Potential Unreviewed Safety Question Affecting Department of Energy Complex Concerning Hydrogen Generation in TRU Waste Drums

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July 18, 2018

After searching for the reasons why four transuranic waste drums ruptured in April 2018, just hours after being repackaged, I came across a report published in 2002 that seemed to provide important clues for the rapid drum overpressurization. The four waste drums had been repackaged by Fluor Idaho, the operating contractor for the Idaho Cleanup Project, under the Department of Energy at the Idaho National Laboratory site.

The information in the 2002 report suggests that the Department of Energy needs to conduct a thorough review of the safety issues pertaining to transuranic (TRU) waste drums not only in Idaho but also at other sites around the DOE Complex including the Waste Isolation Pilot Plant (WIPP) and at the Los Alamos National Laboratory, both in in New Mexico. The emergency response at any location that the waste is transported through may also need to be reviewed.

Cause of the Four Drum Rupture has been a Mystery

So far, the Department of Energy has not offered any explanation for the rapid gas buildup, within hours, from repackaging the waste into new drums. I don't know how far along Fluor Idaho, the Idaho Cleanup contractor, is in determining the cause of the rupture of the four TRU waste drums. I only know that they have not released any information pertaining to analysis of drum contents and that they have communicated to the Idaho Department of Environmental Quality that they do not plan to issue a report until November, several months from now. But in the meantime, shipments to WIPP are continuing.

The Unreviewed Safety Question process is a formal process used by the Department of Energy to document the issues that arise that could mean that their documented safety analysis for their nuclear operations may have understated the likelihood or the consequence of

USQ Issue:

There appears to be an Unreviewed Safety Question concerning TRU waste across the Department of Energy Complex involving inadequate technical bases for concluding there would be no excessive hydrogen buildup when TRU waste containers are opened, intentionally or accidentally, and allowed to take in oxygen.

Why it matters:

Upon waste handling or transportation mishap that allows oxygen into the container, significant heat up and overpressurization may result within 24 hours. This could greatly increase the release and spread of radioactive transuranic waste, affecting workers and the public.

Transuranic Waste:

TRU waste typically includes americium-241 and plutonium-239/240.

an accident.

I hope to prompt the Department of Energy and its contractors to make sure that they assess the report published in 2002 that observed unexpected and excessive hydrogen generation on a transuranic waste sample at ambient temperature.

Currently, there appears to have been the assumption that as long as no incompatible materials were added to the waste and the waste was not subjected to excessive temperatures, there would not be excessive hydrogen generation.

But for the four drums that ruptured, no materials had been added and the drums were being stored at normal temperatures.

Excessive Hydrogen Generation Noted in TRU Sludge Waste in 2002 Report

In the research described in the 2002 report, the transuranic organic waste sludge sample that unexpectedly generated excessive hydrogen apparently had not had material added to the sample or been stirred. The intent of the experiment was to heat the samples and measure hydrogen gas generation. But the hydrogen level was already elevated in one sample when the experiment started. Simply upon unsealing the sample of transuranic sludge waste material, an excessive amount of hydrogen generation was observed. The DOE defunded the research. And it is not clear that the observations were ever followed up on.

In my limited review of the technical bases for concluding that the chemically-laden transuranic sludge waste would not overpressurize drum waste containers, it appears that the technical bases may be awfully thin. It appears that analyses by a single author, John Dick, who tested chemical combinations that had not been exposed to radioactivity, which is normally present in transuranic waste, concluded that as long as the waste materials were not subject to excessively high temperatures and did not have reactive materials added to the waste, that the waste would not overpressurize.

Therefore, there appears to be an Unreviewed Safety Question concerning TRU waste within the Department of Energy Complex involving inadequate technical bases for concluding there would be no excessive hydrogen buildup when TRU waste containers are opened, intentionally or accidentally, and allowed to take in oxygen.

DOE Must Avoid Focusing Too Narrowly on Drum Repackaging in Idaho

It might be narrowly decided that the cause of the April four-drum rupture is limited to the specific chemical constituents present in that waste — or that repackaging the waste into new drums was a necessary condition for the excessive hydrogen generation. But, additional configuration and factors beyond those need to also be considered.

I suggest that the Department of Energy not restrain itself too narrowly during the investigation of the four-drum rupture event. I am concerned about the tendency to continue to rely on an incomplete and now proven to be grossly inadequate technical bases for assuming there would not be significant overpressurization events as long as the waste was stored as

normal ambient temperatures and as long as no addition materials such as organic kitty litter or other reactive waste had not been recently added to the waste.

