

Generation of Hydrogen Gas as a Result of Drilling Within the Saturated Zone

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Abstract

Hydrogen gas was discovered within the steel casing above standing water in a percussion-drilled borehole on the Hanford Site in south-central Washington state. In situ measurements of the borehole fluids indicated anoxic, low-Eh (< -400 mV) conditions. Ground water sampled from adjacent wells in the same formation indicated that the ground water was oxygenated. H_2 was generated during percussion drilling, due to the decomposition of borehole waters as a result of aqueous reactions with drilled sediment and steel from the drilling tools or casing. The generation of H_2 within percussion-drilled boreholes that extend below the water table may be more common than previously realized. The ambient concentration of H_2 produced during drilling was limited by microbial activity within the casing-resident fluids. H_2 was generated abiotically in the laboratory, whereby sterilized borehole slurry samples produced 100 times more H_2 than unsterilized samples. It appears that H_2 is metabolized by microorganisms and concentrations might be significantly greater if not for microbial metabolism.

Introduction

The Yakima Barricade Borehole (YBB), located on the U.S. Department of Energy's (DOE) Hanford Site (Figure 1), was drilled as part of a DOE research program to investigate microbial processes in deep subsurface environments and to evaluate geochemical and geohydrological controls on subsurface microorganisms. The borehole was sited free of nearby surface or ground water contamination, and penetrated a relatively thick (740 feet [225 m]), heterogeneous sedimentary sequence that overlies Columbia River basalt (CRB) (Figure 2) and in which hypotheses relative to the controls of microbial activity could be tested.

A combustible gas, determined to be H_2 , was detected during drilling of the YBB. Tests were performed to evaluate the mechanism by which H_2 was concentrated within the borehole. This paper will present evidence for the generation of H_2 in boreholes during percussion drilling below the water table and propose mechanisms of H_2 generation and their implications for safety during drilling.

Combustible gas was detected in the borehole while drilling within a fluvial, sedimentary sequence of the Neogene-age Ringold Formation. These sediments consisted predominantly of well-rounded, clast-supported gravels in a moderately to well-sorted arkosic, sandy matrix. Gravel-size clasts included detrital basalt of local origin, along with granitic, quartzitic, and volcanic-porphry clasts derived from distant

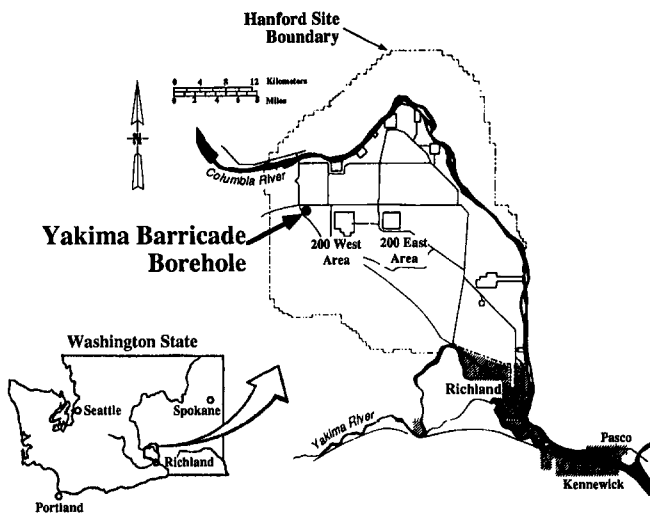


Figure 1. Location map of the Hanford Site and the Yakima Barricade Borehole (YBB).

