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PRIMARY COOLANT CHEMISTRY OF THE PEACH BOTTOM AND FORT ST. VRAIN HIGH-TEMPERATURE GAS-COOLED REACTORS

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PRIMARY COOLANT CHEMISTRY OF THE PEACH BOTTOM AND FORT ST. VRAIN HIGH-TEMPERATURE GAS-COOLED REACTORS*

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ABSTRACT

The chemical impurities in the primary coolants of the Peach Bottom and Fort St. Vrain reactors are discussed. The impurity mixtures in the two plants were quite different because the sources of the impurities were different. In the Peach Bottom reactor, the impurities were dominated by H_2 and CH_4, which are decomposition products of oil. In the Fort St. Vrain reactor, there were high levels of CO, CO_2, and H_2O. Although oil ingress at Peach Bottom created carbon deposits on virtually all surfaces, its effect on reactor operation was negligible. Slow outgassing of water from the thermal insulation at Fort St. Vrain caused delays in reactor startup. The overall graphite oxidation in both plants was negligible.

1. PRIMARY COOLANT SYSTEM

1.1. Peach Bottom

The primary helium coolant system in the 40-MW(e) Peach Bottom high-temperature gas-cooled reactor (HTGR) consisted of a reactor pressure vessel, two steam generators, two oil-lubricated helium compressors, piping, and auxiliary equipment. The steam generators and helium compressors were arranged to form two parallel loops for circulation of the helium coolant at a pressure of 2.4 MPa. The core outlet temperature was nominally 1000 K.

Within the reactor, approximately 80%/h of the main helium stream was withdrawn from the main coolant system through the tubular fuel elements. This purge stream went to the low-temperature trapping system for removal of fission products. In addition, helium was withdrawn from the steam generator tube sheet baffles and was purified by passage through a chemical purification system (Cu/CuO catalyst bed followed by molecular sieve beds) which removed gaseous contaminants such as H_2O, H_2, CO, and CO_2. The total helium flow rate through this system was about 20%/h. The purified helium then joined the fuel element purge stream for gaseous fission product removal.

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The compressor which provided gas flow for this purification system was located downstream of the entire system and was lubricated by oil.

1.2. Fort St. Vrain

The Fort St. Vrain HTGR is a 330-MW(e) plant. The core outlet temperature is 1050 K, and helium pressure is 4.8 MPa. Its primary coolant system is based on the same fundamental principles as the Peach Bottom reactor. However, the Fort St. Vrain reactor does incorporate a number of new design features, the most prominent of which are (1) a prestressed concrete reactor vessel (PCRV); (2) once-through modular steam generators with integral superheaters and reheaters; (3) four steam-driven axial flow helium circulators with water-lubricated bearings; (4) prismatic fuel elements with improved fuel particles; (5) fibrous ceramic insulation adjacent to the PCRV liner; and (6) lack of a fuel element purge system.

Fission product and chemical impurity control is provided by a 12%/h bypass purification stream consisting of (1) a high-temperature-activated carbon bed and a sintered stainless steel filter which removes condensable fission products and particulates; (2) a molecular sieve bed which removes H_2O and CO_2; (3) a liquid-nitrogen-cooled carbon bed which removes xenon, krypton, CO, N_2, and CH_4; and (4) a hot titanium sponge bed which removes H_2 and tritium.

2. COOLANT CHEMISTRY DATA

2.1. Peach Bottom

The Peach Bottom reactor was started up in January 1967, and it achieved full power in June 1967. The coolant impurities during rise to power and steady state are given in Table 1. The steady values persisted throughout the life of the plant (with the exception of occasional transient hydrocarbon ingresses) until shutdown on October 31, 1974. Only one reactor shutdown and rare power reductions were due to excessive hydrocarbon impurities, and reactor startups were seldom delayed because of impurity outgassing. The technical specifications for full-power operation were 10 ppmv of CO, 2 ppmv of CO_2, and 2 ppmv of CH_4. References 1 and 2 present the Peach Bottom impurity data.

