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CHEMICAL IMPURITIES IN THE HELIUM COOLANT

AT THE PEACH BOTTOM HTGR

by

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ABSTRACT

During the operation of Core 1 and part of Core 2 in the Peach Bottom (HTGR) atomic power station, tests were performed to (1) measure the concentration of chemical impurities in the helium coolant and (2) ascertain the sources of the impurities. This report presents the results of these tests.

1. SUMMARY

The purity of the helium coolant in the Peach Bottom HTGR remained satisfactory during the operation of Cores 1 and 2. Core 1 ran for 450 equivalent full power days. Core 2 has accumulated 280 EFPD to date. Although the observed impurity concentrations were far below the limits set by the technical specifications, they have been persistent, which is suggestive of a constant source. The contaminant levels found at steady state were: $H_2 = 10$, $N_2 = 0.5-1.0$, $CO = 0.5$, and $CH_4 = 1.0$ ppmv. Other chemical impurities, O_2 , H_2O , and CO_2 , were found to be immeasurably low, i.e., below ~ 0.05 ppmv.

These data indicate that steam ingress was either nonexistent or quite low. Moreover, the possibility of a separate hydrogen source exists. Possible H_2 sources discussed herein are oil ingress, graphite outgassing, and/or proton diffusion through steam tubes.

2. INTRODUCTION

Maintaining a high degree of purity in the coolant of the High-Temperature Gas-Cooled Reactor (HTGR) is of prime importance. Coolant purity is necessary to preclude reactions of gaseous contaminants with the hot graphite core. Contaminants of chemical importance include H_2O , O_2 , H_2 , CO , CO_2 , and CH_4 . These species may arise from a variety of sources, the most obvious of which are steam ingress, outgassing of reactor materials, and residual air following startup. Other possible sources of contamination include proton diffusion through steam tubes and oil ingress.

Reactions that would occur if these species were present in the coolant include graphite oxidation, carbon transport due to methane formation and decomposition, carbon deposition both in the core and elsewhere in the circuit due to CO disproportionation, and chemical complex formation on graphite surfaces.

Of most concern in the HTGR is graphite oxidation resulting from steam inleakage. The large mass of graphite, however, tolerates considerable steam ingress and subsequent graphite oxidation. In the Peach Bottom reactor, for instance, the design maximum allowable steam inleakage rate to the main coolant is $0.01 \text{ lb } H_2O/\text{hr}$. If leakage of this magnitude continued unchecked during one core life or three years, only about 160 lb of graphite, or 0.4% of the core graphite, would be consumed. (This calculation conservatively assumes that the steam reacts only with fuel element graphite and is not removed by the purification system.)

In all HTGR systems, coolant purity is maintained by continuous bypass purification. Therefore, if impurities persist at steady state,

then a constant source of contamination must exist. Such is the case for the Peach Bottom reactor, where low but persistent levels of impurities were found. These impurity concentrations have been observed after long periods of reactor operation; therefore, transient sources of contamination such as residual air or graphite outgassing must be ruled out.

The data reported herein summarize the gas analyses performed for post-construction surveillance of low-level chemical impurities. The test involved analyses of the Peach Bottom helium coolant at several sample points using a gas chromatograph. In general, the test was performed in addition to the routine analyses accomplished by the reactor operators (Philadelphia Electric Company personnel), and involved the use of a more sensitive analytic technique. The more sensitive procedure was necessary for the determination of the low impurity concentrations found at steady state.

3. SYSTEM DESCRIPTION

3.1 PRIMARY COOLANT SYSTEM

The primary helium coolant system consists of the reactor pressure vessel, two steam generators, two helium compressors, and their related piping and auxiliaries. The steam generators and helium compressors are arranged to form two parallel loops for circulation of the helium coolant, with each loop designed for half the total coolant flow rate of 463,000 lb/hr. Helium flow through the reactor core is common to both loops. The total volume of the primary coolant system is approximately $2.3 \times 10^8 \text{ cm}^3$. The total surface area in the primary system is approximately $2 \times 10^7 \text{ cm}^2$; most of this area is in the steam generators. A simplified schematic diagram of the system is given in Fig. 1.

The primary reactor coolant fluid is essentially pure, dry helium gas. Materials of construction to which the helium is exposed include graphite, austenitic stainless steel, Incoloy-800, Cr-Mo alloy steels, and carbon steel. The level of fission products and chemical contaminants in the helium is controlled by fission product trapping and helium purification systems. Operating pressure is normally 350 psia at the compressor discharge.

Within the reactor, approximately 750 lb/hr of the main helium steam is withdrawn from the main coolant system through the fuel elements. This purge stream goes to the fission product trapping system for removal of fission products. In addition, helium is withdrawn from the steam generator tube sheet baffles and is purified by passage through a chemical purification system, which removes such gaseous contaminants as H_2O , H_2 , CO , and CO_2 . The total helium flow rate through this system is about

Fig. 1. Schematic diagram of primary coolant system

175 lb/hr. The purified helium then joins the low-temperature delay bed for gaseous fission product removal.

3.2 FISSION PRODUCT TRAPPING SYSTEM

The fission product trapping system is shown schematically in Fig. 2. It consists of a series of water-cooled activated carbon beds followed by a series of low-temperature delay beds (Freon cooled). These beds remove fission gases by chromatographic delay and subsequent decay in situ of radioactive species. Since the beds operate at such low temperatures (down to -112°F), they also provide an efficient cleanup mode for CO_2 and H_2O , which are removed quantitatively. In addition, the large mass of carbon in the beds holds by physical adsorption quite large amounts of the noncondensable gases H_2 , N_2 , CO , and CH_4 . The dynamic adsorption coefficients for these gases on activated carbon at -110°F are: $\text{H}_2 = 6 \text{ cm}^3/\text{g}$, $\text{N}_2 = 200 \text{ cm}^3/\text{g}$, $\text{CO} = 600 \text{ cm}^3/\text{g}$, and $\text{CH}_4 = 4000 \text{ cm}^3/\text{g}$. Thus, from these data alone one speculates that, at steady state, the relative concentration of the impurity species in the gas phase should be $\text{H}_2 > \text{N}_2 > \text{CO} > \text{CH}_4 > \text{CO}_2 > \text{H}_2\text{O}$, assuming the quantity of each species is approximately the same.

Downstream of the delay beds is a liquid-nitrogen-cooled carbon bed, which accepts a small bypass stream (50 to 100 lb/hr) from the purified helium exiting the delay beds. This trap quantitatively removes by adsorption all gaseous impurities except H_2 and Ne . The function of the trap is to provide cleanup for species that are not removed elsewhere in the system, in particular Ar , N_2 , CH_4 , and Kr-85 .

3.3 CHEMICAL PURIFICATION SYSTEM

A schematic diagram of the chemical cleanup system or steam generator baffle purge system is shown in Fig. 3. The steam generator baffle purge system provides a means of sweeping the tube sheet weldments with helium, thereby limiting H_2O ingress from weld leaks into the main circuit. This gas is passed through a purification system for removal of water vapor and other chemical impurities. It consists of a bed of CuO catalyst (which

converts CO and H₂ to CO₂ and H₂O) followed by dual beds of molecular sieves (for H₂O and CO₂ removal). The molecular sieve beds are regenerated frequently by back purging the sorbed contaminant H₂O and CO₂ into a caustic scrubber system.

