Radiolytic Hydrogen Generation and Methanogenesis in WIPP: An Empirical Point of View – 11040

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ABSTRACT

Geologic disposal of radioactive waste is internationally recognized as the most prudent management approach to the back end of the nuclear fuel cycle. Alpha-emitting isotopes in waste matrices containing hydrogenous materials generate radiolytic hydrogen, which must be managed to ensure concentrations never exceed flammability limits. In addition, past concerns have been raised that methanogenesis could also present explosion hazards during a geologic repository's operational lifetime.

Early (pre-operational) planning for the Waste Isolation Pilot Plant (WIPP) lead its original design to include explosion walls as part of the closure design in the event of a build-up of hydrogen or methane. This conservative approach simply assumed explosive gases could be present without detailed prediction of their concentration and extent. As the Department of Energy (DOE) emplaced waste after opening, the first two disposal panels were isolated from the ventilation circuit with the previously planned 4-meter thick explosion walls of robust concrete blocks. A separate requirement for an additional massive panel closure structure, which would make the closure system even more robust is also required, however a regulatory decision on their need is proposed for the near future.

When the third disposal panel was filled (WIPP plans a total of 10), DOE petitioned its primary repository regulators (The New Mexico Environment Department – NMED, and the Environmental Protection Agency – EPA) to allow monitoring of gases interior to the disposal panel in lieu of installing explosion walls. DOE argued that by routine monitoring, it could determine if flammable gases were building to potentially explosive levels or not. If concentrations approached action levels or if the monitoring system failed, DOE proposed to construct the explosion walls as originally conceived. This approach allowed DOE to conduct monitoring to potentially demonstrate that explosion walls, and eventually even more robust panel closures, might not be necessary for safe operation of the repository.

This paper describes the results of the first 3 years of hydrogen and methane monitoring in Panels 3 and 4 at WIPP. Flammable volatile organic compounds are also present in many of the waste streams emplaced at WIPP, but liquids are prohibited. Measurements of these flammable organic compounds are also made, but they play a minor role in the argument to eliminate explosion walls as part of the closure design at WIPP. Over 1000 air samples from all interior reaches of Panels 3 and 4 have been collected to date. Every single methane sample has been determined as "Non Detectable" at detection levels of about 30 parts per million. Radiolytically generated hydrogen in these same samples was typically found at levels in the few hundred parts per million, well below the action levels specified in the permit (~4 parts per thousand). The monitoring results indicate that the initial WIPP planning was overly conservative and that explosion walls and robust panel closures may not be needed during the operational lifetime of WIPP.

INTRODUTION

WIPP was constructed and its first disposal panel mined by the end of 1988. Although DOE considered WIPP ready for waste receipt, an 11-year period of regulatory licensing and permitting passed before the first shipment arrived for emplacement (1999). During this delay, several iterations of planning for final disposal panel closure resulted in a design for the panel closures that was based on very conservative assumptions [1].

With limited data on the expected concentrations of volatile organic compounds (VOCs) in the diverse array of transuranic (TRU) waste streams, and limited understanding of the potential for gas generation within the waste, conservative calculations resulted in a proposed design that included a massive concrete structure to be placed in the inlet and outlet drifts of each disposal panel. An assumed potential for a build-up of explosive gases within each panel also led to the proposal to install a massive explosion wall that would itself protect the panel closure from the blast effects so that the closure would continue to serve as a barrier to the VOCs.

In retrospect, these very conservative assumptions and calculations now appear unnecessary. It is prudent to re-examine the need for such robust structures to avoid cost and industrial accident vulnerability. Based on all the monitoring (both within the waste drums before ever shipping to WIPP, and monitoring of conditions in the filled disposal rooms of the repository), it is likely that a much lower cost closure can protectively serve the purpose.

GAS GENERATION MECHANISMS

This section describes the 3 primary sources of flammable gases that might pose a risk to WIPP workers and, to a much lesser extent, potentially exposed members of the public.

Potential Sources of Hydrogen

Hydrogen can be generated by two widely different radiological and chemical processes:

1) Radiolysis (ionizing radiation breaks bonds as it slows in hydrogenous materials), and
2) Corrosion of iron based materials under inundated conditions (no oxygen present).