2.1.1. Moisture Measurements. Except during startup, moisture was not detected in the Peach Bottom helium coolant by ordinary instrumentation. The moisture levels during operation of core 2 were inferred from measurements of gaseous tritium in the primary circuit. The tritium monitors distinguished the HT species from HTO, and by assuming that the HT/HTO and H_2/H_2O ratios were equal, the H_2O concentration could be calculated from measurements of HT, HTO, and H_2. Figure 1 plots HT/HTO versus P_{H_2} and shows that over a wide range of P_{H_2}, the HT/HTO ratio at steady state was 20. Therefore, at 10 ppm H_2, the moisture concentration was estimated to be 0.5 ppmv. During hydrogen injection (Section 4), the HT/HTO ratio increased. These data are in close agreement with those obtained at Dragon at steady state and during H_2 injection (Ref. 3).

2.1.2. Oil Ingress. The first suggestion of a possible oil leak into the primary circuit was the observation of persistent H_2 and CH_4 impurities. Toward the end of core 1 operation, there were occasional high hydrocarbon concentrations (consisting primarily of up to 100 ppmv of CH_4 in the helium coolant). This transient source of hydrocarbon proved to be oil ingress from an oil demister/filter which removed oil vapor and oil mist from the discharge of the helium compressor in the purification system. The filter was saturated with oil, and it was speculated that on occasion, liquid oil or mist was injected into the reactor. This source undoubtedly also contributed to steady oil vapor ingress, since the piping downstream of the filter/demister contained liquid oil with a finite vapor pressure. This steady source could have added 10 to 100 kg of oil vapor per year to the primary circuit.

Another source of oil ingress may have been the oil-lubricated main compressors. A small amount of back diffusion of oil vapor past the helium-buffered labyrinth seals could have contributed to continuous low-level oil ingress.

The final conclusive evidence for oil ingress was the carbon deposit (up to 0.2 mm thick) which coated virtually all the primary circuit metallic surfaces. The carbon scales were layered, indicating possible periodic ingress. The deposits had no discernible effect on the heat exchange properties of the steam generators nor on the metallurgy of the underlying structures. Chemical analysis of the deposits revealed that they contained carbon (80% to 100%), iron (2% to 3%), and traces of chromium and sulfur (Ref. 4). Approximately 80% of the cesium and strontium plateout activity on the steam generator tubes was associated with the carbon deposits (Ref. 5). The density of the carbon deposits was estimated to be 1.0 g/cm^3 and the average thickness 0.05 mm, making the total amount of carbon deposits about 100 kg, which was consistent with the estimated steady-state ingress rate.

Transient high levels of oil vapor or hydrocarbons in the helium coolant contributed to early failure of the moisture monitor cells. These cells were the P_2O_5-coated electrolytic type (similar to Goldsmith hygrometer cells). The hydrocarbons coated the cells with resinous deposits, which caused their response time to increase. Cells with excessive response times were replaced.

2.2. Fort St. Vrain

The coolant impurity mixture at Fort St. Vrain is dominated by H_2O and the graphite oxidation reaction products CO, CO_2, and H_2. The major source of the water is typically the water-lubricated bearings of the main circulators. Water is normally prevented from leaking up the shaft by labyrinth seals and a buffer helium system. During startup and shutdown, the pressure balance between the buffer helium and the primary circuit pressure is sometimes upset, allowing water to flow into the reactor.

Water ingress before and during initial nuclear startup has been frequent and sometimes large. When ingress was large, it was thought that water entered the fibrous ceramic insulation and condensed on the water-cooled PCRV liner. Dry-out prior to restart was often quite slow because of the slow diffusion of water out of the insulation materials. Once the reactor attained high steady power, dry-out of the system was rapid, and the purification system reduced the impurities to acceptable levels.

Table 2 (Refs. 6, 7) summarizes the coolant impurity data obtained to date. Gaseous impurities are given at each power level, since the reactor was brought to power in stages. The concentrations listed were obtained at the beginning and end of each time or power increment. In general, the concentrations were higher at the beginning of each power increment, because of increased outgassing at each temperature increase.