Thus, the Peach Bottom helium purification process consists of three separate bypass systems, each providing cleanup capability for different chemical species, as illustrated in Table 1.

Fig. 3. Schematic diagram of chemical cleanup system

Table 1
PURIFICATION RATE CONSTANTS⁽¹⁾

Species	Note	Constant, hr ⁻¹
H ₂	175 lb/hr from SGBP ⁽²⁾ through oxidizer	0.195
CO	175 lb/hr from SGBP through oxidizer plus 100 lb/hr through LN system ⁽³⁾	0.305
N ₂	100 lb/hr through LN system	0.11
CO ₂	175 lb/hr from SGBP through oxidizer plus 825 lb/hr through LTDB ⁽⁴⁾ system	1.11
H ₂ O	175 lb/hr from SGBP through oxidizer plus 825 lb/hr through LTDB system	1.11
CH ₄	100 lb/hr through LN system	0.11

¹ Purification constant = purification flow/loop inventory (900 lb/He)

² SGBP = steam generator baffle purge system

³ LN system = liquid-nitrogen-cooled sorber

⁴ LTDB = low-temperature delay beds, Freon cooled (~ -110°F)

4. GASEOUS CONTAMINANTS AND SOURCES OF CONTAMINATION

4.1 EXPECTED GASEOUS CONTAMINANTS

The gaseous impurities expected to occur in the helium coolant in the Peach Bottom reactor are H_2 , CO, CO_2 , O_2 , N_2 , CH_4 , H_2O , Ar, and Ne.* These species will arise from several possible sources, the most important of which are listed below.

a) Graphite outgassing	$H_2, CO, CO_2, N_2, CH_4, H_2O$
b) Air ingress (i.e., during shutdown)	O_2, N_2, Ar, CO, CO_2
c) Steam ingress	$H_2, CO, CH_4, CO_2, H_2O$
d) Oil ingress	H_2, CH_4
e) Charging tank contamination	Ne, Ar, H_2O , Air
f) Proton diffusion through steam tubes	H_2

Of the above species, H_2 , CO, CO_2 , CH_4 , O_2 , and H_2O are of chemical importance in the HTGR, and the concentration of each species, in general, will be controlled by its respective ingress rate, reaction in the hot graphite core, and purification rate.

4.2 CHEMICAL REACTIONS OF GASEOUS IMPURITIES IN THE HTGR

The most important chemical reactions in the HTGR are the following:

*This list does not include the fission products Xe and Kr, which normally occur in the HTGR coolant and are therefore not regarded as impurities.

The most important impurity reaction in the HTGR is the steam-graphite reaction (reaction 1 above), because only H_2O can contaminate the main circuit to a significant extent. The other reactions occur secondarily to the steam-graphite reaction.

All of the reactions may be enhanced by the high radiation field of the core at full power. Radiation accelerates these reactions by the formation of metastable species, possibly including H , H_2 , O , O_2 , CO_2 , OH , and H_2O_2 in ionized or excited forms. These species are formed as a result of direct gamma or fast neutron irradiation or transfer of energy from excited helium atoms. The energy transfer mechanism is suggested to be due to both charge exchange and excitation transfer from the electronically excited inert gas atoms.

In the hot regions of the core, reactions 1 through 5 tend to proceed as written, indicating that at steady state, the gases H_2 and CO will predominate over the other species. At lower temperatures the chemical equilibrium shifts to the left (i.e., the reactions tend to reverse), in particular, where either metal catalysis or radiolytic processes are important. (As discussed later (Section 4.3.6), methane may owe its existence in the HTGR to the radiolytically induced reaction of hydrogen with graphite (reaction 4, reverse).)

By far the most important source of contamination should arise from the ingress processes c, d, and f above. The other sources tend to be transient in nature, because of the continuous purification process. Thus, the steady state level of the persistent species depends on the ingress rate, the reactivity of the species with hot graphite, and the purification rate constant. The following equations show the interrelation of these factors for the case of continuous water ingress. At steady state the following relationships hold:

$$P_{H_2O} = \frac{W}{r_w + R_1} \quad (1)$$

$$P_{H_2} = \frac{P_{H_2O} R_1}{r_h + R_4} \quad (2)$$

$$\frac{P_{H_2}}{P_{H_2O}} = \frac{R_1}{r_h + R_4} \quad (3)$$

where P = equilibrium pressure, ppmv

W = water vapor ingress rate, ppmv hr

r_w = purification rate constant for water vapor $\left(\frac{\text{flow rate}}{\text{inventory}}\right) \approx 1.0 \text{ hr}^{-1}$

R_1 = core reactivity to H_2O (reaction 1) $\left(\frac{\text{ppmv } H_2O \text{ reacting}}{\text{ppmv } H_2O \text{ present}}\right) \text{ hr}^{-1}$

r_h = purification rate constant for H_2 = 0.2 hr^{-1}

R_4 = core reactivity to H_2 (reaction 4) $\left(\frac{\text{ppmv } H_2 \text{ reacting}}{\text{ppmv } H_2 \text{ present}}\right) \text{ hr}^{-1}$

Since for all practical purposes reaction 4 (methane formation) can be ignored, Eq. (3) is reduced to

$$\frac{P_{H_2}}{P_{H_2O}} = \frac{R_1}{r_h} \quad (4)$$

From this simple relationship, the integrated chemical core reactivity R_1 for an HTGR can be calculated from H_2 and H_2O measurements during H_2O ingress. This relationship assumes, of course, that the methane reaction (4) and the shift reaction (3) are negligible.

4.3 SOURCES OF CONTAMINATION

4.3.1 Hydrogen

Graphite outgassing is a source of hydrogen. This is not expected to be a major source of hydrogen since the graphite was all fully graphitized above 2500°C and the fuel compacts were annealed at 1800°C. On the other hand, graphite outgassing could prove to be a persistent low-level source of H₂ because of the large mass of reflector graphite at low temperature (~350°C).

Hydrogen will also arise from the steam-graphite reaction (1), if steam leakage occurs. In this case, oxygen species (predominantly CO) will be produced at about the same rate.

A possible source of H₂ has been advanced by Dragon Project personnel, who theorize that hydrogen atoms (protons) diffuse through steam generator tube walls. The source of hydrogen in the steam system is the normal metal corrosion process, reaction (7). They earlier experienced rapid corrosion of mild steel tubes in the heat exchangers. High H₂ content (up to 100 ppmv) in the helium coolant was measured during this time.

The Dragon workers feel that the high corrosion rates were more than adequate for the proton diffusion process to occur. The high corrosion rate of the mild steel tubes was apparently caused by nucleate boiling, rapid bubble collapse, and turbulent steam/water flow conditions in regions where heat transfer rates were very high. The resultant H₂ on the water side is not continuously removed (as in the Peach Bottom reactor) but builds up to fairly high levels in the closed steam circuit.

The arguments against the occurrence of this process at Peach Bottom are:

1. The oxidation of metals by pure water of pH 9 to 10 should be negligible. Experience at other steam plants tends to substantiate this.