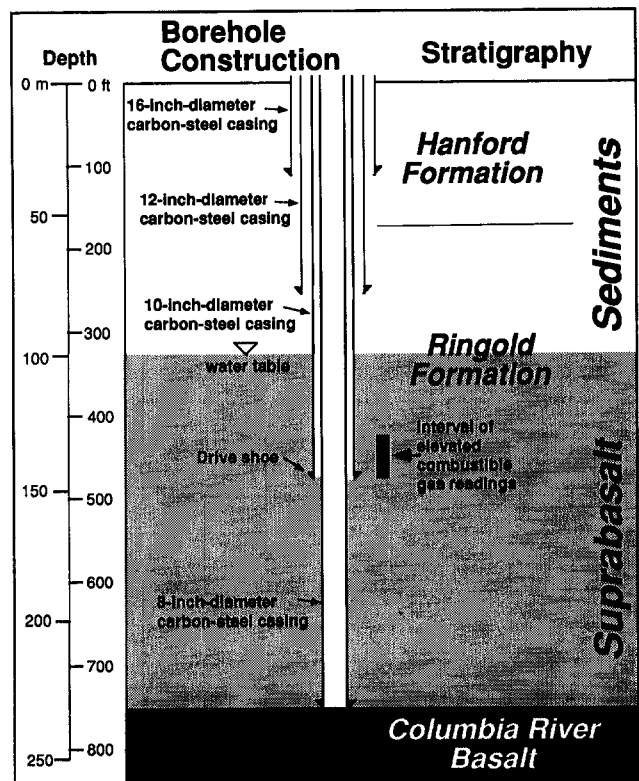


Figure 2. Borehole construction and stratigraphy at the YBB. A total of four strings of telescoping carbon-steel casing was used to advance the borehole to a total depth of 748 feet (227 m). Combustible gas was first detected at the 425-foot (130-m) depth (100 feet [30 m] below the water table) while drilling in saturated Ringold Formation sediments. The levels of combustible gas remained relatively low <20 percent of the LEL after the ~475-foot [144 m] depth.

source areas surrounding the Columbia Plateau (Goodwin 1993). Petrographic analysis of fluvial Ringold gravels from comparable strata in nearby boreholes indicated quartz was the predominant constituent (about 50 percent), with subordinate, subequally abundant feldspar and lithic rock fragments. About half (13 percent) of the lithic clasts were mafic volcanics (i.e., indigenous CRB) followed in abundance by intermediate-to-silicic volcanics, quartzite, and granitic clasts.

The hole was drilled using the percussion cable-tool method. With this method, continuous, telescoping carbon-steel casing was driven downward to maintain the borehole opening within the unconsolidated to semiconsolidated suprabasalt sediments of the Hanford and Ringold formations (Figure 2). The casing was advanced as material from the bottom of the hole was removed with a core barrel. New sections of casing were welded on about every 10 feet as the borehole deepened. Below the water table, fluid within the borehole directly contacted subsurface strata only at the bottom of the casing. Broken small fragments of larger clasts were retrieved from the core barrel after drilling advanced the borehole. During drilling a dark, sediment-laden slurry developed within the cased portion of the borehole below the water table, which lay at a depth of 327 feet (100 m). When the bottom of the borehole was 420 feet (128 m) below the surface and ~100 feet (30 m) below the water table, a small explosion lifted a 1-cm-thick solid steel plate several centimeters off the top of the casing during routine welding operations. After the explosion, a combustible gas analyzer (CGA) used near the top of the casing indicated the presence of a combustible gas. Drilling operations were suspended until the identity and source of the gas(es) could be determined.

Methods

The origin and nature of the combustible gas in the wellbore was investigated with a series of analyses of the borehole gas, borehole fluids, formation ground water, and formation sediments. The borehole gas was

analyzed in the field with Sensodyne™ sampling tubes and in the laboratory using gas chromatography (GC). Headspace samples for GC analysis were collected periodically using a sterile hypodermic needle and a gas-tight syringe. After the explosive gas was first detected, the lower explosive limit (LEL) of the atmosphere within the borehole relative to pentane was measured with the CGA at least twice daily. Subaqueous temperature, dissolved oxygen (D.O.), electrical conductivity, pH, and Eh were measured in situ with the Hydrolab Datasonde-3™ at depths within several feet of the bottom of the borehole. This instrument was calibrated in the laboratory prior to deployment. The platinum oxidation-reduction electrode was calibrated using quinhydrone buffer solutions, and the D.O. cell was calibrated against sparged and atmosphere-saturated tap water; pH and conductivity electrodes were calibrated against purchased standards. The geochemistry of formation water was evaluated by monitoring these hydrochemical parameters near the bottom of the borehole while pumping water from the top of the water column within the casing. The ground water introduced into the casing after pumping was sampled using the downhole AMS Sampler™, which allowed sampling at specific, predetermined depths within the borehole fluid column. Geologic samples from the bottom of the borehole were logged and described at least every 5 feet (1.5 m) or more frequently at changes in lithology.

Selected bulk samples retrieved from the core barrel were analyzed for particle-size distribution by dry-sieving (≥ 62 -micron fraction) and hydrometer analysis (< 62 -micron fraction).

