THE REACTION OF HYDROGEN AND OXYGEN IN THE PRESENCE
OF CONCRETES INCORPORATING SIMULATED RADIOACTIVE WASTE*

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INTRODUCTION

The radiolysis of contained water, with the potential of pressurization due to the accumulation of these radiolytically produced gases, has been identified as a major concern for radioactive wastes fixed in cementitious matrices.¹ The amounts of hydrogen and oxygen produced depends on the type and concentrations of the radioactive species as well as the composition of the matrix. Obviously pressurization of a waste canister or the repository itself must be held to a minimum. One estimate¹ of the pressure build-up is that about 100 atmospheres pressure could accumulate in a standard canister containing alpha waste after 100,000 years. However, even for this pressure, the rate of gas production would be small. For example, a standard 200 liter canister containing 10 g of ²³⁹Pu dispersed in concrete containing normal concentrations of unbound water, would generate a maximum of about 1 ml of H₂ per day. Since the radiolysis of concrete is dependent on the amount of unbound or free water present in the system, removal of all or most of this water would greatly reduce this rate.² Radiolysis due to beta and gamma emitting nuclides were neglected because it has been shown their contribution to long term pressurization would be small. Regardless of the production rate however, pressurization from the accumulation of hydrogen and oxygen would be avoided if there were sufficient recombination of these gases as, or after, they were generated. These studies were undertaken to determine the recombination rates obtained with special cementitious matrices.

Concrete is one of the more viable alternate waste form concepts. This waste host is being investigated at the Oak Ridge National Laboratory in a program directed at the investigation of FUETAP (Formed Under Elevated

Temperature And Pressure) concrete.³ This material, because of the composition and method of preparation, offers some distinct advantages of standard concretes as a waste fixation medium. FUETAP is solidified and cured for 24 hr at 100 to 250°C and ≤ 4.1 MPa (600 psi). The properties that are demonstrated by specimens containing simulated waste and prepared under these conditions include good physical strength, excellent resistance to the leaching of the contained nuclides, a tolerance for some nitrate in the waste, and a very low free water concentration. In essence, the product can be classified as a low temperature ceramic. The present paper presents the results of an investigation of the reaction of hydrogen and oxygen in the presence of FUETAP concrete.

The subject of the reaction of hydrogen and oxygen has been exhaustively studied.^{4,5,6} These elements do not combine in the gaseous state at ambient temperatures. However, they do interact when the gases are in contact with a catalytic surface with a recombination rate that is directly related to the surface area and the temperature. Thus the basis for this study was the realization that FUETAP concrete containing radioactive waste or perhaps some other added constituent could provide a surface to catalyze the recombination of any radiolytically produced hydrogen and oxygen.

EXPERIMENTAL PROCEDURE

In this investigation, the rate of reaction between hydrogen and oxygen was measured by determining the yield of water or the depletion of oxygen, as mixture of these gases flowed through a bed of the test material. Three cementitious mixtures were examined, a neat cement paste and two FUETAP concretes. The FUETAP concretes (Table 1) were prepared with and without 2.8 wt % NaNO_3 present. Alumina and ferric oxide were used as reference materials (Table 2). The concrete specimens were crushed and a

Table 2. Substrates selected for study of the hydrogen-oxygen reaction rate

	FUETAP concrete substrate				Ferric Oxide
	Neat paste	Simulated waste w/o nitrate	Simulated waste with 2.8% nitrate	Alumina	
% Waste solids added	0	14.8	14.3	0	0
Test quantity, g	300	300	300	300	2*
Substrate form	1 to 10 cm fragments	1 to 10 cm fragments	1 to 10 cm fragments	15-20 mesh crystals	10 m ² /g powder

*The 2 g of ferric oxide was mixed with 18 g of 15-20 mesh alumina.