2. Significant hydrogen diffusion through metal walls should not occur unless there is an appreciable H_2 concentration gradient. This means that H_2 on the steam side must be much higher than on the helium side. Hydrogen, however, cannot accumulate in the steam at Peach Bottom since it is continuously released to the atmosphere (at the air ejector). (It is counter argued that diffusion of corrosion products or "nascent" hydrogen can occur regardless of the relative concentrations of H_2 on either side.)

Another theory is the H_2 could arise from some nuclear process, perhaps by n,p reactions, tritium production, radiolysis of water, or normal neutron decay. A simple calculation, however, shows that if all neutrons decayed to hydrogen, the H_2 production rate in Peach Bottom would only be $\sim 10 \text{ cm}^3/\text{min}$ (or less than 1 ppmv at steady state), which is a negligible amount. This calculation shows that no nuclear process can contribute a significant amount of H_2 in an HTGR.

Another possible source of hydrogen in the Peach Bottom reactor is thermal decomposition of oil vapor. Oil could leak into the system from the main compressor lube oil system, the purified helium compressors, or perhaps the control rod drive mechanisms.

Thermal decomposition of oil would occur on graphite above 500°C . The solid residue left on the graphite might contain an appreciable quantity of hydrogen. This material is known to degas over a relatively long period of time even at temperatures to 1000°C . One expects, moreover, that a significant quantity of hydrogen in the core (as hydrogenous coke residues) would enhance neutron moderation. Thus, the oil ingress mechanism would lead to hydrogen in the gas phase as well as hydrogen in the core, which could cause an increase in nuclear reactivity.

4.3.2 Carbon Monoxide

The main source of CO in the HTGR coolant is the steam-graphite reaction following a steam leak. CO is also an outgassing product.

If CO arises from a steam leak, then an approximately equimolar amount of H_2 should also be apparent. The H_2O level in the helium should also be observable (except for very small steam leaks) because the reactivity of the graphite core to steam is not so great as to consume all of the water that leaks in. In general, the CO/H_2O ratio is expected to be about equal to the H_2/H_2O ratio approximately described by Eq. (4).

Recent analyses⁽¹⁾ of the chemical reactivity of the HTGR core to water vapor (R_1) indicate that H_2/H_2O or CO/H_2O should fall within the range 1 to 10 (impurity sources other than H_2O ingress are neglected).

4.3.3 Water Vapor

Water vapor can exist in the main coolant to a significant extent only if water ingress occurs. (H_2O vapor as a graphite outgassing product is negligible above $300^\circ C$.) The partial pressure of H_2O present for a continuous steam leak is given by Eqs. (1) and (4). Analyses show that at steady state the fraction of H_2O reacted will fall in the range 0.5 to 0.9 (i.e., $H_2/H_2O = 1$ to 10).

4.3.4 Carbon Dioxide

CO_2 is an outgassing product of graphite at temperatures below around $700^\circ C$. Above this temperature CO is the major product. CO_2 reacts with hot graphite by reaction (2). This reaction should eliminate essentially all CO_2 from the coolant.

The carbon deposition reaction (the reverse of (1) and (2)), however, can occur on heat exchanger surfaces (after long exposure to relatively high H_2 and CO levels) and may eventually contribute to CO_2 impurity in the main loop.

The radiolytically induced shift reaction (3) may also lead to CO_2 impurity. By either process, CO_2 can exist only in equilibrium with a relatively high CO concentration.

4.3.5 Oxygen

O₂ impurity will occur only during and shortly after reactor startup because of residual air in the main system. O₂ cannot persist in the helium system during reactor operation because of rapid reaction with hot graphite. (The O₂ + C reaction is about 10⁵ times faster than reactions (1) and (2).)

4.3.6 Methane

Methane is a minor graphite outgassing product. In addition, if the H₂ level is sufficiently high, methane can arise via reaction (4). It is of interest, however, that considering the thermodynamic equilibrium of reaction (4), methane should be virtually nonexistent in the HTGR. It is calculated that at the lowest reactor graphite temperature in the Peach Bottom reactor (~600°K, 620°F), 10 ppm H₂ would yield only about 0.2 ppm CH₄. Moreover, higher graphite temperatures would tend to cause an even lower methane concentration. Since the actual concentration of methane in the main loop was observed to remain relatively constant at around 1 ppm, it is speculated that radiolytic processes have created a quasi-steady state in which methane formation is faster than by ordinary thermally activated reactions resulting in an increased methane yield. Indeed, in a high radiation field, thermodynamic equilibria often do not apply because of the abnormally high concentration of ions, free radicals, atoms and other excited species.

4.3.7 Nitrogen

Nitrogen arises from air ingress and core outgassing. Nitrogen usually outgasses from graphite quite readily and completely and should pose no particular problem in an HTGR coolant if the liquid-nitrogen-cooled sorber unit is adequately sized and working properly.

4.3.8 Neon

Neon is a normal impurity in tank helium. Concentrations of 10 or 20 ppmv are not uncommon. Neon in the main coolant poses no particular problem except as a slight nuisance. An excessive amount of neon could

be bothersome because of the activation product, 38-sec Ne-23. Neon is an additional minor problem because it elutes from the usual gas chromatograph columns along with H₂. Thus, in order to analyze for H₂ using a gas chromatograph with ordinary thermal conductivity detectors, a special H₂-Ne separation column must be utilized. At Peach Bottom a 25 ft long, 1/4 in. OD charcoal column at ambient temperature has been used with good success.

4.3.9 Argon

Argon arises from air ingress during reactor outage. Ar-41 is an activation product which could raise the main coolant activity somewhat until the argon is removed by the liquid nitrogen sorber. Gas chromatographic analysis for argon or O₂ requires a special column for O₂-Ar separation. A 6 ft long, 1/4 in. OD column filled with 5A molecular sieve at -78°C provided ample separation in tests at Peach Bottom.

5. CHEMICAL IMPURITY MEASUREMENTS

5.1 ROUTINE ANALYSES OF MAIN LOOP IMPURITIES

Measurements using the ordinary plant analyzers have, in general, showed low or immeasurable concentrations of gas impurities except during periods of reactor startup or during abnormal conditions such as liquid nitrogen sorber system breakthrough. The sensitivity of the plant instrumentation for the gaseous components is 1 to 5 ppmv for CO, N₂, CO₂, and CH₄, and 50 to 100 ppmv for H₂. During the latter part of 1967, however, CO levels close to instrument sensitivity (2 to 3 ppmv) were recorded both on the chromatographs and the IR analyzer. Accordingly, it was decided to install more sensitive instruments in order to accurately assess the chemical impurities in the loop helium.

5.2 LOW-LEVEL ANALYSIS OF MAIN LOOP IMPURITIES

Three special analyzers were installed in the Peach Bottom reactor to measure low-level impurities in the main coolant. A Goldsmith electrolytic hygrometer was installed in the diffusion probe bypass line of steam generator loop No. 1. The monitor operates at full reactor pressure and is therefore approximately 10 times more sensitive than a low-pressure monitor. Moreover, the monitor is operated on a more sensitive scale (0 to 10 ppm) than the main loop monitors (0 to 1000 ppm). Moisture levels below 0.1 ppm can be measured.

The second instrument is an auxiliary gas chromatograph (Loenco Model 15A), which is installed next to the XSM 310 gas sample concentration device, and there is an additional column for H₂-Ne separation. Using this instrument, 0.5 ppm H₂ can be detected. The sensitivity for the gases N₂, CO, CO₂, and CH₄ is around 0.05 ppm.