Several experiments were conducted with the borehole slurries to determine their role in H_2 production. The borehole slurry was characterized by analysis of its density, particle-size distribution, and clay mineralogy. Density was determined as the mass per unit volume of borehole fluid. Particle-size distribution for suspended slurries was measured using the hydrometer technique (Gee and Bauder 1986). Clay mineralogies were determined by x-ray diffraction. Borehole fluids were also analyzed for H_2 and CH_4 by transferring 125-mL subsamples of water from the downhole sampler into glass gas-sampling tubes immediately upon recovery. A 5-mL bubble of pure nitrogen gas was introduced by syringe, displacing 5 mL of slurry. Gases were extracted after vigorous shaking for 120 seconds by transferring the gas bubble to a tube containing N_2 -saturated water; 1 atm pressure was maintained by displacing equivalent volumes during the transfer. The extracted samples were transported to the laboratory (approximately 30 minutes travel time) and analyzed by GC with thermal conductivity detection on a Hewlett-Packard 5890 Series II chromatograph with a Supelco 100/120 mesh Carbosieve S II molecular sieve 10-inch \times 0.125-inch stainless steel column. The carrier gas was N_2 , at a flow rate of 30 mL/min. The injector temperature was 120 C, the detector temperature was 250 C, and the oven temperature was incrementally increased from 50 C to 250 C at 20 degrees per minute. The detector polarity was negative.

Borehole slurry samples were either used as received or autoclaved (i.e., sterilized) before use so that the role of microorganisms in the generation or consumption of H_2 could be assessed. The most probable number (MPN) of aerobic bacteria was determined in these samples. Samples were degassed initially and then incubated in closed vials in the laboratory at room temperature in both air and N_2 atmospheres over a two-week period.

Results and Discussion

A number of tests confirmed the presence of H_2 . A sampling tube specific to H_2 was lowered into the borehole headspace and indicated ≥ 2 percent H_2 . Additional confirmation came from two samples, collected from 6 m below the top of the casing on consecutive days, which indicated concentrations of 1.2 and 1.5 percent H_2 (Table 1). During the collection of these gas samples, CGA readings taken at the sample depth registered 40 percent of the LEL (equivalent to 1.6 percent H_2), in agreement with the laboratory results (Table 1). Monitoring with the CGA indicated combustible gas at levels ranging from 0 to 100 percent of the LEL from depths of 3 to 25 feet (1 to 8 m) below the top of the casing (Figure 3). Because the atmosphere near the top of the casing may not represent borehole headspace with depth, only those LEL measurements taken > 12 feet (4 m) from the top of the casing are shown in Figure 3.

	Sample #1	Sample #2
Collection Date:	6/8/92	6/9/92
Analytical Method:	Mass spectrometry (%)	Thermal conductivity detector (TCD) (%)
N_2	80.5	82.5
O_2	18.3	15.9
CO_2	0.03	0.03
CH_4	< 0.01	0.03
H_2	1.2	1.5

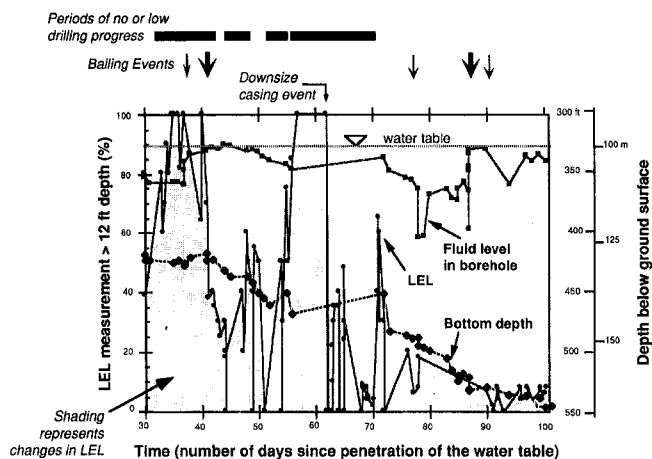


Figure 3. Plot of the LEL, fluid level, and bottom depth vs. time.

Hydrogen gas is combustible over a greater range in concentration (4.0 percent to 74.2 percent) than pentane gas (1.4 percent to 7.8 percent), which was used to calibrate the CGA (CRC 1965). Therefore the LEL readings measured with the CGA are 35 percent greater than the actual LEL for hydrogen gas in the borehole, but still provide a relative measure of H_2 concentration in the borehole headspace. The results of CGA measurements with and without a carbon filter were the same, indicating that the combustible gas was of low molecular weight (i.e., complex hydrocarbons were not present).