All impurities decreased (with the possible exception of CO) as the reactor was brought to higher powers and temperatures, indicating the combined effects of graphite outgassing and decreasing amounts of water vapor leaving the insulation materials. In general, whenever moisture was measurable (indicating ingress), the H_2/H_2O ratio was low, indicating low overall oxidation reactivity of the core. The persistent concentration of CO_2 indicates possible contributions from the radiolytic shift reaction $H_2O + CO = H_2 + CO_2$.

The detection limit of the dew point meters for H_2O is about 1 ppmv. A single measurement of moisture was made at 50% power using the HT/HTO method described above. The calculated P_{H_2O} was 0.2 ppmv, indicating that dry-out of the primary circuit was indeed possible.

The anticipated consequences of moisture ingress into the Fort St. Vrain HTGR are (1) oxidation of graphite structures, (2) hydrolysis of exposed carbide fuel particles, and (3) oxidation of metallic surfaces.

The degree of graphite oxidation to date has been minimal because the impurity concentrations have been reduced to low levels for reactor operation at high temperature. For example, whenever the core outlet temperature is $\geq$922 K, the maximum allowed impurity concentration is 10 ppm total oxidants, which includes the impurities $CO + CO_2 + H_2O$. For temperatures below 922 K, the limit is based on a moisture content which is allowed to increase with decreasing temperature. Thus, the reactor operator must bring the reactor to power slowly and in stages to ensure that the impurity limit is not exceeded. As a result of this limit, most of the moisture exposure has been at relatively low temperatures, where graphite oxidation is not a problem.

The total amount of oxidation to date may be inferred from the quantity of gaseous carbon species removed by the purification system (Table 3). An overall oxidation of 1.4×10^{-4} fraction after 174 effective full-power days (EFPD) can be calculated by dividing the number of moles of gasified carbon ($CO + CO_2$) by the number of moles of carbon in the core and lower reflector. This calculation is conservative because it assumes that all gaseous carbon is from oxidation rather than outgassing. Outgassing of the entire Fort St. Vrain graphite inventory, i.e., 5.7×10^5 kg, could account for a large part of the gaseous carbon observed to date.

Hydrolysis of exposed carbide fuel particles would cause a large increase in the rate of fission gas release (R/B) and could therefore be easily detected by routine monitoring of the circulating activity in the primary circuit. The overall core R/B has remained relatively constant and very low; hence, in-service fuel failure to date appears negligible.

The H_2/H_2O ratio in the primary circuit has remained quite low during almost all reactor operation. Thus, the metallic components in the primary circuit are expected to have oxide films. This is undoubtedly beneficial because it precludes corrosion processes such as carbon deposition and carburization and possible sulfidation reactions.

3. PURIFICATION SYSTEM PERFORMANCE

3.1. Peach Bottom

The Peach Bottom helium purification system operated efficiently throughout the life of the reactor. It maintained the circulating activity of xenon and krypton at less than 1 Ci and the chemical impurities at the levels in Table 1. Table 3 lists the total impurities removed by the system during core 2 operation. H_2 was the major species removed. The overall core oxidation was $\leq 3 \times 10^{-4}$, assuming that CO and CO_2 were generated by graphite oxidation. Near the end of core 1 life (452 EFPD), the CuO catalyst bed was no longer effective in oxidizing hydrogen, although it still oxidized CO. In situ regeneration of the catalyst was accomplished by adding oxygen to the bed inlet.

3.2. Fort St. Vrain

The Fort St. Vrain purification system has performed well to date, especially considering the large amounts of water removed by the dryer beds (Table 3). An exception to the excellent performance of this system is the titanium H_2 getter beds, which have been in service only sporadically. These beds are located downstream of the liquid-nitrogen-cooled carbon beds and are therefore in theory exposed to only pure dry helium and H_2. In practice, however, the beds have occasionally become contaminated with nitrogen, which reduces the H_2 removal efficiency. This has not caused a large increase in H_2 in the primary circuit, and it appears that the excess hydrogen may be absorbed by the graphite components.