A third instrument is a Cambridge hydrogen analyzer, which was installed and operated by Philadelphia Electric Company personnel to monitor hydrogen in the steam system.

In addition to these analyses, tests were performed to determine whether oil ingress is occurring to a significant extent. The tests involved analysis of the helium coolant for oil vapor, visual inspection of likely low spots in the plumbing for liquid oil, and chemical analysis of Peach Bottom graphite for oil residues (by hydrogen analysis).

5.2.1 Results of Low-Level Analyses

The Peach Bottom reactor was first brought to full power in May 1967 and started commercial operation on June 1. Prior to this, however, the reactor was operated at reduced power levels for normal shakedown purposes. The first power escalation of note occurred in January 1967, when 35 MW(t) was attained. During this initial period at 35 MW(t), it was anticipated that major outgassing of the core and other reactor components would occur. Table 2 shows the gaseous contaminant concentrations during this period for several power levels. Hydrogen is not included in this list because the low level analyzers were not yet installed.

The next set of data were obtained in December 1967, using the special low-level analyzers, following 4600 hr of full power operation. Table 3 lists the data obtained at two power levels, 30% and 100%.

Although the concentrations of the gaseous contaminants were not alarming, their persistence after such a long time at full power prompted further speculation and investigation into their possible sources. It was realized for the first time that steady inleakage of contamination must be occurring.

The reactor experienced a scheduled outage for core and reactor component examination during the period January to May 1968.

The reactor was again brought to full power on May 10, 1968. Extensive gas chromatographic analysis of the helium coolant during power escalation showed a significant increase in coolant impurities, due to

Table 2
GASEOUS IMPURITY CONCENTRATIONS IN PEACH
BOTTOM DURING INITIAL APPROACH TO POWER
JANUARY 1967

Date	Reactor Power (MW(t))	Gaseous Contaminants (ppmv)			
		N ₂	CH ₄	CO	CO ₂
1-22-67	0	7.0	0	0	0.3
1-24-67	2	15	0.05	0.05	0.5
1-25-67	5	--	0.08	0.05	0.4
1-26-67	3	15	0.05	0.6	0.3
1-27-67	1	16	0.09	0.5	0.3
1-28-67	5	27	0.4	0.4	0.5
1-29-67	20	50	1.8	1.8	1.7
1-30-67	35	40	1.0	4.1	1.8

Table 3
GASEOUS IMPURITY CONCENTRATIONS IN PEACH BOTTOM
COOLANT AFTER 4600 HOURS AT FULL POWER
DECEMBER 1967

Date	Reactor Power (%)	Sample Point	Gaseous Contaminants (ppmv)			
			H ₂	N ₂	CH ₄	CO
12-9-67	30	Main loop	3	0.8	0.7	0.5
12-10-67	30	Main loop	3.4	0.9	0.65	0.44
12-10-67	30	LTDB outlet	---	0.8	0.24	0.3
12-11-67	100	Main loop	9.5	0.5	0.6	0.55
12-11-67	100	LTDB outlet	9	0.65	0.2	0.3
12-12-67	100	Main loop	9	0.5	0.6	0.5

Analyses of helium from the dump tanks showed normal levels of impurities. The liquid-nitrogen-cooled sorber outlet helium was found to be free of all impurities except H₂. The oxidizer outlet contained no H₂ and CO and the drier beds (molecular sieves) showed no H₂O or CO₂, indicating that those systems were working properly. In addition no CO₂ nor H₂O was found in mainloop samples.

outgassing of the system. (During the extended outage, some air ingress and subsequent adsorption occurred which undoubtedly contributed somewhat to outgassing upon heatup.)

In June 1968, the reactor was again shut down for minor repairs. Gas analyses were performed following the escalation to 95% power later in June.

The data for the periods described above are given in Tables 4 (May 1968) and 5 (June 1968). Data for these periods are also shown in Figs. 4 through 6, where gaseous contamination is plotted vs. time and power level.

Figures 4 and 5 are of interest because they show impurity concentrations as a function of reactor power. The initial increase at each new increase in reactor power is believed to be due to the outgassing effects. (Laboratory experiments on the outgassing of graphite have shown similar behavior; that is, as the temperature is brought up in steps, a "burst" of gas is invariably observed at each temperature increment.) However, during each power escalation, the purge stream hydrogen level is higher than the main loop. Since the fuel is much hotter than the rest of the graphite, it would respond (i.e., outgas) more rapidly to changes in temperature than the rest of the core.

Figure 6 shows the data for the main loop contaminants during June 1968. These measurements were started two days after the reactor had been brought to power, when initial outgassing was essentially complete. These data show that H_2 and CH_4 remained essentially constant during the twelve days of measurements, while CO and N_2 were gradually cleaned up. The apparent purification factors determined from Fig. 6 for CO and N_2 are $3 \times 10^{-3} \text{ hr}^{-1}$ and $7 \times 10^{-3} \text{ hr}^{-1}$, respectively. These are in contrast to the actual cleanup constants given in Table 1, 0.3 and 0.1 hr^{-1} for CO and N_2 , respectively, and indicate that during initial periods of startup there is a considerable source of CO and N_2 , which is undoubtedly outgassing of core components and the large mass of chilled carbon in the low-temperature delay beds.

Table 4

HELIUM CHEMISTRY DURING MAY 1968

Date, Time	Sample Point	Reactor Power (%)	Fuel Temp (°F)	Misc. Conditions	Gaseous Impurities (ppmv) ^a					
					H ₂	N ₂	CH ₄	CO	Total H ₂ ^b	H ₂ /O ^c
5/9/68, 0900-1300	Main loop A-304	78	1635	Normal	11	4.5	0.7	4.4	12.4	2.8
		78	1635	Normal	11.3	6.4	0.47	4.7	13.2	2.8
5/9/68, 1200-1600	Main loop A-304	78	1505	Core overcooled	8.7	---	---	---	---	---
		78	1505		7.5	---	---	---	---	---
5/9/68, 1700-1800	Main loop A-304	78	1505	Core overcooled;	7.8	---	---	---	---	---
		78	1505	purge reduced to 450 lb/hr	---	---	---	---	---	---
5/10/68, 0600-0730	Main loop A-304	78	1505	Core overcooled;	7.0	4.8	0.8	3.7	8.6	2.3
		78	1505	purge flow 850 lb/hr	7.3	---	---	---	---	---
5/10/68, 0730-1100	Main loop A-304	78	1505	Core overcooled;	7.2	---	---	---	---	---
		78	1505	purge reduced to 450 lb/hr	5.8	---	---	---	---	---
5/10/68, 1100-1200	Main loop A-304	78	1505	Core overcooled;	7.0	---	---	---	---	---
		78	1505	purge flow 850 lb/hr	6.8	---	---	---	---	---
5/10/68, 1200-1500	Main loop A-304	78	1505	Core overcooled;	7.3	6.3	0.91	4.3	9.1	2.1
		78	1505	buffer He Δp reduced 1 to 0.6 psi	7.4	7.0	0.68	3.8	8.8	2.3
5/10/68, 1700-1800	Main loop	95	1700	Core overcooled	11.5	5.8	0.61	4.9	12.7	2.6

^aA-304 is a sample of the purge stream downstream of the first LTDB, A-304. The data have been corrected for dilution of purified He, (175 lb/hr).