In light of the TRU waste overpressurization at WIPP in 2014 and now in light of four TRU waste drums that overpressurized at the Idaho National Laboratory site at the Idaho Cleanup Project in April 2018, the 2002 report that identified excessive hydrogen buildup in TRU waste samples is particularly important. Because of the WIPP event being thought to be due to the addition of organic absorbent, a wheat-based kitty litter, initial responses to the Idaho four-drum rupture event in April were to point out that no organic materials had been added to the drum when it was repackaged.

The particle size of the TRU radionuclides as well as the amount of ionizing radiation and neutron radiation and possible reasons for inadequate radioactive material assay also need to be examined. Even for so-called "homogeneous" sludge waste from Rocky Flats, the original waste in the drum would not necessarily have been well mixed which could result in radiation assay underestimation of the TRU material present in the drum. The way that Portland cement and other materials were added to the original TRU waste drums from Rocky Flats (or a supplier to Rocky Flats) might not be well mixed and could result in underestimating the radioactive material present. It would appear that the incorrect assay of the amount of TRU radioactive material present may have been a significant factor in the 2014 WIPP drum explosion.

Poorly Characterized Waste Stream

The transuranic waste involved in the rupture of four drums at the Idaho Cleanup project appears to have involved a waste stream that was particularly poorly understood. This characteristic seems to be the only reason they have offered for deeming it acceptable to continue other shipments to WIPP.

A long listing of chemicals that might be in the waste that was in the four drums that ruptured had been assigned but there was no physical sampling to determine which of the chemicals were in the waste prior to its repackaging. Nonetheless, the contractor, the DOE, and the Idaho Department of Environmental Quality deemed the process safe enough based on their very limited knowledge of what was in these drums of "homogenous" sludge.

Awfully Thin Technical Bases For Current Assumptions

The bases for concluding that hydrogen generation in the TRU drums should not be a problem appears to stem from analyses largely by the same analyst, John Dick, who concluded that the TRU waste would not overpressurize when ambient temperatures for storing the waste would maintained. It appears that his research regarding mixing of chemicals did not include actual TRU waste and thus would not reflect the possible increased susceptibility to hydrogen generation of chemicals long exposed to radiation.

The four drums that ruptured had been repackaged in Idaho did not add new material. The contents of the drums were mixed around in a trough and then repackaged into new drums.

These drums were stored in areas of the facility where no worker respiratory protection would have normally been provided. There was no expectation that these drums were vulnerable to over-pressurization and rupture. If not for the good luck of the timing of the drum ruptures being during the off hours when no workers were in the facility, many workers would have had significant inhalation of radioactive material. And these drums could have been moved from this facility to other locations that also would have put workers and/or the environment at risk.

Possible Reasons for Excessive Hydrogen Buildup

The question of why there was excessive hydrogen buildup might be explained by research conducted at ANL-W and reported in 2002. The report by David B. Barber and Kevin P. Carney and Jack C. Demirgian is "Observation of Excessive Hydrogen from Transuranic Waste Type IV Solidified Organics." This work was funded by DOE's Transuranic and Mixed Waste Focus Area under contract W-31-109-ENG-38.

However, upon finding unexplained excessive hydrogen buildup in actual TRU waste samples, the research was defunded.

While this research did not make final conclusions of the cause of excessive hydrogen buildup in some TRU samples, they did offer possible reasons.

The reasons can include variation in chemical contents of the TRU waste, variation in the amount of ionizing radiation in the sample, increased susceptibility of the compounds to release gases at lower temperatures because of long term exposure to ionizing radiation resulting in "thermal cracking," and the presence of free radicals formed by the ongoing ionizing radiation.

In the 2002 report by Barber et al., simply opening the container of the TRU sample which allowed in oxygen (and no mention of stirring or mixing the waste) was enough to, in a noted case, result in unexpected and excessive hydrogen gas generation.

Had this finding been further and adequately researched, additional precautions might have been put in place to monitor hydrogen off-gassing (and temperature). So, some of the precautions that have been put in place at least temporarily at the ARP V now, after the four-drum accident, could have been identified years earlier.

The historical bases for the assumption that opening drums, stirring drum material, and repackaging drums and/or storing the drums would not develop pressures that would overpressurize the drums and release large amount of TRU waste material appear to be inadequate.

