RADIOLYTIC GAS GENERATION IN CONCRETE MADE WITH
INCINERATOR ASH CONTAINING TRANSURANIUM NUCLIDES

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ABSTRACT

The effects of various factors on H₂ generation by alpha radiolysis of concrete containing TRU incinerator ash were studied. Methods for reducing H₂ generation were investigated. Samples of portland and high-alumina cement containing up to 30% calcined ash (dry basis) were doped with ²³⁸PuO₂. Gas pressures were measured as a function of radiation dose; gas compositions were determined. Gas yields were calculated in terms of G values (molecules produced per 100 eV of alpha energy absorbed). These yields were used to estimate pressures in containers of radioactive concrete waste during storage.

INTRODUCTION

The action of α , β , or γ radiation on water produces hydrogen gas.¹ Thus, nuclear waste forms, such as concrete, that contain H₂O can produce H₂. Potentially, this can lead to pressurization of storage containers, or to the production of flammable or explosive gaseous mixtures.

This paper summarizes results of an extensive investigation² of the radiolysis of concrete with α particles to estimate the rate of H₂ evolution from concrete containing TRU waste. Other studies showed that ⁶⁰Co- γ and ³H- β radiolysis of concrete produce H₂.³⁻⁵

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With γ radiolysis of concrete waste, the radiolytically-generated pressure reached a low equilibrium value because of a back reaction between H_2 and OH radicals. Earlier studies with α radiation^{3,5} showed that an equilibrium pressure was not attained at H_2 pressures up to 160 psi indicating considerable H_2 accumulation in the container.

The present study was initiated to estimate radiolytic gas production from concrete containing TRU incinerator ash during long term storage in the Waste Isolation Pilot Plant in New Mexico.⁶ The effects of various factors on this rate, along with methods to reduce it, were investigated.

EXPERIMENTAL PROCEDURE

Portland Type I cement (P-I) and high-alumina cement (HAC) were investigated. Simulated TRU incinerator waste was prepared by calcining at 800°C the ash from incineration of typical combustible laboratory wastes such as tissues or polyethylene tubing. Principle components of the ash were Ca (added as heat retardant to the plastics) and Ti (added as whitener). Carbon content of the ash was nominally <1%.

Mixtures of 70 wt % cement and 30 wt % ash (dry basis) were prepared with a known amount of $^{238}\text{PuO}_2$. After thorough mixing, sufficient water was added to give a workable paste (initial water/cement = 0.8) which was then poured into a cylindrical steel mold (10 cm x 2 cm O.D.). After curing 5 to 30 days at ambient conditions, the final composition of the specimens (total weight = 60 g) was nominally 50 wt % cement, 20 wt % ash, and 30 wt % water containing 0.1 to 1.0 Ci of ^{238}Pu . In the presence of air, the specimen was sealed to a pressure transducer and the pressure increase recorded. After a known time, the gas was sampled and its composition determined by gas chromatography.

G values (molecules produced/100 eV of α energy absorbed) were calculated from both the final gas composition and from the rate of pressure increase using the ideal gas law, the void volume in the container, and the amount of ^{238}Pu present.

GAS YIELDS

Typical pressure increases for three concretes are shown in Figure 1. Sample P-1 and HAC-1 contained simulated ash doped with $^{238}\text{PuO}_2$, and sample HAC-2 contained ash prepared from incineration of waste contaminated with a ^{238}Pu solution. Thus, HAC-2 resembles more closely an actual waste form. These three samples were cured unsealed at ambient conditions for approximately a month. When nonradioactive concretes were sealed to the transducer, no pressure was produced, confirming that radiolysis caused the pressure increases.

Fig. 1. Pressure Increase from α Radiolysis of Portland or High Alumina Concrete Containing ^{238}Pu

The slopes of the three lines in Figure 1 differ because of differences in the G values and dose rates for the three concretes. $G(H_2)$ and $G(O_2)$ values were calculated from the changes in the partial pressures of H_2 and O_2 during the test. The partial pressure of N_2 was unchanged by radiolysis. $G(\text{total})$ is the 100-eV yield of all gaseous molecules and was calculated from the slopes of the lines. Within experimental error, $G(H_2) + G(O_2) = G(\text{total})$ as expected if the N_2 pressure is unchanged.