Of the three primary types of ionizing radiation, radiolytic production of hydrogen is dominated by alpha radiation because of its high energy deposition rate as the alpha particles slow down in a solid matrix. This high energy deposition rate also comes with a short stopping range. The reader may recall their high school physics lesson when shown that a piece of paper is adequate to shield from alpha radiation. All the hydrogen bonds that the alpha particle can break are in the first few microns of the sheet of paper because the alpha radiation does not penetrate further into the solid. This short range also leads to another attribute of radiolysis in a solid matrix that is typically ignored. Because there is no physical movement of the matrix to expose new hydrogen atoms within the solid, radiolytic hydrogen generation rates monotonically decrease over time in all solids. This effect, known as “matrix depletion” occurs because the alpha radiation is coming from a solid source. In the case of transuranic (TRU) waste destined for disposal in WIPP, the dominant source of radiation is plutonium. Plutonium in intimate contact with organic matter (e.g., paper or plastic) will generate hydrogen at a rate that continually declines over time as more and more available hydrogen is released from the matrix. Because the source doesn’t move with respect to the available hydrogen atoms, the probability of breaking a hydrogen bond and releasing that proton declines over time (and in direct proportion to cumulative dose deposited.

Note this decline in hydrogen generation rate is not associated with the radioactive lifetime of the source. The matrix depletion effect is more a measure of the homogeneity of mixing the radioactive source material within the hydrogenous matrix than of the specific radioactivity of the source [2].

In addition to radiolysis, hydrogen can be generated by anoxic (without oxygen) corrosion of various metal components of the waste and packaging (primarily iron and aluminum based materials). Anoxic conditions can only be expected under inundated conditions, where brine has somehow accumulated and completely surrounds the waste [3]. It should be noted that aluminum and aluminum alloy corrosion rates are much slower than those for iron based materials. Estimates of the rates of hydrogen production under anoxic and fully brine inundated conditions may be made, however these rates are quite uncertain in the short-term during disposal operations, and the likelihood of inundating brine accumulation in this time frame is highly unlikely in light of its observed absence since the first disposal rooms was mined over 20 years ago.

Other arguments against significant hydrogen generation by corrosion include the obvious fact that waste containers (typically drums) are painted. Initially corrosion will be inhibited until painted drum surfaces become exposed and internal steel components become accessible. In addition, after initial closure of a panel, oxygen-rich conditions will prevail, and the iron will oxidize (rust) with no hydrogen generation possible until all of the oxygen has been consumed. The oxidation rate is highly dependent on humidity as well [4]. The low humidity in deep reaches of the WIPP (away from fresh air intakes) minimizes oxidation, even of unpainted steel surfaces. This is evidenced from observation of un-rusted surfaces on many pieces of equipment or structures installed when the first openings were mined at WIPP in the early 1980's. In the routinely low humidity levels found in WIPP, steel surfaces become passivated and oxidation slows. Therefore, oxygen depletion in closed disposal panels is not expected quickly. But only after oxygen is depleted and in the presence of brine, could anoxic corrosion be expected to generate significant hydrogen.

In 2007, a calculation was made to bound the upper limit of hydrogen generation in panel 3 [5]. This radiolysis estimate was based on the actual waste types that had been emplaced at the time, and used the actual hydrogen measurements of head-space gas in individual payload containers made to demonstrate compliance with the license requirements of the shipping containers. That conservative estimate of the production rate of hydrogen by radiolysis was about 4.5E-05 moles per second for the entire inventory of waste in panel 3 (about 1 ml/s). Generation at this rate would lead to an average concentration of 4% by volume in an air-tight sealed panel in about 20 years (neglecting any loss of hydrogen by diffusion). This should be considered a lower bound on the time required to reach a lower flammability limit since the accumulation of hydrogen is mitigated by its ease of diffusion through even highly impermeable materials. The reader is also reminded of the many fractures and openings in the disturbed rock zone of a salt mine, which will not completely heal for many decades after disposal operations cease.

Potential Source of Methane

Methanogenesis or biomethanation is the formation of methane by microbes known as methanogens. Methanogenesis in microbes is a form of anaerobic respiration [6]. Methanogens do not use oxygen to breathe; in fact, oxygen inhibits the growth of methanogens. Organisms capable of producing methane have been identified only from the domain Archaea, a group

phylogenetically distinct from both eukaryotes and bacteria, although many live in close association with anaerobic bacteria. The production of methane is an important and widespread form of microbial metabolism. In most environments in the biosphere, it is the final step in the decomposition of biomass.

In addition, methanogenesis also requires the presence of liquid water, within which the methanogens metabolize. If there is oxygen present, methanogenesis is not. Conversely, if liquid water is not present, neither is methanogenesis. Therefore, just like hydrogen generation via anoxic iron corrosion, no methane can be expected as long as oxygen is present and inundating brine is not.