Depth to water and depth to the bottom of the borehole are also plotted in Figure 3 to show the relationship between drilling activities and the LEL. Fluid levels within the borehole fluctuated dramatically depending on the density of the slurry; densities increased with time since bailing. The variation of LEL with time clearly shows that LEL was highest when little or no progress was made in deepening the borehole. During such times the slurry stagnated within the borehole casing. In most cases sharp declines in the LEL correlate with borehole bailing, which allowed fresh formation water to enter through the bottom of the casing; the introduction of oxygenated water reduced or arrested H_2 generation. For example, the first LEL peak occurred during a period (beginning after ~ 35 days)

Table 2
In Situ Borehole Fluid Measurements Performed Before and After Bailing/Pumping

Date	State of Borehole Fluid	D.O. (mg/L)	Eh (mV)	pH	Temp. (C)	H ₂ (ppm)	CH ₄ (ppm)
Before Bailing/Pumping (stagnant)							
8/14/92	Dense slurry after drilling	0	-456	8.0	22.5	43,000	103
8/17/92	Dense slurry after drilling	0	-409	8.0	21.1	37,000	76
After Bailing/Pumping (introduction of formation waters)							
8/4/92	Bailed and pumped overnight	4.9	184	7.5	20.8	88	0
8/18/92	Bailed and pumped	3.1	250	7.6	21.1	390	0

when little drilling progress was made because of extensive sampling and difficult drilling conditions. Elevated LEL levels ended after a bailing event (40 to 45 days) that was followed immediately by a more normal rate of drilling advance. Another example of the correspondence between bailing and LEL occurred at approximately 77 days. Some short reductions in drilling progress corresponded with spikes in LEL (e.g., the spike occurring at 47 days). An abrupt decrease in LEL that occurred at 62 days coincided with placement of the 8-inch-diameter casing inside the 10-inch-diameter casing. Such a dramatic decrease in LEL suggests that combustible gas was being generated by reactions between the borehole fluids and the casing lining the inside of the borehole. The LEL remained relatively low except for a few short peaks that followed within 10 days of downsizing the casing. The new casing was apparently responsible for decreasing the LEL, since the condition of the slurry did not change and no bailing took place during or soon after downsizing the casing.

In situ measurements of casing-resident borehole fluids indicated that the fluids were anoxic and highly reducing. In contrast, samples of ground water, derived from the formation after bailing and pumping, contained significant concentrations of D.O. and displayed positive Eh values (Table 2). In situ measurements were performed several times with a Hydrolab Datasonde-3™ lowered to within several feet of the bottom of the borehole. Introduction of fresh water at the bottom of the casing caused a rapid response in the datasonde (Figures 4A and 4B), with D.O. and Eh quickly rising from 0.2 to 4.9 mg/L and 90 to 184 mV, respectively, and then stabilizing over a short period of pumping (less than 30 minutes). To reduce the quantity of fine-grained particles suspended in the aqueous samples, the borehole was bailed prior to pumping. The slightly oxidative conditions within the casing at the start of pumping may have been established by the introduction of oxygenated formation water into the borehole during bailing. In a subsequent test, pumping was stopped, and D.O. and Eh of the borehole fluid dropped dramatically and stabilized at an anoxic, reducing state after 400 minutes (6.6 hours) (Figures 4C and 4D). The pH also increased slightly with time, as ground water reacted with suspended solids within the casing.

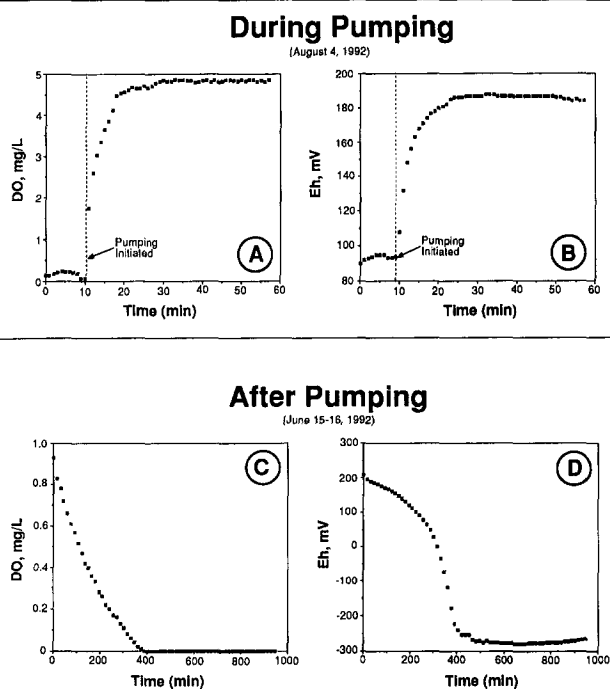


Figure 4. Changes in oxidation-reduction potential and dissolved oxygen within borehole fluids before (A and B) and after (C and D) pumping of fluids from the borehole. A and B show an abrupt change in borehole conditions induced by introduction of formation water by pumping and discharging at the surface. C and D demonstrate a slow return to anoxic, reducing conditions within the borehole after the pump was shut off.