Less than a stoichiometric amount of O_2 was formed, as indicated by the ratio $G(O_2)/G(H_2)$ being less than 0.5 (Figure 1). This agrees with the α radiolysis of liquid water where $G(O_2)/G(H_2)$ is only 0.13.⁷ Oxygen has also been formed by the α radiolysis of concrete containing simulated high level waste sludges.³ The reason for O_2 not being produced with HAC-2 at this time is unknown. Less than a stoichiometric amount of O_2 being formed indicates that some other oxidation product of water is being formed. Perhaps this is H_2O_2 as it is in liquid water. Another study showed evidence of this species in γ irradiated concrete.³

Dose rates for the tests shown in Figure 1 were nominally 10^{17} eV/(min) (gram of concrete), with HAC-2 having the lowest rate. This dose rate is about 1000 times larger than that expected in actual waste. For example, the dose rate in a 55 gallon drum 90% full of concrete containing 200 g ^{239}Pu is only 4×10^{14} eV/(min) (gram of concrete). To determine if this is a dose rate effect, a test was performed at 10^{16} eV/(min) (gram of concrete). No dose rate effect on $G(\text{H}_2)$ was evident. If H_2 is formed as it is in liquid water (recombination of H atoms or hydrated electrons), no change in $G(\text{H}_2)$ at lower dose rates is predicted.

Tests at 23, 70, and 100°C showed that $G(\text{H}_2)$ was independent of these temperatures for concretes that had the same water content. This agrees with the radiolysis of liquid H_2O where $G(\text{H}_2)$ is not significantly affected by temperature.¹

REDUCTION OF $G(\text{H}_2)$

Lower rates of H_2 production would be desirable both for short and long term considerations. Two methods were found to reduce $G(\text{H}_2)$: either an addition of H atom scavengers to concrete, or a removal of H_2O by heating concrete or using pressed concrete. The latter methods would be effective over the long term only if water were excluded from the concrete during storage.

The two best scavengers for reducing $G(\text{H}_2)$ were NO_3^- and NO_2^- ions. Both of these ions reduce $G(\text{H}_2)$ in the radiolysis of liquid water. These were easily added to the concrete by using NO_3^- or NO_2^- solutions. For NO_3^- ions, the maximum concentration in the solution used to make the concrete was 6M; this reduced $G(\text{H}_2)$ to 0.03. (However, O_2 from radiolysis of the NO_3^- ion was formed with a G value of 0.37 so there was little reduction in the overall radiolytic pressurization rate.) For NO_2^- ions, the maximum concentration in the solution used to make the concrete was 5M; this reduced $G(\text{H}_2)$ to 0.053. Also, when NO_2^- ions were present, O_2 present in the air sealed with the concrete was consumed [$G(-\text{O}_2) = 0.08$]; thus, the pressurization rate decreased considerably. Also, a slight amount of N_2O was produced [$G(\text{N}_2\text{O}) = 0.04$], indicating reduction of the NO_2^- ions.

Relative decreases in $G(\text{H}_2)$ upon addition of NO_3^- or NO_2^- ions are shown in Figure 2. The data for NO_3^- ions follow the trend shown by the solid line for the effect of these ions in the α radiolysis of liquid water.⁷ This similarity indicates that these ions are reacting as they do in liquid water. Further, this suggests that the reaction for H_2 formation from α radiolysis of concrete may be identical to that for liquid water. The effect of NO_2^- ions on $G(\text{H}_2)$ from α radiolysis of liquid water has not been determined.

Fig. 2. Lowering of $G(\text{H}_2)$ in α Radiolysis of Concrete by Addition of NO_3^- or NO_2^- Ions

One method of lowering the water content of concrete is to prepare pressed concrete. This concrete is prepared by pressing a cement-ash pellet containing very little water (about 2 wt %), at 25,000 psi.⁸ Gas production from three pressed concretes containing portland Type I cement doped with $^{238}\text{PuO}_2$ was measured. Two concretes contained simulated TRU incinerator ash. The third contained bone char (a material for absorbing Pu from waste streams). $G(\text{H}_2)$ values measured from the amount of H_2 produced were 0.009 and 0.005 for the concretes containing ash and 0.003 for the one containing bone char. Pressure increases were insufficient to calculate values for $G(\text{total})$ because of the relative large void volumes of the containers. To determine the consequence of this concrete becoming wet, pressure measurements were made while the concrete was submerged in water. $G(\text{H}_2)$ increased to 0.13. O_2 was produced [$G(\text{O}_2) = 0.03$] and $G(\text{total})$ was 0.16. Weight measurements indicated that the sample had sorbed 16 wt % H_2O . Clearly, to retain the low rate of H_2 production, water must be excluded from the concrete during storage.