Flammable Volatile Organic Compounds

There are flammable VOCs in the waste. However these represent a fixed source which will deplete over time, and a source which is limited to levels well below flammability by the transportation requirements. Thus, flammable VOC components in filled panels are expected to remain quite small and further diminish over time. Hence they are not considered a significant issue related to the development of an explosive atmosphere in a full panel.

GAS MONITORING PROGRAM DESCRIPTION

In 2001, the National Academy of Sciences recommended DOE conduct pre-closure monitoring of gases in WIPP [7]:

> *The committee recommends pre-closure monitoring of gas generation rates, as well as the volume of hydrogen, carbon dioxide, and methane produced. Such monitoring could enhance confidence in the performance of the repository, especially if no gas generation is observed. Observation should continue at least until the repository shafts are sealed and longer if possible. The results of the gas generation monitoring program should be used to improve the performance assessment for recertification purposes.*

Then in 2003 [8] and again in 2004 [9], Congress directed the DOE to change the process used to characterize waste for WIPP (these statutes are referred to as Section 311 in this paper). Using nearly identical language in both years, Congress stated:

> *(a) The Secretary of Energy is directed to file a permit modification to the Waste Analysis Plan (WAP) and associated provisions contained in the Hazardous Waste Facility Permit for the Waste Isolation Pilot Plant (WIPP) …. (b) Compliance with the disposal room performance standards of the WAP hereafter shall be demonstrated exclusively by monitoring airborne volatile organic compounds in underground disposal rooms in which waste has been emplaced until panel closure.*

Section (b) essentially directed DOE to monitor VOC concentrations in the WIPP underground in lieu of the intrusive sampling and analysis required under the permit from the NMED. This gave DOE a way to conduct the hydrogen and methane monitoring recommended by the National Academy of Science by using the same sampling lines that were mandated by Section 311 for monitoring VOC concentrations in closed disposal rooms. While unrelated, the Section 311 permit modification was linked to approval to dispose of remote-handled waste at WIPP,

which was strongly rejected by WIPP critics. This delayed implementation of the sampling program until the modification became effective in October 2006, and sampling for VOCs began shortly thereafter in Panel 3, the active disposal unit at that time. It took several more months to obtain a permit modification to delay construction of explosion walls in panel 3 and begin making hydrogen and methane measurements in lieu of installing explosion walls. Sampling for hydrogen and methane began in August 2007.

The sampling is performed using long stainless steel tubing with a passivated inner surface and ~7mm in diameter. Sampling tubes were installed along the outer walls of each disposal room after panel excavation, and before waste emplacement operations began. There are two sampling tubes per disposal room; one that terminates at the inlet side of each room and another that terminates at the outlet side. Each sampling line terminates at a 3-way splitter that allows air to be simultaneously drawn from locations about 50 cm above the floor, 50 cm below the roof, and approximately at the mid-height of each room. Figure 1 schematically shows the sampling line network in a typical disposal panel (blue diamonds represent sample intake locations).