Table 1. FUETAP concrete formulation

Component	wt %
Cement	38.9
Fly ash	9.3
Clay	9.3
Quick-gel	0.4
Water	27.3
Simulated waste ^a	14.8

^aComposed of 75.2% Fe_2O_3 , 14.9% Al_2O_3 , 4.9% Cr_2O_3 , 4.8% NiO , 0.14% SrO , and 0.04 % CeO .

300 g sample of the fragments were placed in a stainless steel flow-through reactor. The alumina reference material consisted of 300 g of 15-20 mesh particles and the ferric oxide of two g of 10^2 μ/g surface area material diluted with 18 g of alumina. The alumina was a nonreactive substrate and the ferric oxide was used as a reactive substrate for comparison with the two FUETAP concretes containing waste.

Three dynamic flow test systems were used to determine the reaction rate between hydrogen and oxygen. They differed principally in the type and range of the analyzer. The first was a magnetic susceptibility instrument capable of measuring the oxygen content in the 0 to 5% range. The other two were electrolytic water sensor units, one with a range from 0 to 20,000 ppm and the second with a range from 0 to 1000 ppm.

Oxygen Depletion Tests

A schematic diagram of the experimental layout used to measure the difference in oxygen concentration after passing gas over the substrates in question is shown in Fig. 1. The measurements were made by sampling the gas before and after it had passed over the substrate or bypassed the sample. The feed gas,

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Fig. 1 OXYGEN DEPLETION TEST SYSTEM

which was flowing at a rate of 75 ml/min. was 75% hydrogen and 25% air. Steady state conditions were achieved by flowing the gas mixture through the substrate for a period of 24 hrs. The oxygen depletion, which was calculated from the difference in oxygen content of the gas stream alternately directed through the substrate and the bypass was then plotted against the system temperature.

The oxygen depletion for the FUETAP samples containing simulated waste was significant and exceeded 20% of the available oxygen at temperatures above 130°C. Extrapolation of the data to ambient temperatures indicates that about 0.1% of the available oxygen would have been depleted on contacting the gas and the waste containing substrates for 80 seconds. Results with the neat cement paste substrate were very low and essentially undetectable at temperatures below 140° (Fig. 2).

Water Yield Test-High Range

The schematic-diagram of the experimental arrangement used to measure the yield of water in the range of 0 to 20,000 ppm is shown in Fig. 3. Operation with this detector required that the gas flow be maintained at 20 ml/min. and a relatively long time was required to achieve steady-state condition. In some cases corrections were necessary to compensate for long term flow rate drift. The measurements at ambient temperatures were carried out on substrates which had been conditioned at 200°C in a stream of dry gas. This was necessary to reduce the background to less than 5 ppm.

These results (Table 3) substantiated that a significant catalytic reaction occurs at ambient as well as at higher temperatures in the presence of FUETAP concrete specimens containing waste. Neat cement paste yielded a

Fig. 2. DATA USING OXYGEN DEPLETION TEST SYSTEM

Fig. 3. TEST SYSTEM FOR HIGH-RANGE WATER YIELD

Table 3. Data obtained with 0-20,000 ppm water yield test system

Test feed gas: 4.1% hydrogen, 1.7% oxygen and 94.2% nitrogen

Background feed gas: 100% nitrogen

Residence time: 3 ± 0.5 minutes

Type concrete substrate:	Water yield, ppm					
	Neat		With waste, no nitrate		With waste, with nitrate	
Feed gas:	<u>Test</u>	<u>N₂</u>	<u>Test</u>	<u>N₂</u>	<u>Test</u>	<u>N₂</u>
Test temperature, °C;						
27	23	20	7,700	20	6,400	20
28			5,600	30	6,700	20
100-110			5,200	100	6,700	30
120-130	900	35	7,700	100	7,700	100

significantly lower recombination rate. In these experiments, the feed gas was composed of 4.1% hydrogen, 1.7% oxygen, and 94.2% nitrogen. The typical residence time within the reactor was 3 ± 0.5 minutes.