Another method to reduce the water content and lower the rate of gas production is to heat the concrete after it has cured for a sufficient time to remove free water. Most of the H_2O in concrete is added to achieve a workable paste that can be poured or cast rather than to cause the hydration reactions that give concrete its strength.⁹ The drastic reduction in the pressurization rate caused by heating at 200°C to remove H_2O is shown in Figure 3.

Fig. 3. Effect of Lowering the H₂O Content on Pressure Increase by α Radiolysis of a Portland Concrete Sample Heated at 90°C and then at 200°C

Heating at 90°C did reduce the G values, but not as significantly as heating at 200°C. The concrete used to obtain the results in Figure 3 had been cured at room temperature in a moist environment for 36 days before it was heated and thus had attained at least 70% of its final strength. It was dried by heating in an oven in the steel cylinder into which it was cast. At 90°C, the sample showed a continuous weight loss as long as it was heated (34 hr). At 200°C no more weight was lost after 16 hours of heating. In both tests, the temperature of the concrete had returned to ambient before the sample was sealed to the transducer.

A very low value for G(H₂) was obtained after the concrete had been heated to 200°C. Low G(H₂) values were also found for other concretes heated at 200°C. For HAC-2 (Figure 1) and for a pressed concrete, G(H₂) values of 5×10^{-4} and 3×10^{-4} respectively were obtained. The pressure above these samples also decreases as shown in Figure 3. This was also observed after a nonradioactive concrete had been heated to 200°C.

The results in Figure 3 indicate that the water driven off concrete at temperatures less than 200°C is more easily radiolytically reduced than that remaining water. The remaining water is probably involved in the hydration reactions that give the concrete its strength. When water was again added to the concrete used for Figure 3, $G(H_2)$ and $G(O_2)$ increased to nearly their original values, 0.34 and 0.18, respectively.

RADIOLYTIC PRESSURES IN STORAGE CONTAINERS

The above G values can be used to calculate pressures generated by radiolysis in a storage container of concrete containing TRU waste. The equation for a concrete containing several TRU isotopes is

$$P = \frac{[(1.2 \times 10^{18} \text{ } \alpha/\text{year})(Ci)] [G(\text{total})] RT}{100 \text{ NV}} \sum_i \frac{Ci_i E_i (1 - e^{-\lambda_i t})}{\lambda_i}$$

where Ci_i , E_i , and λ_i are the number of curies, the α energy, and the α decay constant, respectively of the i -th isotope. Pressures for H_2 and O_2 can also be calculated using $G(H_2)$ or $G(O_2)$. Results for H_2 generation in a 55 gallon container 90% full of concrete (10% porosity) containing 200 g of ^{239}Pu are shown for various values of $G(H_2)$ in Figure 4. The lines were calculated by assuming that $G(H_2)$ was not affected by the H_2 pressure and that a slow thermal recombination reaction of H_2 and O_2 was not occurring over the long storage times. A previous α -radiolysis test has shown that $G(H_2)$ is not significantly affected by H_2 pressures up to 160 psi.³

Fig. 4. Calculated Radiolytic H_2 Pressure in a 55 Gallon Container 90% Full of Portland Concrete and 200 g ^{239}Pu

Also, no evidence for a thermally induced recombination reaction has been observed at the α dose rates used thus far.

8

The effect of adding NO_2^- to the concrete or drying the concrete is clearly evident in Figure 4. With untreated concrete, considerable H_2 pressures can be generated after intermediate storage times. Also, with the untreated concrete, a flammable mixture (4% H_2 in air) can be present after only about 40 days. With concrete dried at 200°C , more than 10^2 years would be necessary to generate a flammable mixture. If less ^{239}Pu is present, longer times would be necessary.

CONCLUSIONS

H_2 and O_2 will be produced by α radiolysis during storage of canisters of portland or high alumina concrete containing TRU waste. The rate of H_2 production can be decreased by adding NO_3^- or NO_2^- ions to the concrete or by drying the concrete. NO_3^- addition increases O_2 production while NO_2^- addition decreases O_2 production. Drying at 200°C reduces the rate of H_2 production by a factor of approximately 2000 while reducing the water content by only approximately a factor of 5. If H_2O is again added to the concrete, the gas production rates return to nearly their original values.

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