4. HYDROGEN INJECTION EXPERIMENT

There was concern that in future HTGRs used for process heat, hydrogen diffusion from the process side to the helium side could cause high levels of hydrogen in the primary coolant. It was conjectured that the hydrogen would react with graphite to form high concentrations of methane, which is an undesirable carburizing agent. Hence, a hydrogen injection test at Peach

Bottom was performed while the reactor was at 55% power. Hydrogen was injected at 3.35 liters/min in two pulse tests of 3.5 and 2.5 h. A steady-state test at 1.4 liters/min which lasted for 72 h was also accomplished. At the end of the steady run, the reactor was brought to 80% power. Figure 2 presents data from these tests. The data indicate that the concentration of methane in Peach Bottom was proportional to $(PH_2)^{1/3}$, suggesting that high concentrations of hydrogen can be tolerated without concern about high methane concentrations. These results are in general agreement with those of the Dragon injection tests (Ref. 3).

5. TRITIUM BEHAVIOR

The tritium concentrations in the primary coolant at Peach Bottom and Fort St. Vrain have been measured by grab sample and continuous monitor devices. Table 4 gives the results of the tritium measurements. The tritium concentration in the Peach Bottom primary circuit increased by a factor of 10 during core 2 operation. The initial concentration was roughly equivalent to that expected from He-3 activation (using He-3/He-4 = 2×10^{-7}). The increase in the tritium released to the primary coolant reflects the release from (1) fuel (ternary fission), which is influenced by increased fuel temperatures toward end of life; (2) control materials (B-10 activation); and (3) graphite (Li-6 activation). The total amount of tritium produced in core 2 during 897 EFPD was about 1900 Ci. The total amount released to the primary coolant during 3 yr of operation was about 600 Ci, for an overall release fraction of 0.32.

A total of 307 Ci of tritium as HTO was removed from Fort St. Vrain by the purification system after 101 EFPD. Another unknown amount was removed by the titanium getters, which operated sporadically. During this iniital period, most of the tritium was in the form of HTO because of the low H_2/H_2O ratio. The 307 Ci of HTO is roughly equal to the amount produced by He-3 activation.

6. CONCLUSIONS

The following conclusions can be drawn from the Peach Bottom and Fort St. Vrain coolant chemistry data:

1. HTGR systems can be designed and operated with low concentrations of chemical impurities in the primary circuit.
2. The concept of bypass purification has been proven.
3. High methane concentration as a consequence of high hydrogen concentration is not expected.
4. Using currently available grades of nuclear graphite, outgassing of graphite components is a transient source of impurities during startup. Long-term graphite outgassing is an insignificant source of gaseous impurities at steady state.

5. With the exception of contamination of the moisture monitor cells, small amounts of oil ingress have little effect on reactor operation.

6. The Fort St. Vrain coolant impurities have had no measurable effect on fuel, graphite or metal component performance to date.

7. Frequent moisture ingress can cause expensive delays in plant startup and should be minimized.

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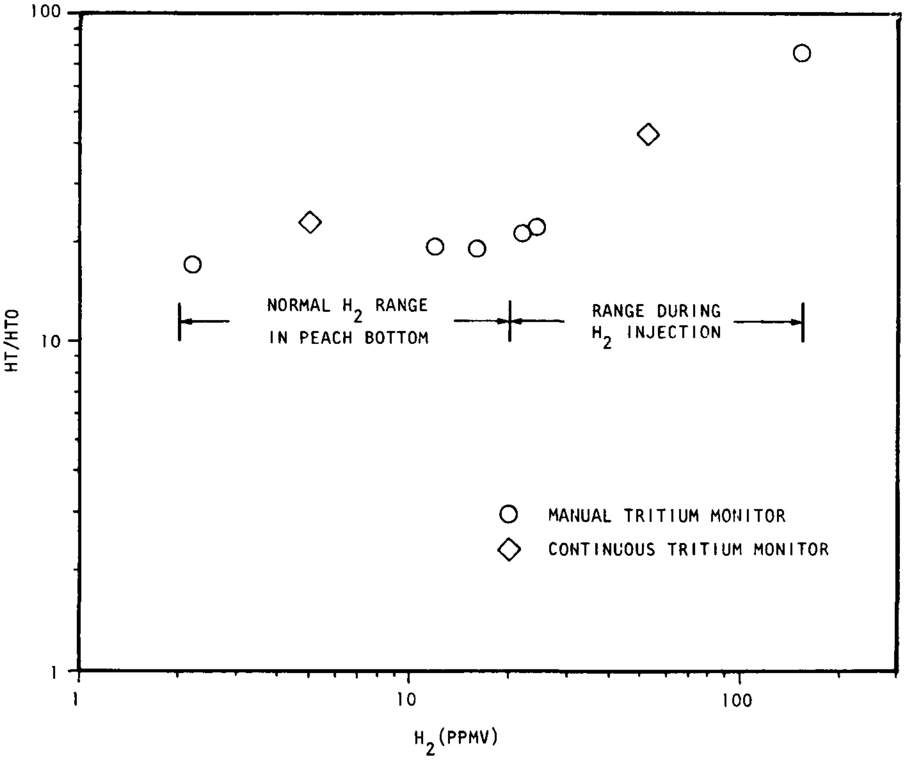