^bTotal H₂ = H₂ + 2 CH₄.

^cH₂/O = total H₂/CO.

Table 5

HELIUM CHEMISTRY DURING JUNE 1968

Date	Sample Point ^a	Reactor Power (%)	Misc. Reactor Conditions	Gaseous Impurities(ppmv)					
				H ₂	N ₂	CH ₄	CO	Total H ₂ ^b	H ₂ /O ^c
6/6/68	Main loop A-303	94	Normal	11.8	3.2	1.0	2.9	13.8	4.8
				9.6	2.8	0.4	2.6	10.4	4.0
6/7/68	Main loop A-303	94	Normal	8.0	2.4	0.39	2.4	8.8	3.7
				10.0	2.2	0	2.2	10.0	4.6
6/10/68	Main loop A-303	94	Steam generator baffle purge No. 2 = 150 ppm H ₂ O	10.3	1.0	0.96	2.3	12.3	5.4
				10.3	1.1	0.23	2.0	10.8	5.4
6/11/68	Main loop A-303	94	Steam generator baffle purge No. 2 = 150 ppm H ₂ O	9.5	0.86	1.04	2.3	11.5	5.0
				11.2	0.70	0.23	1.8	11.7	6.5
6/12/68	Main loop A-303	94	Steam generator baffle purge No. 2 = 150 ppm H ₂ O	7.6	0.64	1.1	2.0	9.8	4.9
				9.8	0.57	0.17	1.6	10.1	6.3
6/12/68	Main loop A-303	94	Purge flow = 522 lb/hr	7.9	0.64	0.76	2.1	9.4	4.5
				10.6	0.50	0.26	2.1	11.1	5.3
6/13/68	Main loop A-303	96	Normal	7.9	0.49	1.05	1.6	10.1	6.3
				12.1	0.41	0.19	1.3	12.5	9.6
	Main loop A-303	85	Reduced power and core temperature	6.3	0.45	0.87	1.5	8.0	5.3
				4.5	0.41	0.24	1.1	5.0	4.5
	Main loop A-303	92	Overcooled core	6.3	0.47	0.86	1.5	8.0	5.3
				7.6	0.40	0.30	1.2	8.2	6.8

^aA-303 is a sample of the purge stream at the effluent of the second water-cooled delay bed A-303.

^bTotal H₂ = H₂ + 2 CH₄.

^cH₂/O = total H₂/CO.

Fig. 4. H₂ concentration in main loop and purge stream during May 1968

Fig. 5. Gas impurity concentrations in main loop during May 1968

Fig. 6. Main loop contaminants during June 1968

Two sets of helium chemistry data were obtained in October 1968, just before the scheduled shutdown on October 23. These data are of particular interest because they were obtained after the reactor had operated at full power for an additional 3170 hr, following the June 1968 startup. These analyses are shown in Table 6. They indicate again that the coolant contamination is persistent and that a steady ingress of impurities must be occurring.

Impurity concentrations during the operation of Core 2 are given in Table 7. Core 2 achieved full power on July 14, 1970, and has been in operation since then except for a scheduled outage from April 22 to July 12, 1971. The data given in Table 7 appear quite erratic, particularly with regard to hydrogen levels. High hydrogen concentration is attributed to breakthrough of H_2 in the oxidizer unit. This was verified by the observation of identical H_2 concentrations at the inlet and outlet of the Cu/CuO bed. It is of interest, however, that whereas the CuO bed had periodically become saturated with respect to oxidation of H_2 , the unit was still effective in CO oxidation and removal. This was determined by comparing the CO concentration in the main loop, 0.4 ppmv, to that in the oxidizer effluent, < 0.05 ppmv. Another indication of CO oxidation and removal by the system was the observation that CO levels in the main loop had not increased above the normal level of about 0.5 ppmv. Why the oxidizer should be effective in CO oxidation and not H_2 oxidation is not fully explained.

During the latter part of December 1970, the oxidizer was regenerated by the addition of oxygen, after which hydrogen levels were observed to drop to about 10 to 15 ppmv. This regeneration proved to be quite insufficient because during the early part of January, hydrogen in the main loop was again observed to increase. This was not totally unexpected because the regeneration process was known to be less than complete due to oxygen leakage from the oxygen manifold. Another partial regeneration of the oxidizer was accomplished in January 1971 and H_2 levels once again decreased and remained low for several days. On January 26, 1971, the

Table 6
CHEMICAL IMPURITIES IN HELIUM COOLANT (PPMV) OCTOBER 1968

Sample Point	Date	H ₂	Ar	N ₂	CH ₄	CO	CO ₂
Main loop	Oct. 11	10	0.1	0.5	1.0	0.65	<0.02
A303 exit	Oct. 11		0.1	0.4	0.2	0.4	~0.06
A304 exit	Oct. 11	10	0.1	0.4	0.4	0.33	0.3
LTDB exit	Oct. 11		0.1	0.4	0.4	0.17	0.02
Main loop	Oct. 22	12	0.2	0.8	1.0	0.6	<0.02
LTDB exit	Oct. 22	12	0.1	0.4	0.4	0.15	<0.02

Table 7
GASEOUS IMPURITIES IN CORE 2 OPERATION

Date	Impurity Concentration (ppmv)			
	H ₂	N ₂	CH ₄	CO
11/25/70	86	1.4	2.2	0.4
11/30/70	110	1.5	2.0	<0.04
12/15/70	-	2.9	1.6	0.7
12/18/70 ^a	106	1.7	2.2	0.4
12/24/70	46	2.2	0.6	0.4
12/29/70	20	1.8	0.6	0.9
1/6/71 ^a	60	1.6	0.8	0.6
1/12/71	15	1.0	0.7	0.6
1/18/71	11	1.7	0.7	0.7
1/26/71	12	-	-	-
1/27/71	30	1.7	1.0	0.4
2/2/71	49	1.8	1.4	0.7
2/4/71	90	-	-	-
2/8/71	140	1.6	1.9	0.4
2/18/71 ^a	28	0.4	0.3	0.1
2/23/71	17	1.0	0.8	0.4
3/5/71	11	0.6	0.1	0.3
3/10/71	< 9	3.2	1.2	0.1
3/14/71	14	3.2	0.3	<0.05
3/29/71	135	6.0	1.2	0.1
4/5/71 ^a	62	6.0	2.2	1.8
4/12/71	30	5.9	0.4	0.7
4/22/71 ^b	18	4.9	1.5	1.2
7/26/71 ^b	12	8.8	1.6	1.8
8/10/71	40	7.0	2.6	0.8
8/18/71	36	2.5	1.7	0.8
8/19/71	48	3.7	2.1	0.6

^a The Cu/CuO oxidizer unit was partially regenerated following these dates.

^b Scheduled reactor outage 4/22/71 to 7/12/71.

H₂ concentration started to increase again and rose to about 140 ppmv. A partial regeneration of the oxidizer material on February 9, 1971, brought the H₂ level again, only to rise again on March 22. A fourth regeneration was performed prior to the shutdown on April 22.

Following the startup on July 12, 1971, the hydrogen levels have increased to nearly 50 ppmv. A complete regeneration of the Cu/CuO material was under consideration at the time this report was written.