Other research has noted increased hydrogen generation levels, characterized by G-value, for mixed chemicals.

TRU Drum Handling Risks Beyond Repackaging, Include Transportation

The safety analyses must also address safety issues concerning unintended opening TRU waste packages, allowing oxygen entry to the previous oxygen deprived drum.

The wrong conclusion which was that the TRU waste, now opened after a long oxygen limited environment, would not have excessive hydrogen buildup that would result in container drum rupture, has been a very dangerous error made by the Department of Energy.

I implore the Department of Energy to perform adequate analysis review of the bases for concluding that there was no or minimal risk from the newly opened and repackaged drums. This issue pertains not only to the repackaging of transuranic waste drums, it also pertains to the necessary precautions and emergency response regarding an accidental drum breach. Forklift tines puncturing a drum, could, for instance, allow oxygen into the drum and put the drum at more risk of an overpressurization within a few hours of the initial breach. The possible build up of excessive temperature (300 F) in the waste and possible drum lid popping pressures need to be understood and mitigated in drum handling and transportation incidents.

Summary

A thorough review of the inadequacy of the technical bases for assuming that there was little risk of drum overpressurization needs to be conducted. The old assumptions — that unless new materials were added to the drum, the drum would not overpressurize at ambient temperatures — are flawed.

Additional vulnerability of TRU drums at lower than previously assumed temperatures also needs to be revisited. Many assumptions made in the documented safety analysis for handling of TRU waste appear to be without sound technical bases. Without sound technical bases, the necessary mitigations and controls had not been put in place.

The multitude of drum storage and handling configurations and incidents such as puncturing a waste drum also appear to potentially pose a higher likelihood and consequence from potential rapid overpressurization such as would cause additional drum rupture or lids to pop off the drums, during the response to a drum incident that had allowed oxygen to enter to drum.

Selected References

Keith Ridler, *The Idaho Statesman*, "Officials say radioactive sludge barrel ruptures now total 4," April 25, 2018. http://www.idahostatesman.com/latest-news/article209827149.html

David B. Barber and Kevin P. Carney, Argonne National Laboratory, "Observations of Excessive Hydrogen from Transuranic Waste Type IV Solidified Organics," January 2002. Funded by the DOE's Transuranic and Mixed Waste Focus Area. https://www.researchgate.net/publication/238614280_Observations_of_excessive_hydrogen_from_transuranic_waste_type_IV_solidified_organics The paper describes unexpectedly high levels of hydrogen generation in tests conducted of transuranic Type IV solidified organics. There is a variety of materials present in the sludge (oil, inert and volatile organic compounds) and variation in the localized and drum-total ionizing radiation doses, variation in storage conditions, and variation in radiolysis, recombination and matrix depletion effects. "It has certainly proven difficult to isolate mechanisms for hydrogen production and release from these

organic systems. The three mechanisms discussed previously, i.e., storage-and-release, cracking of radiation-produced organic compounds and radiocatalysis, as well as other causes may be at play. Several research paths including inerted sampling remain to be pursued to resolve these questions." The Department of Energy's funding for this research was terminated.

John R. Dick and Brent N. Burton, INEEL, "Evaluation of Chemical Compatibilities of the OU 7-10 Glovebox Excavator Method Project," INEEL/EXT-01-01587, June 2002. https://ar.icp.doe.gov/images/pdf/200304/2003041100126KAH.pdf See also John R. Dick, INEEL/EXT-01-00265 and INEEL/EXT-03-00471 cited in ICP/EXT-04-00248.

North Wind Inc. for U.S. Department of Energy, Environmental Management, "Historical Background Report for Rocky Flats Plant Waste Shipped to the INEEL and Buried in the SDA from 1954 to 1971," ICP/EXT-04-00248, Revision 1, February 2005. https://ar.icp.doe.gov/images/pdf/200504/2005040400022KAH.pdf

B. L. Anderson et al., Hydrogen Generation in TRU Waste Transportation Packages, NUREG/CR-6673, UCRL-ID-13852, Lawrence Livermore National Laboratory, February 2000, https://www.nrc.gov/docs/ML0037/ML003723404.pdf p. 77 "Aromatic hydrocarbons, such as benzene, toluene, and cyclohexene protect TBP from radiolysis, while saturated hydrocarbons such as hexane, cyclohexane, and dodecane sensitize TBP to radiolytic degradation (Barney and Bouse 1977). Carbon tetrachloride has also been found to sensitize TBP radiolysis."