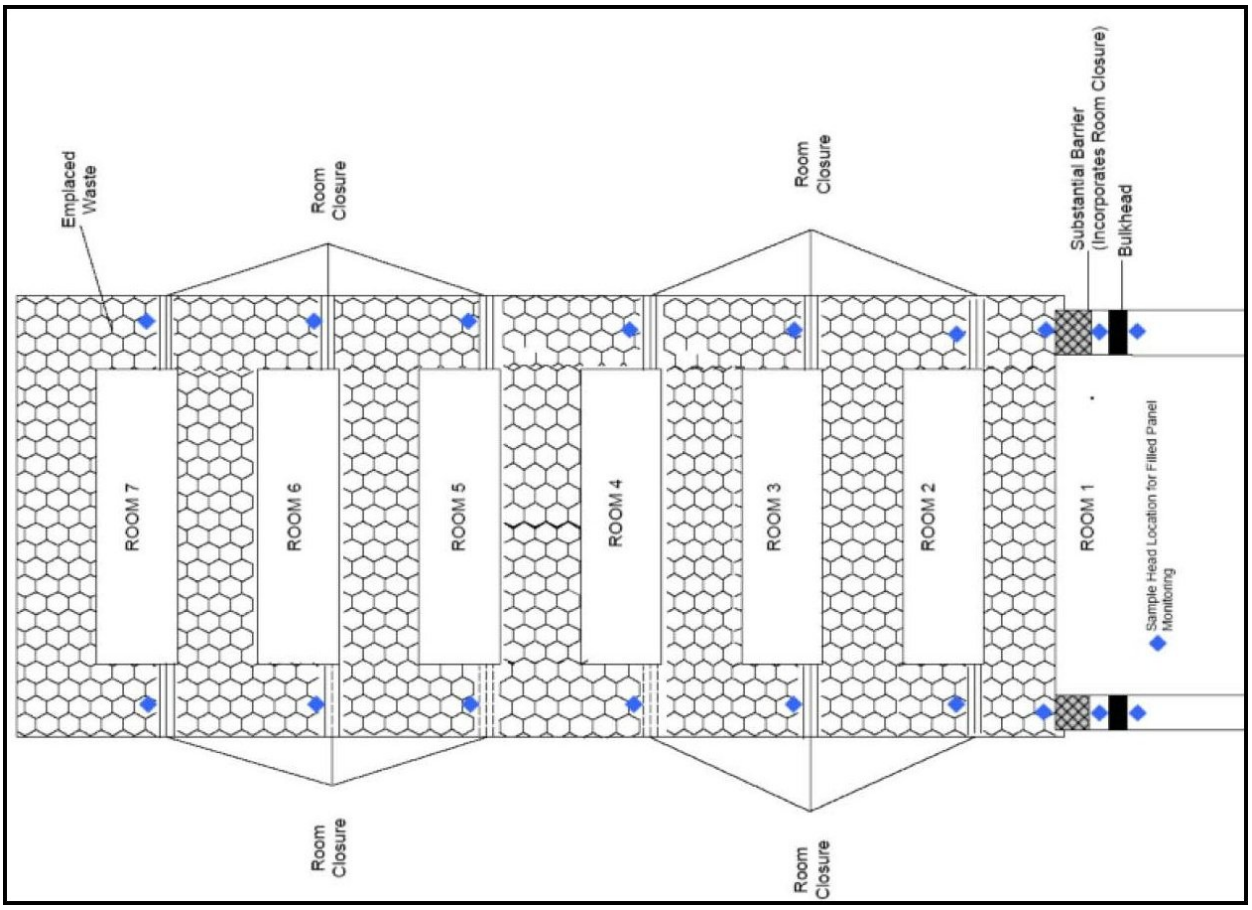

Fig. 1 Plan view of typical disposal panel showing disposal rooms separated by brattice cloth ventilation barriers (room closures) and gas sampling locations in the inlet and outlet sides of each of the seven disposal rooms.

In addition to the VOC monitoring lines, five more sampling locations are used to monitor for hydrogen and methane. These additional locations use a single inlet sampling point placed near the roof and include:

- the inlet of room 1,
- the waste side of the exhaust bulkhead,
- the accessible side of the exhaust bulkhead,
- the waste side of the intake bulkhead,
- the accessible side of the intake bulkhead.

Samples for analysis of hydrogen and methane concentrations are collected using the sub-atmospheric pressure grab sampling technique described in EPA Method TO-15 [10]. This method, which is the same for VOC sampling, uses an evacuated canister under vacuum (~0.05 mmHg) to draw an air sample through sample lines into a ~6 liter stainless steel canister with passivated interior surfaces. The passivation of tubing and canisters effectively seals the inner walls and prevents compounds from being retained on the surfaces of the sampling equipment. Sample lines are purged prior to collection as recommended by the method (about 3 times the sample line volume). At the end of each sampling period (about 6 minute grab sample at ~1 lpm), the canisters reach near atmospheric pressure.

There are no EPA-specific analytical methods which address hydrogen or methane. However, non-EPA methods are available. For the hydrogen and methane sampling, DOE uses a specially developed analytical test method for determination of hydrogen and methane using Gas Chromatography/Thermal Conductivity Detection.

The permit provisions include Action Levels based on the lower flammability limits for hydrogen and methane, referred to in the permit as lower explosive limits (LELs). In air, the lower flammability limit for hydrogen is generally considered to be 4 percent while that for methane is 5 percent. Both limits assume atmospheric oxygen levels are present.

The permit Action Level 1 for hydrogen and methane in a panel is 10 percent of the LEL which, for hydrogen, is 0.4 percent or 4000 ppm and for methane is 0.5 percent or 5000 ppm. If this Action Level is reached or exceeded, the monitoring will be increased to weekly. If the concentrations measured in subsequent sampling fall back below Action Level 1, the sampling frequency relaxes back from weekly to monthly.