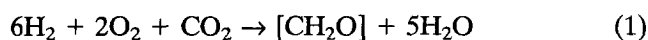
During drilling, fine particles from the formation and drilling process were mixed into the standing column of borehole fluid, creating a dense slurry. Thus, with drilling time and with no substantial influx of formation water, the density of the borehole fluid increased. Variations in the density of the slurry caused fluid levels within the casing to vary by as much as 80 feet (25 m) (Figure 3). Both smectitic and illitic clays and quartz were identified in the slurry. Density measurements of the borehole slurry ranged from 1.20 to 1.35 g/cm³. Assuming an average particle density of 2.65 g/mL, the suspension was calculated to consist of approximately 12 volume percent sediment. The larger clasts retrieved from the core barrel were compared with Ringold Formation gravels collected from outcrop, which were generally well rounded and unbroken. Drilled gravels showed smaller average clast size and

increased angularity. Particle-size distributions also showed a decrease in particle size (i.e., an increase in sand fraction and decrease in gravel fraction) as a result of pulverization during drilling (Figure 5). The suspension thus contained some drilling fragmented gravels along with sediment fines.

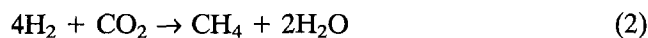
Hydrogen and methane detected in borehole slurry samples did not originate from the formation ground water. This is demonstrated in Table 2, which shows that formation water obtained after bailing is low in H₂ and devoid of CH₄. Historical data indicated that wells developed in the unconfined aquifer elsewhere on the Hanford Site were also low in H₂ (Early et al. 1986). Borehole slurry samples, on the other hand, contained up to 4.3 percent H₂ and small amounts of CH₄ (Table 2). Methane was probably produced in the borehole slurry by anaerobic bacterial consumption of H₂ and, possibly, by oxidation of the carbon-steel casing (Daniels et al. 1987).

Laboratory Generation of Hydrogen Gas

To confirm that H₂ could be produced at low temperatures by the interaction of crushed detrital material and steel shavings with ground water, H₂ was produced in the laboratory from borehole slurry samples (Figure 6). In unsterilized slurry samples, H₂ concentrations were ≤1 percent of the headspace, regardless of whether the headspace was air or N₂. In the autoclaved (i.e., sterilized) slurry, H₂ concentrations approached 10 percent of headspace volume (N₂ headspace) within two weeks. These results suggested that H₂ was generated via reactions in the slurry and not by the microbial fermentation of organic matter. It is common for microorganisms to utilize H₂ as an energy source (Atlas and Bartha 1993). Analysis of the unsterilized borehole slurry indicated microbial populations of >10⁶ MPN of aerobic H₂-utilizing bacteria/cm³. These results suggest that hydrogenotrophic bacteria present in the borehole slurry are capable of growing on H₂ via such reactions as:



where [CH₂O] is taken to represent biomass, or



under anoxic conditions where anaerobes convert H₂ to CH₄. Reaction 2 may lead to accelerated corrosion of the steel casing (Daniels et al. 1987).

Hydrogen Gas Generation in the Subsurface

Previously Reported Sources of Hydrogen Gas

The origin of H₂ at numerous locations worldwide is uncertain; possible causes of H₂ generation range from mantle degassing to chemical interaction between clastic sediments and ground water following deposition (Molchanov 1968). An extensive survey of deep (>3300 feet [1000 m]) subsurface fluids in the former Soviet Union indicated that normal background concentrations for

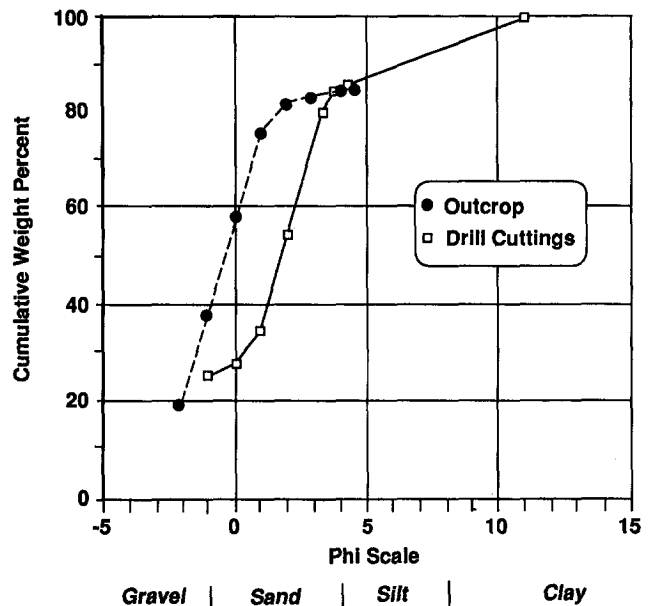


Figure 5. Comparison of particle-size distributions between disturbed (drill cuttings) and undisturbed (outcrop) Ringold Formation coarse-grained sediments.