Figure 1. HT/HTO vs P_{H_2} in Peach Bottom

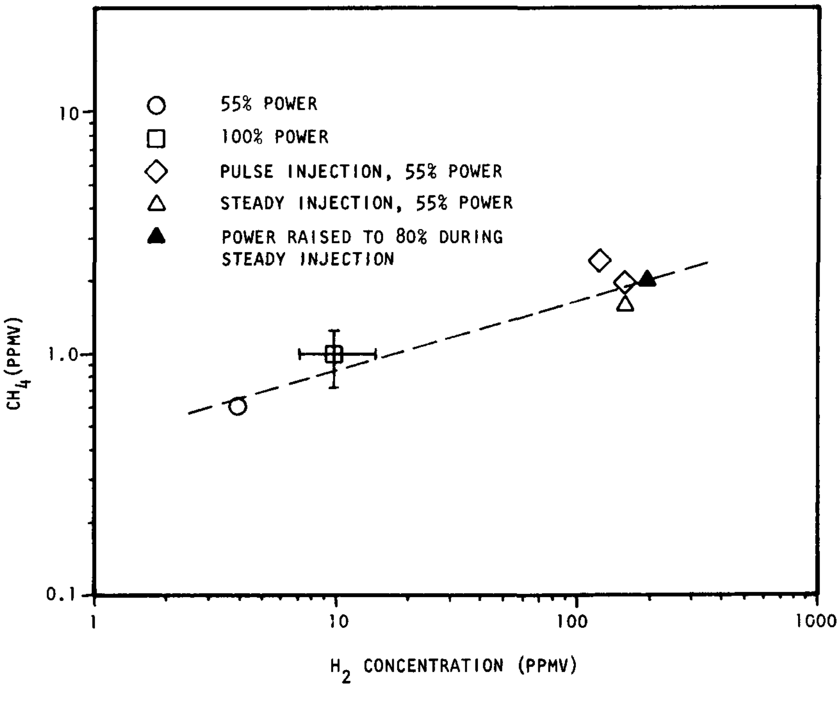

Figure 2. Results of hydrogen injection experiments at Peach Bottom

TABLE 1
GASEOUS IMPURITY CONCENTRATIONS IN PEACH BOTTOM DURING INITIAL APPROACH TO POWER AND AFTER 4600 HOURS AT FULL POWER

Date	Reactor Power (%)	Gaseous Contaminant(ppmv)					
		H_2	N_2	CH_4	CO	CO_2	H_2O
				Core 1			
1- 1-67	0	--	--	--	--	--	55
1-22-67	0	--	7.0	0	0	0.3	5
1-24-67	2	--	15	0.05	0.05	0.5	--
1-25-67	5	--	--	0.08	0.05	0.4	5
1-26-67	3	--	15	0.05	0.6	0.3	--
1-27-67	1	--	16	0.09	0.5	0.3	7
1-28-67	5	--	27	0.4	0.4	0.5	3
1-29-67	20	--	50	1.8	1.8	1.7	5
1-30-67	30	--	40	1.0	4.1	1.8	2
12- 9-67	30	3	0.8	0.7	0.5	<0.05	<1
12-12-67	100	9	0.5	0.6	0.5	<0.05	<1
				Core 2[a]			
1971-1974	100	10	0.5	1.0	0.5	<0.05	~0.5[b]

[a] Average steady-state values.