Action Level 2 for hydrogen and methane in a panel is 20 percent of the LEL which, for hydrogen is 0.8 percent or 8000 ppm and for methane is 1 percent or 10,000 ppm. If Action Level 2 is achieved or exceeded for two successive weekly samples, the permit requires that monitoring cease and DOE is required to install the explosion isolation walls within 180 days.

When two flammable gases are mixed, the mixture may exhibit a different LEL than the individual gases. This is referred to as the composite LEL for the mixture. DOE evaluated whether or not the composite LEL should be used in determining the Action Levels and concluded that using the 10 percent and 20 percent thresholds was sufficiently conservative to assure action would be taken before potentially explosive levels of hydrogen or methane built up in filled panels. The additional conservatism added by using the composite LEL was not justified considering the additional complexity for demonstrating compliance (i.e., compliance using the composite value is based upon application of a mathematical formula and not on fixed, tabulated values in the permit).

As waste emplacement operations progress and each disposal room is filled within a panel, the filled room is cut off from ventilation by a barrier called a brattice curtain (or cloth), which is a simple canvas-like cloth suspended from the roof and attached to the sides and floor of the drift to effectively cut off the filled room from air ventilation underground. While some attention is given to sealing air flow from going around the barrier, the brattice cloth is by no means an air-tight seal. Small (millimeter scale) gaps remain. After panels 3 and 4 were filled, a metal bulkhead was constructed in both the inlet and outlet drifts (see Figure 1). This final ventilation barrier in each panel was augmented by a rubber (conveyor belt material) gasket bolted to the salt and bulkhead to form a seal. Again, small gaps remained. The reader is reminded that the salt creep process results in fractures and partings within the rock salt walls themselves that make the concept of a perfect gas seal impossible during the operational phase of the repository. Figure 2 shows photos of typical brattice cloth and metal bulkhead construction in WIPP.

Fig. 2 Photos of a typical ventilation barrier called a brattice curtain (top) separating each disposal room, and of a typical metal bulkhead (bottom) “sealing” the inlet and outlet drifts of each disposal panel from ventilation air in the rest of the mine.

DOE believes the use of the bulkhead, the accompanying monitoring, and related Action Levels will maintain safe and protective operations by ensuring that:

- physical access to the full panel is prevented,
- the panel is removed from active ventilation, and
- conditions inside the panel are regularly monitored so that preventive actions can be taken well in advance of the existence of a hazardous condition.

MONITORING RESULTS

Panel 3 was filled and closed in August 2007, while panel 4 was filled and closed in May 2009. Monthly hydrogen and methane sampling began in both panels the same month they were closed. Two results from over 1,000 samples collected since then stand out:

- All samples assayed less than the minimum detectable level for methane (<~20-30 ppm).
- Hydrogen results typically assay at several hundred ppm, when detected at all.

The monthly monitoring results for hydrogen in panels 3 and 4 are presented in Figures 3 and 4, respectively.

