit those shown here for  $CO_t$  and  $H_a$ . They do, however, show a marked deviation from the lines established at the higher flow indicating much more dilution of the cavity gas by influx of formation gas. This observation corresponds to the observed increase in cavity pressure during the low-flow rate flaring.

The gas quality program at Lawrence Radiation Laboratory is continuing its investigations in an effort to gain a better understanding of the complex interactions of the Gasbuggy gas with itself and its environment. These results, and the interpretations which can be drawn from them, will be publicly available in the future.



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Figure 9. Change in chemical composition of gas during 11-day flow test in June-July 1968

#### Acknowledgemeni

The authors wish to acknowledge the assistance of Mr. R. Crawford of the Lawrence Analytical Chemistry Group who performed the chemical analysis by mass spectrometry.

#### REFERENCE

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## GASBUGGY CLASSIFICATION GUIDE (A-40979)

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#### ADDENDUM #2

October 27, 1967

The Division of Classification has authorized the following change of Topic 4.2 of the CLASSIFIED version of the GASBUGGY Classification Guide dated September 19, 1967:

4.2

MHRHMPHIAAS (JI:3P HKAW ( FENFUNCD)

The total amount of post shot tritium wherever located expected to be present is about 4 grams.

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JOANN -Looks to me or if Total T in bran buggy was 4 grows and that 95+ 70 of it was HTD. See Discussion p286 6. The bocumentary photography is interesting. cheb