Moisture levels as indicated by the Goldsmith hygrometer have been consistently low (i.e., ≤ 0.05 ppmv). Other data, however, tend to corroborate these apparent low moisture levels.

The additional information is the observation of an extremely small amount of fuel carbide oxidation in the fractured fuel element D06-01 which was removed for examination after 300 EFPD.⁽⁴⁾ Metallographic examination of fuel compacts revealed that 80 to 98 percent of the carbide kernels were exposed but that only about 8 percent of the kernels in the top compact (No. 30) were partially or completely oxidized. Below the top compact, kernel oxidation was immeasurably small, except for compact 8 in which a small number of oxidized particles (about 1 percent) were observed. Compact 8 was located in the fracture zone of the fuel element and thus received some direct coolant flow during part of the year. Moreover, the oxidized particles in those compacts were all on or near the surface.

These observations suggest that oxidizing coolant impurities were gettered by the exposed carbide kernels in those compacts (Nos. 8 and 30) which received direct coolant flow. Moreover, the oxidant in question was clearly not CO, since CO was only slightly depleted in the purge stream (see Tables 4, 5 and 6).

The oxidizing impurity which has some lifetime in the HTGR core (i.e., is not completely gettered by the hot graphite) and will react rapidly and quantitatively with exposed (Th,U)C₂ is H₂O. Thus, from the observation of a small amount of oxidized fuel, one can estimate

the average steady state water vapor concentration during the first year of operation.

Assuming that all of the water vapor that entered the fuel element purge system was gettered by about 10% of the carbide fuel in the first compact, it is calculated that the steady state partial pressure of water during the first year of operation was about 0.07 ppm. This low value is consistent with the low moisture levels indicated by the Goldsmith hygrometer.

Gas analyses as indicated in Tables 2-6 were performed during escalation to power, during steady state at various powers and following long times at full power. In addition, data were obtained while other reactor parameters were deliberately varied in order to aid in ascertaining the sources of contamination. The following discussion outlines the conditions of each analysis and the results of each.

5.2.1.1 Reactor Power and Core Temperature. Gas analyses were performed during escalation to full power and at several incremental steps. Data obtained during initial startup (Table 2) or following reactor outages or installation of new fuel elements (Tables 4 and 5 and Figs. 4, 5 and 6) show definite evidence of graphite outgassing. Data obtained after long-term operation at full power (Tables 3, 6, and 7) are deemed most informative since outgassing should be essentially complete (or at least the outgassing rate should have decreased to a low value). The steady state level of the four components of chemical importance at full power is given in Table 8.

Table 8
GASEOUS IMPURITIES AT FULL POWER AND
STEADY STATE

Impurity	Observed (ppmv)	Design	Tech. Spec. (Upper Limit)
H ₂	10 ± 2	10	None
CO	0.5 ± 0.2	10	10
CH ₄	1.0 ± 0.2	1	2
CO ₂	<0.05	1	2
H ₂ O	<0.05	1	*

Analyses obtained at other power levels were not for steady state operation; however, the data indicate a significant and rapid change in coolant contamination with change in power level (and temperature). Tables 3, 4, and 5 show this effect. These observations indicate a rapid adsorption-desorption process in which the core graphite is a large sink-source for the gaseous impurities. It does not necessarily suggest that the core is the ultimate source, but that the core is a sink in which relatively large amounts of each component are stored by adsorption.

5.2.1.2 Core Temperature. Data were obtained before and after the core was "overcooled" while reactor power was held constant at 78% (see Table 4). Measured fuel temperatures dropped about 130°F as a result of the overcooled condition. These data confirm the findings summarized above and suggest that coolant impurity concentrations are dependent primarily on core temperature and not core power alone.

5.2.1.3 Purge Flow Rate. Three separate reduced purge flow experiments were performed to ascertain whether the source of H_2 is in the fuel or elsewhere. If the fuel is a hydrogen source, the H_2 level in the purge should increase with reduced purge flow. If the source is elsewhere in the main loop, the H_2 concentration should remain constant.

The data given in Tables 4 and 5 show the results of the reduced purge experiments. It is seen that H_2 levels in the purge remained essentially constant at both full and partial purge rate.

5.2.1.4 Buffer Helium Flow. If main compressor oil normally leaks in through the buffer helium-labyrinth seal system, more oil should leak in during periods of low buffer helium flow. Higher oil ingress rate should also result in higher H_2 levels in the main loop. Accordingly, measurements of H_2 level were performed during a period in which the buffer helium Δp was reduced from 1 psi to 0.6 psi for 2 hr. No change in H_2 concentration in the main loop helium was observed during these tests.

5.2.1.5 Apparent Steam Leak Conditions. Gas analyses were obtained shortly before and after an apparent steam leak into the No. 2 steam generator baffle purge stream (see Table 5). No change in coolant contamination was observed, indicating that the baffle purge system efficiently reduces water ingress into the main coolant from leaking tube sheet weldments.

5.3 OIL CONTAMINATION MEASUREMENTS

Oil contamination in the Peach Bottom reactor was investigated in three ways. The steps taken and the results of each are listed below.

5.3.1 Oil Drains

It was assumed that if oil ingress occurred, then low spots in the system might accumulate liquid oil. Accordingly, the drains from the No. 1 expansion loop and from the liquid nitrogen heat exchanger were opened. No oil was found.

5.3.2 Oil Vapor Measurements

Oil vapor cold trap samples were obtained from the main loop and purified helium header. The technique was to pass helium gas from these sample points through a steel trap chilled to 0°C. A plug of glass wool in the trap was used as the condensing surface. The glass wool plug was examined for oil by using an ultraviolet lamp. (Oil fluoresces in UV light.)

No positive indication of oil vapor was detected in the trap following a total sample flow of 5000 liters through the sample collection system. An oil vapor pressure of less than 0.02 ppmv was estimated for these analyses (the vapor pressure of DTE797 oil at 25°C has been measured at 0.3 ppmv).

5.3.3 Measurements of Oil Residues on Core Graphite

If there is a continuous oil leak into the main loop helium, most of the oil should decompose on the hot graphite surfaces of the core. The coke residue left on the fuel elements would contain relatively large amounts of hydrogen. Analyses of hydrogen in fuel element graphite after 150 and 300 EFPD are given in Table 9. These data show normal hydrogen concentrations, (i.e., approximately 10 ppm (wt)). There is no indication of coke residues which would arise from thermal decomposition of oil vapor.

5.4 ANALYSES OF HYDROGEN IN THE STEAM SYSTEM

The results of the Cambridge hydrogen analyzer indicated 4 ppb (wt) H_2 in both steam loops. In addition, no H_2 was found in the condensate pump discharge, which is downstream of the air ejector. This means that H_2 (or other gases) cannot accumulate in the steam system because of the efficiency of the air ejector.

Table 9

HYDROGEN CONTENT OF CORE MATERIALS

Core Component	Weight (lb)	Hydrogen Content (1), (2)							
		Initial		After 150 EFPD B13-05		After 300 EFPD			
						D06-01		C08-01	
		ppm	lb	ppm	lb	ppm	lb	ppm	lb
Upper reflector	1.1×10^4	20	0.2	6	0.6	8	0.09		
Fuel element graphite, sleeve	2.3×10^4	20	0.5			12	0.3		
Fuel element graphite, spine	1.1×10^4	20	0.2						
Lower reflector graphite	7.8×10^3	20	0.2			13	0.1		
Side reflector graphite	8.5×10^4	20	1.7					8	0.7
Fuel compacts ⁽³⁾	1.9×10^4	300	5.5						

(1) Total hydrogen in core graphite initially ~ 7.8 lb.
Total hydrogen in core graphite after 300 EFPD ~ 4.5 lb.