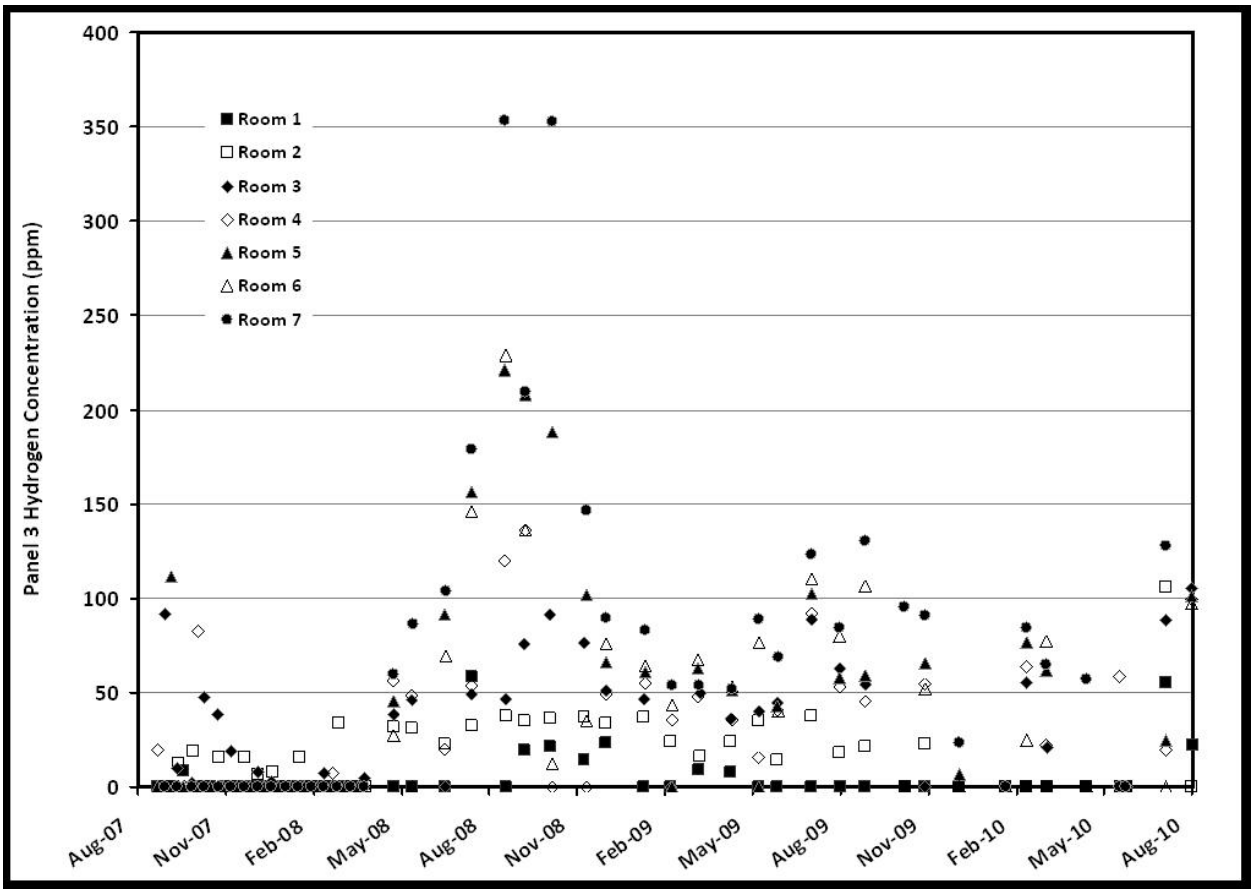

Fig. 3 Time series history of hydrogen monitoring results taken from the outlet sides of disposal rooms in closed panel 3 over a 3-year period.

In these time series plots, only the results from sampling the outlet sides of each disposal room are plotted. Only a handful (out of over 500) of samples taken from the inlet side assayed above the minimum detectable limit for hydrogen (~20-30 ppm), and therefore are not plotted. When outlet sample results assayed below the minimum detectable limit, the value was plotted at a concentration of zero in Figures 3 and 4.