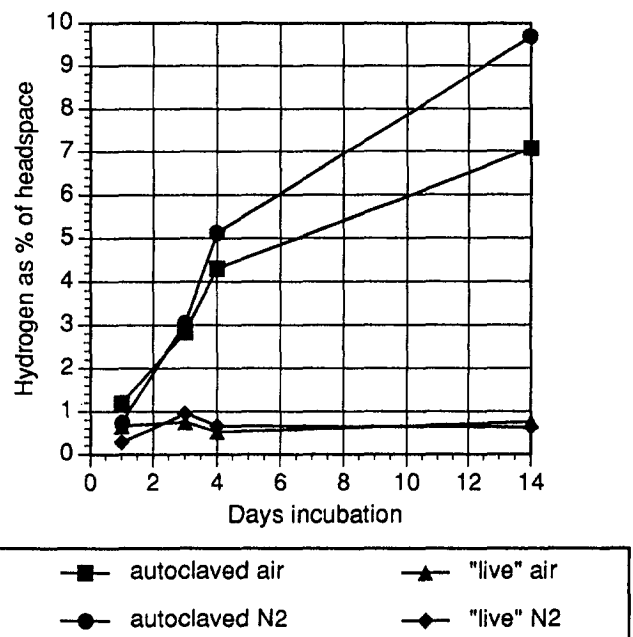


Figure 6. Laboratory production of H₂ gas in slurry samples from the YBB. Unsterilized ("live") samples yielded smaller quantities of H₂ than sterilized (autoclaved) samples, suggesting H₂ generation is abiotic. Headspace gas (N₂ or air) did not significantly affect the results.

dissolved H₂ were on the order of a few mL/L, but there were wide regions where concentrations of hundreds of mL/L or more were detected (Shcherbakov and Kozlova 1986). These regions of very high H₂ concentration coincided with major fault zones that might act as conduits for gas migration from depth. Anomalously high concentrations of H₂ (up to 99 percent) have been observed bubbling out of springs in areas of serpentinization in Oman (Neal and Stanger 1983) and California (Barnes et al. 1972). Up to 3 percent H₂ concentrations have been measured along faults following tectonic activity in Japan (Wakita et al. 1980).