(2) Each number is average of 3-4 separate analyses.

(3) Hydrogen analysis of irradiated fuel compacts or spine was not performed. Based on the other analyses, it is estimated that 1/2 of the initial hydrogen remains in these components after irradiation.

6. DISCUSSION OF CHEMICAL IMPURITY DATA

The salient features of the gaseous impurity data thus far accumulated are listed below.

1. There is a steady source of impurities in the main loop, as shown in Tables 3 and 6 where ~ 10 ppmv H_2 and ~ 0.5 ppmv CO were observed after 4600 and 7500 hr of Core 1 full power operation. Similar impurity levels were found in the Core 2 coolant during steady state operation when the He purification system functioned properly (see Table 7).
2. The ratio of hydrogen species to oxygen species remains high ($H_2/O = 20$ for the steady state cases given in Tables 3, 6, and 7). The following phenomena are suggested as reasons for the high H_2/O :
 - a) Long-term outgassing of the core components.
 - b) A small steam leak, and faster cleanup for oxygen species than for hydrogen species.
 - c) A separate source of hydrogen such as proton diffusion through steam tube walls or oil ingress.

These possible sources of chemical contaminants are discussed in detail in Section 7.

3. The impurity levels in the main loop are not affected by any change in reactor parameters, except graphite temperature, where the effect is large (see Tables 3, 4, and 5). This indicates an adsorption-desorption process where impurity gases rapidly established new equilibria at each different

temperature. This does not suggest that the core is necessarily the source of contaminants, but is a sink in which gas impurities are held in relatively large quantities. Moreover, adsorption may be enhanced by radiolytic processes which transform the impurity gases into more reactive species. These reactive species then can react with graphite surfaces to form chemical complexes which may be relatively thermally stable.

4. The fact that no increase in impurity gases in the loop helium occurred following the steam leak into the steam generator baffle purge No. 2 on June 10, 1968 (see Table 5) indicates that the tube sheet baffle purge system is efficient.
5. No evidence supporting oil ingress as a source of hydrogen contamination was found. No oil vapor was found in the main loop or the purified helium header cold trap samples. Oil drains were negative. The hydrogen level in the main loop did not increase when the buffer helium flow was reduced. Oil cracking residues were not found by hydrogen analysis on two fuel elements and one side reflector element removed from the Peach Bottom core.
6. The measurements of hydrogen in the steam neither support nor reject the theory that hydrogen is diffusing through the steam generator tubes. Details on this mechanism are given in Section 7.4.
7. Measurement of methane at the fuel element purge stream exit (downstream of the water-cooled delay beds) indicates that methane cracking occurs in the purge channels (or in the water-cooled delay beds). The data show that only 20% to 50% of the methane entering the purge survives. Assuming the methane cracks in the purge grooves, adjacent to the hot fuel, the amount of carbon deposited therein is calculated to be about 13 lb after 8000 hr of full power operation.

8. The data indicate that carbon monoxide is partially removed in the purge channels. Since no CO_2 is seen, the reverse of reactions (2) and (3) (see Section 4.2) can be ruled out. The CO removal could be a result of the radiolytic reverse reaction (1) or oxidation of the exposed fuel.

7. DISCUSSION OF POSSIBLE SOURCES OF COOLANT CONTAMINATION

7.1 OUTGASSING OF CORE COMPONENTS

The hydrogen content of the core components before and after irradiation has been measured and is shown in Table 9.

The data in Table 9 show that approximately 3.3 lb of H_2 has been degassed from core materials during 450 EFPD. This is compared to the amount of H_2 removed by the purification system during this period, calculated to be about 10 lb. Thus, outgassing apparently is not the sole source of H_2 in the coolant. Furthermore, the hydrogen content observed in Core 1 graphite after 150 and 300 EFPD is consistent with the measurements of Thomas,⁽²⁾ who determined hydrogen sorption isotherms on graphite at temperature and pressure conditions similar to those in the reactor (i.e., temperature = 300° to 750°C; H_2 partial pressure = 0.175 mm Hg).

Moreover, the persistency of the hydrogen levels in the main coolant at steady state is not consistent with graphite outgassing phenomena. Laboratory experiments show that graphite outgassing is rapid during the initial rise to temperature followed by a period in which the gas evolution rate decreases rapidly. After a relatively few days, the outgassing rate in a reactor should be negligible. It is postulated, therefore, that an additional source of hydrogen exists.

7.2 OIL INGRESS THEORY

The potential for oil ingress exists in Peach Bottom from two major sources, the main coolant blowers and the purified helium compressor, both of which are oil lubricated. The main blowers, however, are provided with labyrinth seals through which high-pressure helium is pumped, thereby back-purging oil vapor into the lube system. The purified helium compressor is provided with an oil demister and activated carbon sorbent beds which should preclude oil vapor entering the primary circuit.

Nevertheless, it is recognized that these protective devices could fail or at best allow a slight amount of oil vapor contamination.

There is no evidence, however, that positively indicates oil contamination in the Peach Bottom main circuit. The oil searches (discussed in Section 5.3) were negative. In addition, gas analyses performed while the main compressor buffer helium pressure was deliberately decreased showed no increase in H_2 levels.

Moreover, hydrogen analyses of irradiated fuel elements from the Peach Bottom reactor (see Table 9) do not show excessive hydrogen content, which would be indicative of hydrocarbon deposition. Experimental work⁽³⁾ has shown that the thermal decomposition of lube oil on graphite at 750°C produced hydrogen-rich coke deposits which are relatively stable (with respect to outgassing) at fuel element temperatures.

7.3 WATER INGRESS THEORY

This concept assumes (1) the existence of a small steam leak, (2) reaction of the water with graphite to form H_2 and oxygen-containing species (mainly CO), and (3) higher removal rate for the oxygen species. A total oxygen species removal rate in the system about 20 times faster than the hydrogen cleanup would result in the observed steady state H_2/O ratio of approximately 20. Possible cleanup modes for oxygen species include:

1. Oxidation of metal surfaces.
2. Oxidation of fuel or fission products.
3. Quantitative removal of CO_2 in the low-temperature delay beds.
4. Partial removal of CO in the low-temperature delay beds (by radiolytic conversion to CO_2 or by normal low-temperature adsorption processes).

CO cleanup via normal purification processes is faster than H_2 cleanup by a factor of approximately 1.5 (see Table 1, Section 3.3).

The effect of purification rate on steady state levels of gaseous species is given by the relation

$$P_i = \frac{I_i}{r_i}$$

where P_i = steady state partial pressure of the species i (ppmv)

I_i = ingress rate of species i (ppmv/hr)

r_i = cleanup rate constant of i , hr^{-1}

If the ingress rates for H_2 and O are equal, as in the case of H_2O in-leakage, then the resultant partial pressures of H_2 and CO will be inversely proportional to their respective purification rates.