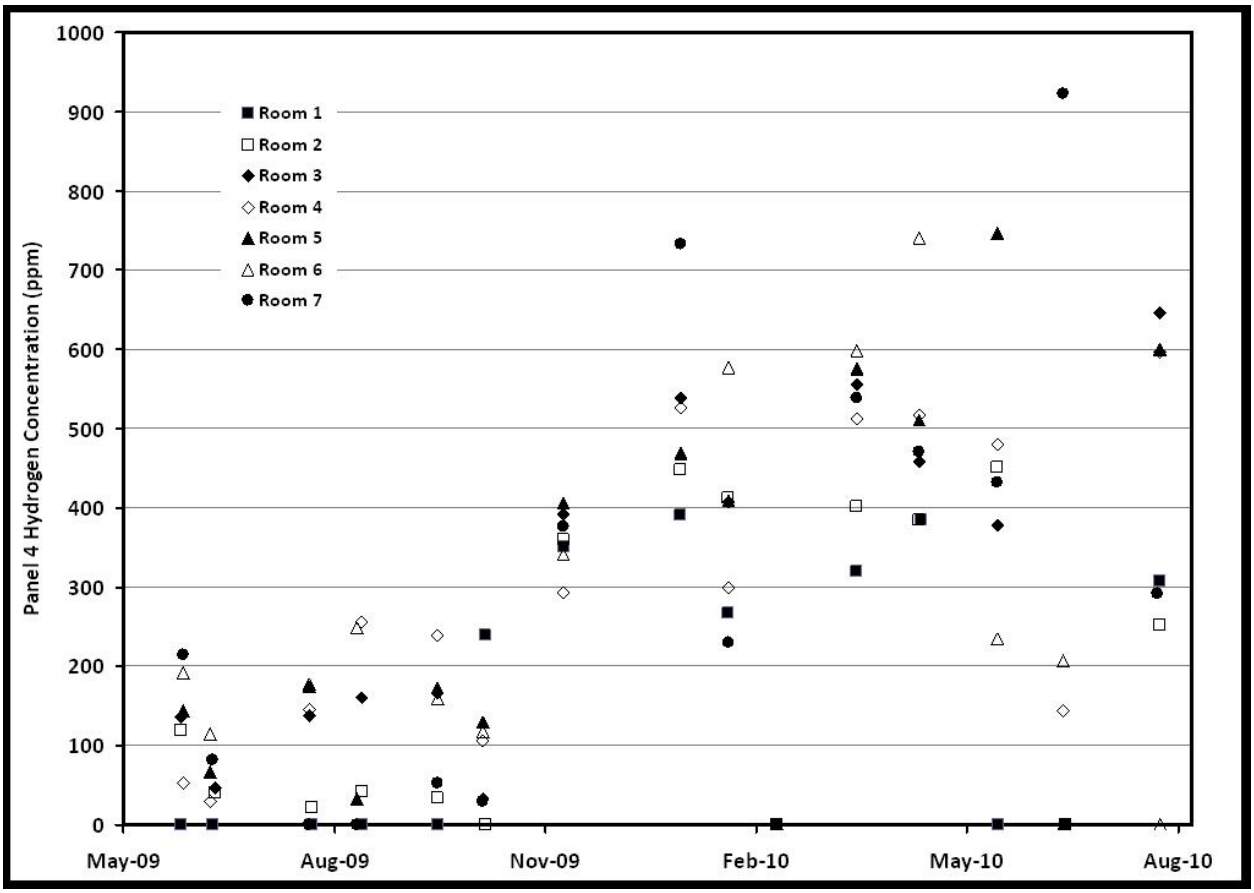

Fig. 4 Time series history of hydrogen monitoring results taken from the outlet side of disposal rooms in closed panel 4 over an 18-month period.

Interpreting these results is easy. There is no detectable methanogenesis occurring in either panels 3 or 4, and thereby by inference, no methanogenesis in panels 1 or 2 either. In contrast hydrogen generation by radiolysis is occurring and at levels easily detected by the analytic method used for assay. No steadily rising concentrations imply that the hydrogen is removed from the disposal rooms on a continuous basis. The removal process appears to be two-fold. The fact that the results from samples collected on the inlet side almost always assay below minimum detectable limits and those from the outlet side typically range in the few hundred ppm levels implies that there is a leakage flow due to differential pressure between the inlet and outlet sides of each disposal panel. The high sample-to-sample variability from each location implies that the release of hydrogen from the waste containers themselves varies over periods of weeks to months. This can be explained by normal barometric breathing.

The highest value of hydrogen measured to date was 923 ppm at the outlet side of room 7 (furthest into the disposal panel) in panel 4 in June 2010. This value is 25% of the Action Level 1 for hydrogen established in the permit (which in turn is 10% of the concentration considered

flammable - if oxygen were present at atmospheric levels). It should be noted that actions to minimize leakage ventilation through panel 4 began in earnest in November 2009, when running annual average carbon tetrachloride levels in the exhaust flow from the entire underground began climbing. A companion paper in session 063 (11039) at this symposium describes this effort in more detail [11].

Active disposal operations with high carbon tetrachloride content were ongoing in panel 5 at that time, but it was prudent to assume that some of the carbon tetrachloride originated from leakage flow through closed panel 4 since it held some of the high carbon tetrachloride waste as well. Therefore, DOE built an additional bulkhead at the inlet and outlet drifts of panel 4 and made extra efforts to seal panel 4 from leakage ventilation. These efforts were coincident with the slight step increase in the peak hydrogen concentration results as seen in Figure 4 in November 2009. The apparent increase may be attributed to the enhanced sealing efforts to minimize carbon tetrachloride leakage out of panel 4. However, the fact that hydrogen concentrations vary so much from one sample to the next indicates that it easily escapes the systems designed to block the carbon tetrachloride.