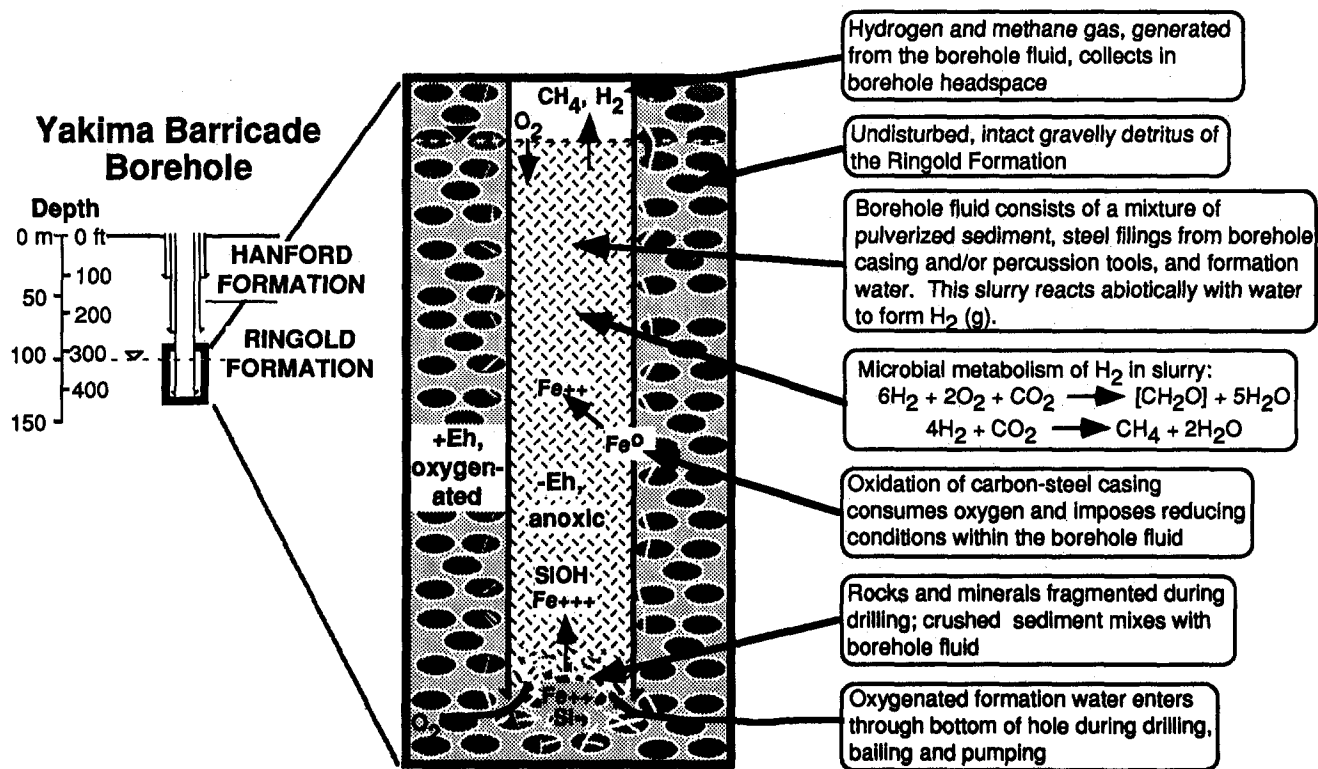


Figure 7. Model of H₂ generation during percussion drilling.

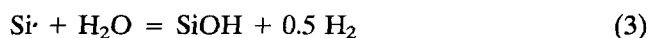
Chemical reactions that might yield H₂ include (1) oxidation of transition metal oxides or hydroxides either in the presence of heated water (Arnorsson 1986; Freund 1984) or in lower-temperature serpentinization reactions (Barnes et al. 1972; Neal and Stanger 1983; Goebel et al. 1984; Angino et al. 1984); (2) reaction of ground water with broken-bond oxygen radicals at mineral faces following mechanical deformation (e.g., faulting) (Kita et al. 1982); (3) release of molecular hydrogen from its point of formation at oxide mineral crystal-lattice defects (Freund et al. 1981; Freund 1984); and (4) dissolution from within mantle minerals (Bai and Kohlstedt 1992).

Although the formation of H₂ at near-surface temperatures is generally considered to be unlikely, field evidence suggests that low-temperature hydrogen gas generation can occur (Molchanov 1968). Goebel et al. (1984) considered several H₂-generating sources and processes in Kansas and concluded that low-temperature serpentinization reactions were the most likely cause. On the basis of isotopic analyses, Neal and Stanger (1983) concluded that low-temperature formation of H₂ during weathering of ultramafic rocks was the source of elevated H₂ in ground water in Oman. Their calculations also ruled out the possibility that significant concentrations of H₂ might come from a high-temperature source.

In general, few mechanisms have been identified whereby H₂ could be generated via rock-water interactions. A hypothesis advanced by Neal and Stanger (1983) and others suggests that the reduction of oxygen and the abiotic generation of H₂ via chemical interactions between rock and water depend on the availability of reduced (ferrous) iron. Assuming an appropriate

redox status, a hydrogen-producing reaction can take place at ambient temperatures and pressures (Shcherbakov and Kozlova 1986) when ferrous iron oxide reacts with water.

The crushing of silicate minerals, themselves, may also lead to H₂ generation. The breaking of silicate bonds during crushing of the sediment, and the associated production of Si[·] and Si-O[·] radicals, has been suggested as a hydrogen-producing reaction by Wakita et al. (1980) and Kita et al. (1982). The chemical reaction between H₂O and fresh rock and mineral surfaces exposed during crushing generates H₂ at room temperature and pressure by the following reaction:



where Si[·] represents an ephemerally charged species at the silicate mineral surface. As these free radical sites are neutralized, H₂ generation will cease. This reaction mechanism has produced small quantities of H₂ gas in the laboratory (Kita et al. 1982) and may be significant in tectonically active areas with regional fault zones capable of transmitting and concentrating H₂ in the subsurface.

Source(s) of Hydrogen Gas at the Yakima Barricade Borehole

Hydrogen at the YBB was assumed to have originated by either (1) low-temperature interactions between ground water and the crushed detritus in the borehole slurry (rock fragments and steel shavings from the casing and percussion tools, suspended in formation water); or (2) concentration of dissolved H₂ from degassing of the surrounding strata. The origin of the H₂ at the YBB was thus considered to result from drilling activities or

undetermined geochemical processes peculiar to the strata being penetrated.