[b] H_2O calculated from (HTO/HT) x H_2.

TABLE 2
PRIMARY COOLANT IMPURITIES DURING RISE TO POWER AT FORT ST. VRAIN

Date	Power (%)	Outlet Temperature (K)	Concentration (ppmv)					
			H_2	H_2O	CO	CO_2	CH_4	H_2/H_2O
July 3-6, 1976	2	490	2-15	240-70	0.2	2-1.8	0.6	0.01-0.2
July 24-28, 1976	11	590	45-35	50-25	4-2	6-1	5-3	0.9-1.4
July 28-30, 1976	21	700	40-90	180-80	2-4	4-10	3-6	0.2-1
July 30 - Aug 2, 1976	26	785	85-30	140-76	4-3	6-10	6-2	0.6-0.4
Dec 10 - Jan 9, 1977	28	895	10	40-4	1.5-3	3.5-1	0.5-0.6	0.25-0.25
Sept 16 - Oct 24, 1977	38	895	3-2	<1(a)	4-2	3-2	0.2	>3
Oct 29-31, 1977	50	945	3	0.2(b)	6-5	1-1.5	0.4-0.2	15
Apr 28 - May 4, 1978	65	980	5-4	<1	10-7	3-2	0.8-0.4	>5
Dec 10 - Jan 27, 1979	63	945	2-7	<1	1-3	0.5-1	0.2-0.1	>3

(a) Limit of detection of dew point moisture monitors ~ 1 ppmv.

(b) H_2O calculated from HTO, HT, and H_2 measurements: $H_2O = \frac{(HTO)(H_2)}{(HT)}$.

TABLE 3
IMPURITIES REMOVED BY THE FORT ST. VRAIN AND
PEACH BOTTOM PURIFICATION SYSTEMS

	Total Concentration (g-mole)	
	Fort St. Vrain(a)	Peach Bottom(b)
H_2O	12,260(c)	1,260(d)
H_2	2,475	6,900
CO	1,310(e)	340(f)
CO_2	1,040(e)	$\leq$120(f)
CH_4	240	250
Total C (CO + CO_2 + CH_4)	2,590	590-710
Total O (CO + $2CO_2$)	3,390	340-580
Total H_2 (H_2 + $2CH_4$)	2,955	7,400

(a) 0%-65% power through May 1978 (174 EFPD).

(b) Based on average impurity data, core 2 operation, 897 EFPD.

(c) Includes moisture removed during power operation.

(d) Estimated from HT/HTO measurements.

(e) Fraction of Fort St. Vrain core graphite oxidized (~1 yr) = 2350 ÷ $1.7 \times 10^7 = 1.4 \times 10^{-4}$. Includes fuel element and lower reflector graphite, but neglects contribution of outgassing.

(f) Fraction of Peach Bottom core 2 graphite oxidized (~3 yr) = 460 ÷ $1.6 \times 10^6 \leq 3 \times 10^{-4}$. Includes fuel element and lower reflector graphite, but neglects contribution of outgassing.

TABLE 4
TRITIUM DATA FROM FORT ST. VRAIN AND PEACH BOTTOM

Year	Peach Bottom		Fort St. Vrain	
	Primary Circuit (μCi/cm^3 He)	Secondary Circuit (μCi/cm^3 H_2O)	Primary Circuit (μCi/cm^3 He)	Secondary Circuit (μCi/cm^3 H_2O)
1	1×10^{-5}	10^{-4}	5×10^{-5}	2×10^{-4}
2	5×10^{-5}	3×10^{-4}	--	--
3	1×10^{-4}	3×10^{-4}	--	--