Water Yield Test-Low Range

The use of a lower range water analyzer (0-1000 ppm) permitted a flow rate of 100 ml/min and thus steady state conditions were obtained more rapidly than in the higher range test (Fig. 4). As before, the substrates used were pretreated at 200°C with a flow of dry gas until a background of less than 1 ppm was achieved at ambient temperatures. Three substrates were used with this system; alumina, ferric oxide, and FUETAP concrete with simulated waste but no nitrate. The feed gas composition was $\geq 95\%$ hydrogen, 0.1-1% oxygen, and the remainder nitrogen except in the alumina test. Here, the gas mixture was maintained at 95% hydrogen, 1.2% oxygen, and 3.8% nitrogen.

Although the results from the system show high rates of recombination over the FUETAP concretes and the ferric oxide (Table 4), in both cases the water yield did not reach a steady state. At temperatures below 60°C, the water yield slowly increased and then exceeded 1000 ppm. In the 60 to 100° range, the yield of water varied in a cyclic manner as shown in Fig. 5. The results from the inert alumina substrate were consistently low and showed only a slight increase with temperature. As for the cyclic behavior, the periods ranged from 20 minutes to greater than 40 hours depending on the hydrogen to air (i.e., oxygen) ratio. Each cycle was characterized by a gradual rise to 300 ppm and then a rapid rise to over 1000 ppm. After a short time at this level the yield dropped rapidly to approximately 100 ppm and the cycle resumed. Such cyclic behavior has been observed in other catalytic studies.⁷ The behavior was explained by the existence of two or more possible reaction routes which proceed

Fig. 4. TEST SYSTEM FOR LOW-RANGE WATER YIELD

Table 4. Data obtained with 0-1,000 ppm water yield test system
 Test Feed Gas: >95% hydrogen, 0.1 to 1% oxygen, remainder nitrogen (for
 concretes and ferric oxide) 95% hydrogen, 1.2% oxygen, 3.8% nitrogen (for alumina)
 Background feed gas: 100% hydrogen
 Residence time: 1 minute for concrete and alumina, 0.1 minute for ferric oxide

Temperature, °C,	ppm Water yield over test substrate		
	Concrete with waste, no nitrate	15-20 mesh Alumina	10 m ² /g Ferric oxide
25-60	100 to >1000		100 to >1000
60-100	100 to 1000-cyclic		100 to >1000 - cyclic
170	>1000	0.2	>1000
190	>1000	0.4	>1000
210	>1000	3	>1000

Fig. 5. CYCLIC REACTION OF HYDROGEN AND OXYGEN

at different rates and for which a triggering mechanism exists. It was beyond the scope of this investigation to determine the mechanism responsible for this particular cyclic behavior.

CONCLUSIONS

The data obtained with each of the three experimental systems show that there is a high hydrogen-oxygen recombination rate in presence of FUETAP concretes containing simulated waste (Table 5). A 300 g sample will catalyze the recombination of greater than 8 ml of H_2 per day (Table 5). Since the radiolytic gas produced by 10 g of ^{239}Pu dispersed in 200 liters of ordinary concrete is of the order of only 1 ml of hydrogen per day, the data suggest that gas pressurization may not be a problem with FUETAP concretes containing waste, if one can ensure that adequate contact is maintained between the gases and the available solid surfaces.

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Table 5. Summary of combination data for hydrogen and oxygen over 300 gram sample of fragmented containing waste concrete (no nitrate) at ambient temperatures

	Test		
	Oxygen depletion	High range	Low range
Gas flow, ml/min	75	20-35	100
Gas composition:			
% hydrogen	75	4.1	>95
% oxygen	5	1.7	0.1 to 0.5
Residence time,	80 seconds	3.3	1
Yield	250 ppm	7,000 ppm H ₂ O	100 to >1,000 ppm H ₂ O
Yield calculated as ml H ₂ /day	>8	250	14 to 140