The results of this study demonstrated that H₂ could indeed have been generated abiotically by mechanical and physicochemical processes within the cased portion of the borehole, as suggested by Angino et al. (1984). Our conceptual model of H₂ generation in the YBB is shown in Figure 7. H₂ is generated by percussion drilling below the water table as a result of chemical interactions between formation water and steel casing, steel shavings, and lithic fragments. Dissolved oxygen originates with oxygenated ground water entering the borehole at the base of the casing and dissolving where the water table interfaced with the overlying air column; reactions occurring within the slurry and between the ground water and casing consume oxygen and lower the Eh. Water is disassociated by reaction with ferrous and metallic iron after consumption of available O₂. Dissolved H₂ could not have originated from formation water at the YBB, since H₂ decreased dramatically and CH₄ was undetectable after bailing and pumping (Table 2). Bailing and pumping forced fresh water from the formation into the bottom of the borehole to replace stagnant fluids.

Other potential sources for H₂ in the subsurface environment near the YBB are similarly not plausible. Migration of organic and inorganic contaminants and their degradation products is unlikely because the YBB is located hydraulically upgradient of known contaminant sources or plumes, and analysis of the fluids within the borehole did not indicate the presence of any contaminants. Tectonic activity near the YBB, venting of H₂ from deeper sources, and microbial fermentation can be eliminated as mechanisms of H₂ generation because ground water in the aquifer does not contain significant amounts of H₂. The ground water sampled from developed wells within the unconfined aquifer elsewhere at Hanford also had a much higher redox potential (-175 to +225 mV) (Early et al. 1986) than the stagnant borehole fluids (Table 2), which has inhibited H₂ generation. Furthermore, microbial fermentation of organic matter at the YBB is an unlikely mechanism for H₂ generation because the experimental evidence indicated that microbial activity consumed H₂ in the borehole slurry. Broken-bond oxygen radicals at the surfaces of crushed sediments as a controlling process in H₂ generation was unlikely because free radicals are probably short-lived within the YBB; elevated LEL (i.e., elevated H₂ concentrations) coincided with periods of poor drilling progress when little freshly crushed suspended material was generated (Figure 3).

The reaction of steel casing and/or steel shavings generated during percussion drilling with formation waters is a possible source of H₂ at the YBB. Steel shavings may be produced by the percussion tools during repeated movement of the tools during drilling. This is corroborated by Pearson et al. (1989), who concluded that excess hydrogen is generated from the corrosion of metallic iron in the borehole, based on the oxidation potential of the hydrogen couple (H⁺/H₂).

The freshly exposed rock and mineral surfaces, derived from the pulverization of suprabasalt sediments and mixed with the water from the formation during drilling, may accelerate the reduction of both oxygen and water within the borehole fluids. Neal and Stanger (1983) reached a similar conclusion with regard to a dissimilatory stage of ground water evolution: "Whilst this second stage mechanism (i.e., decomposition of water) might at first seem implausible at low temperatures, there is convincing laboratory and theoretical evidence to show that it can take place, albeit erratically, in the presence of a catalyst such as some transition metal hydroxides." Neal and Stanger (1983) suggest that the presence of nickel-iron alloys, natural in the ultramafic source rocks within their study area, could also act as catalysts for H₂ generation. It is possible that the carbon-steel alloy composition of the casing plays a similar role in generating H₂ at the YBB.

Summary and Conclusions

Field analyses and laboratory experiments indicate that H₂ is generated at ambient temperatures and pressures via mechanical and physicochemical processes occurring during percussion drilling below the water table. In view of the common use of carbon-steel casing and the pulverization associated with percussion drilling, the phenomenon of H₂ generation during drilling may be more common than had previously been realized (Angino et al. 1984). At the Hanford Site, dozens of boreholes have been drilled via percussion methods to significant depths below the water table with no documented reports of hydrogen gas. However, H₂ is not routinely monitored and the presence of explosive gases would likely have been erroneously attributed to the buildup of other compounds (e.g., methane). Combustible gases may also have been undetected because they were in concentrations below the explosive limit, perhaps due to microorganisms metabolizing the H₂ as an energy source.

At sufficient concentrations, H₂ generated during drilling could be a safety concern, especially in percussion-drilling operations. Hydrogen may not be a significant concern with other types of drilling, or where significant numbers of H₂-utilizing bacteria are present. If microorganisms are inhibited within the borehole by environmental conditions (e.g., low temperatures, toxic substances, abrupt shift to anoxic conditions), H₂ concentrations may rise. During percussion-drilling operations in saturated systems, precautions should be taken to monitor borehole headspace for hydrogen gas. Frequent bailing or pumping during drilling may help to avoid elevated H₂ concentrations. Specific mechanisms of H₂ generation via sediment-water interactions within the borehole have not been identified but will be the subject of further study.

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