ELIMINATING EXPLOSION WALLS AND OPTIMIZING PANEL CLOSURES

Based on the monitoring results from 2007 to date, it would seem that massive panel closures and explosion walls to protect those closures might not be necessary and yet still be protective of workers and the environment. A companion paper in session 063 at this symposium discusses DOE's plans to seek regulatory approval to modify the massive closure design and replace it with a simple 30 meter long wall of run of mine salt [12]. Such a panel closure would likely be a better barrier in preventing panel-to-panel hydrologic communication in an assumed future human intrusion scenario, and would be a lot less costly. Upon filling a disposal panel with waste, the run of mine salt closure would simply be placed in the inlet and outlet drifts. A blower may be used to bring the pile up to the full height of the drifts. While this closure would not be air-tight, it would behave at least as well as the metal bulkheads in panels 3 and 4 described herein (the same leaky pathways around the closure through the disturbed rock zone would exist). Over time (a few decades), the salt creep closure would compact and begin reconsolidating the run of mine salt. Within a few hundred years, this panel closure would resemble the properties of intact salt. In contrast a massive monolith of concrete (the current panel closure stipulated for WIPP by its regulators) would not exhibit the immeasurably low permeability of healed intact salt, but would be considered more permeable.

CONCLUSIONS

Although basic knowledge and laboratory measurements made during the licensing and permitting phase showed that little or no gas generation would occur during the operational life of WIPP, in an abundance of caution, DOE and its regulators still proposed massive panel closures and large explosion walls to protect them. Based on monitoring results (at least for panel 3 and 4), these do not appear to be necessary, since levels of flammable gases and VOCs are present in only trace levels. The only VOC present in significant amounts in the TRU waste stream inventory (and then only in a small fraction of drums) is carbon tetrachloride, which ironically is not flammable.

Over 1000 gas samples collected in all areas of panels 3 and 4 show undetectable levels of methane, thereby confirming the expectation that methanogenesis is not occurring (oxygen is

present, and brine inundation is not). Hydrogen levels in those same samples are in the few hundred ppm range and vary significantly from sample to sample, thereby implying a continuous source, but an intermittent pathway out. This is consistent with barometric pumping of waste containers, superimposed on a steady leakage air flow, even through the further back disposal rooms in a panel.

DOE will continue to monitor for flammable gases in filled disposal panels and take steps to protect workers and the environment if levels rise and explosions walls become necessary. In the meantime, DOE will continue to make the case that there are more prudent and cost effective panel closure designs that should be considered.

REFERENCES

1. Conceptual Design for Operational Phase Panel Closure Systems, DOE-WIPP-95-2057, US Department of Energy, 1995.
2. Idaho National Engineering and Environmental Laboratory, 1990, "TRUPACT-II Matrix Depletion Program Final Report," INEL/EXT-98-00987, Rev. 1, prepared for the U.S. Department of Energy, Idaho Operations Office, Idaho Falls, Idaho.
3. Francis, A.J., Gillow, J.B., and M.R. Giles, 1997. Microbial Gas Generation Under Expected Waste Isolation Pilot Plant Repository Conditions. SAND96-2582, Sandia National Laboratories, Albuquerque, New Mexico.
4. Gillow, J.B. and A.J. Francis, 2002, Re-Evaluation of Microbial Gas Generation Under Expected Waste Isolation Pilot Plant Conditions, Data Summary and Progress Report (February 1 – July 15, 2002). Section 3.1 of Sandia Technical Baseline Report, July 31, 2002. Sandia National Laboratories, Albuquerque, New Mexico.
5. Devarakonda, M., Estimation of Hydrogen Generation Rates From Radiolysis in WIPP Panels, Letter from Washington TRU Solutions to D. Mercer, TS:06:02012, July 20, 2006
6. Thauer, R. K., Biochemistry of Methanogenesis, Microbiology, 1998, volume 144, pages 2377-2406.
7. National Academy of Sciences, 2001, Improving Operations and Long-Term Safety of the Waste Isolation Pilot Plant, Board on Radioactive Waste Management.
8. Section 311 of the Energy and Water Development Appropriations Act, 2004, Public Law 108-137 (December 1, 2003)
9. Section 310 of the Consolidated Appropriations Act for 2005, Public Law 108-447 (December 8, 2004)
10. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Methods TO-15, Second Edition, US Environmental Protection Agency, Research Triangle Park, NC, January 1999; EPA 600/625/R-96/010b.
11. Nelson, R.A., WIPP Status and Plans – 2010, Waste Management 2011 Conference, Phoenix, AZ, March, 2011.
12. Patterson, R.L., S. Kouba, and T. Klein, Panel Closure: A Change in WIPP's Future Operations through Regulatory Compliance, Waste Management 2011 Conference, Phoenix, AZ, March 2011.