It is impossible to assess accurately the importance of metal oxidation (oxygen cleanup mode 1 above) because of the inaccessibility of the steam generators. Incoloy samples removed from diffusion probes, however, showed an oxide scale about 2 μm thick after 3000 hour exposure. A calculation shows that this degree of oxidation could be caused by as little as about 5 lb of water (assuming the oxide scale is uniformly distributed over the Incoloy superheater tubes, $2.6 \times 10^6 \text{ cm}^2$). Furthermore, metal oxidation should diminish with time because of the protective nature of the oxide film.

There is little evidence supporting mode 2, oxidation of carbide fuel, as an important oxygen cleanup process. As discussed in Section 5.2.1, the observation of such a small amount of fuel oxidation in fuel element D06-01 suggests both that CO , under these conditions, is not an effective $(\text{Th,U})\text{C}_2$ oxidant and that the average steady state vapor concentration was only about 0.07 ppmv.

Adsorption of CO_2 in the low-temperature delay beds (mode 3 above) cannot be an important oxygen cleanup mode because the CO_2 level in the coolant is very low.

Evidence supporting mode 4, sorption of CO in the low-temperature delay bed system, is given in Tables 3 through 6, where the CO levels in the water-cooled beds or the delay bed outlet are observed to be less than at the inlet (or main loop).

The following calculation takes into account possible CO removal phenomena suggested by modes 2 and 4. Using the data in Table 6, the CO ingress rate is given by

$$0.65 \text{ ppmv} \times \left(0.82^{(a)} \times \frac{0.48^{(b)}}{0.65} \right) + 0.2^{(c)} = 0.52 \text{ ppmv CO/hr}$$

The H₂ ingress rate is

$$10 \text{ ppmv} \times 0.2^{(d)} = 2 \text{ ppmv H}_2/\text{hr}$$

Thus, the H₂ ingress rate is about four times greater than that of CO, which is not particularly suggestive of a steam leak.

Thus, because the observed H₂/CO ratio has remained high, and because water vapor measurements and fuel oxidation observations suggest that the helium coolant has been extremely dry, it is concluded that steam ingress into the main coolant has been virtually non-existent.

7.4 PROTON DIFFUSION THEORY

The H₂ generation rate in the helium coolant is calculated to be

$$10 \text{ ppmv} \times 10^{-6} \times 5.5 \times 10^{-5}^{(e)} \text{ sec}^{-1} \times 2 \times 10^9 \text{ cm}^3^{(f)} = 1.1 \text{ cm}^3 \text{ H}_2/\text{sec}$$

-
- (a) Fraction helium flow in purge system (hr⁻¹)
 - (b) Fraction CO removed in purge system (see Table 6)
 - (c) CO purification fraction through oxidizer, hr⁻¹
 - (d) H₂ purification fraction through oxidizer, hr⁻¹
 - (e) H₂ purification constant
 - (f) Helium main loop inventory

The H_2 partial pressure in the helium is given by

$$10 \text{ ppmv} \times 10^{-6} \times 23 \text{ atm} = 2.3 \times 10^{-4} \text{ atm } H_2$$

From the Cambridge H_2 analyzer results, one calculates the H_2 generation rate in the steam:

$$\frac{4 \text{ ppb} \times 10^{-9} \times 3 \times 10^5 \text{ (g)} \text{ lb/hr} \times 454 \text{ g/lb} \times 2.24 \times 10^4 \text{ cm}^3/\text{mole}}{2 \text{ g/mole} \times 3.6 \times 10^3 \text{ sec/hr}} = 2.0 \text{ cm}^3 \text{ sec}$$

The H_2 partial pressure on the steam side is

$$\frac{4 \text{ ppb} \times 10^{-9} \times 18 \text{ g/mole} \times 1500 \text{ psi}}{2 \text{ g/mole} \times 14.7 \text{ psi atm}} = 4 \times 10^{-6} \text{ atm}$$

The observation of hydrogen in the steam system is not unexpected because of normal corrosion reactions (see reaction (7) Section 4.2). The following discussion, however, indicates that much of the observed H_2 in the steam system may arise from hydrazine decomposition. Hydrazine is added to the steam system at Peach Bottom for the purpose of scavenging O_2 .

Experimental work by Dickinson, Felgar, and Pirsh⁽⁵⁾ showed that hydrazine begins to decompose at 400°F by the process $2N_2H_4 = N_2 + H_2 + 2NH_3$. They found that at 600°F N_2H_4 is 90% decomposed in less than 1 min. In observations at Peach Bottom, no hydrazine is found in the saturated steam. Therefore, decomposition occurs between the evaporator and inlet to the superheater. Some hydrazine, of course, reacts with oxygen, but oxygen levels are only 5 to 15 ppb at the condensate pump discharge and 0 to 2 ppb downstream from the deaerator. Thus, it is reasonable to expect that hydrazine in the steam system at Peach Bottom decomposes completely via the above reaction during each circuit.

Hydrazine is added continuously at Peach Bottom at approximately 25 g/hr. From this, one calculates

(g) Total steam flow rate

$$\frac{25 \text{ g/hr}}{3.6 \times 10^5 \text{ lb/hr} \times 454 \text{ g/lb}} = 153 \text{ ppb N}_2\text{H}_4$$

Moreover, the steady decomposition of 153 ppb N_2H_4 by the above reaction results in an H_2 concentration of 4.8 ppb (which is essentially equal to the H_2 analysis results above).

The above calculations show that although the hydrogen generation rate in the steam is twice that in the helium, the steady partial pressure of H_2 is much higher on the helium side. This would tend to rule out ordinary Fick's law diffusion, which implies that a pressure gradient must exist across a barrier for diffusion to occur. Indeed, from these statements, one expects that H_2 diffusion should occur from helium to steam, not the reverse.

It is speculated, however, that proton diffusion could occur as a result of corrosion reactions. A theoretical study by Knoedler and Dalgaard⁽⁶⁾ suggests that under certain conditions, virtually all hydrogen produced from steam side corrosion will diffuse through the tube walls.* A specific condition known to catalyze this process is the presence of electron donor materials which poison the magnetite film, thereby not allowing hydrogen to chemisorb thereon and subsequently be swept away by the steam coolant. Knoedler and Dalgaard further point out that if protons are blocked from chemisorption, then they must take the alternate route, which is through the tube wall.

Hydrazine, of course, is a strong reducing agent and therefore an electron donor. One speculates, therefore, on whether hydrazine catalyzes the diffusion of protons through the tube walls.

*Assuming that all H_2 in the He arises from diffusion of corrosion protons, the corrosion rate averaged over the entire mild steel surface area in the economizer-evaporator is calculated to be $\sim 0.3\%/yr$ or 0.0004 in./yr .

8. CONCLUSIONS

The chemical impurities in the helium coolant of the Peach Bottom HTGR have remained low but persistent. It is theorized that a continuous impurity source exists, the location of which is not proven. Both oil and/or water ingress and outgassing of graphite and charcoal could contribute to some of the observed impurities. In addition, hydrogen in the main coolant could possibly come from proton diffusion through heat exchanger tubes following steam side corrosion. There is, however, no reasonable proof (aside from the existence of the impurities) that any of these processes (except outgassing) are occurring in the Peach Bottom HTGR. It is concluded, therefore, that until further data are obtained, the true sources of gaseous impurities in the Peach Bottom reactor are not entirely explained.

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