

Joseph A. Legare
August 11, 1998
98-RF-04028
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pyro-oxidized waste, Rocky Flats contracted with outside experts knowledgeable in the field to provide an explanation for the event. The experts agreed that any mercury compound that could survive the pyro-oxidation process (e.g., vigorous stirring at 850°C for two hours) would be extremely non-volatile at room temperatures, and that preservation of any samples at the required 4°C would not contribute to ultimate data quality. The United States Environmental Protection Agency requires cooling to preserve mercury samples. Elemental mercury and other mercury compounds have significant vapor pressures at room temperature, and cooling the sample mitigates the loss of mercury from the sample during the time between sample collection and analysis. Since the mercury in the samples of pyro-oxidized salt is not volatile at room temperature, cooling the samples would not contribute to constituent preservation. As such, the conclusion of the original request still holds true that eliminating the need for 4°C sample preservation will not affect data quality. Attachment # 1 provides a summary of the additional information and the expert opinions on the subject.

Please forward this information to CAO to allow them to re-evaluate their original exemption approval. Ideally, we would like to have this issue resolved prior to their arrival for the salt program audit scheduled to begin on August 31, 1998, to avoid a situation where this could be identified as a condition adverse to quality.

Questions and comments should be directed to Scott Anderson at X9645.



Alan D. Rodgers
Division Manager
Waste Remediation Operations
Kaiser-Hill Company, L.L.C.

SAA:pmm

Attachment:
As Stated

Orig. and 1 cc – Joseph A. Legare

cc:

Roger Ballenger	w/o attach.
David French	w/o attach.
Gerald O'Leary	w/o attach.
Michael Rivera	w/o attach.
John Schierloh	w/o attach.
Martin Wheeler	w/o attach.
Lam Xuan	w/o attach.

ANALYSIS OF THE REQUIREMENT FOR SAMPLE PRESERVATION FOR MERCURY IN PYRO-OXIDIZED SALTS

Safe Sites of Colorado (SSOC) is pyro-oxidizing Item Description Code (IDC) 414, Direct Oxide Reduction Salt (DOR) — Unoxidized calcium, to oxidize any calcium metal that may be present in the waste matrix. Originally, process knowledge indicated that mercury would not be present in the final pyro-oxidized waste matrix. However, two samples were detected to have mercury in the final waste matrix. Both detections for mercury were low level, approximately 433 parts per billion and two parts per million, respectively, and both were from wastes generated in the Research and Development (R&D) laboratory. The cause of the mercury contamination in the two samples has not been determined. The only sources of mercury in gloveboxes where DOR operations took place included (1) a possible mercury switch on or near the DOR furnace, (2) mercury from a broken thermometer, or (3) mercury from a broken fluorescent light. Mercury was not part of the DOR process in either the production lines or in the R&D gloveboxes.

Because of mercury detection in the two samples of processed IDC 414, SSOC has determined that sampling for mercury will continue. However, sampling and sample handling for Waste Isolation Pilot Plant (WIPP) certified waste requires sample preservation for the mercury analysis. Specifically, sample preservation for mercury requires cooling the sample to 4°C plus or minus 2°C per the Environmental Protection Agency (EPA) protocol in the "Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846) Third Edition" which is referenced as a requirement by the WIPP Quality Assurance Program Plan (QAPP).

Sample preservation for mercury is designed to reduce the volatility of mercury in a sample until it can be analyzed. According to SW-846, samples should be stored at 4°C plus or minus 2°C until analyzed. For pyro-oxidation, the sample is removed from the furnace when the furnace cool-down cycle has been completed after each run. The temperature at which the sample is removed from the furnace is at approximately room temperature or a slightly above (i.e., in general, around 25°C to 28°C). The sample is transported to the laboratory as soon as possible. In the laboratory, the samples are stored until analysis at 4°C plus or minus 2°C. However, the samples are not chilled to 4°C, while in the glovebox. Cooling the sample to 4°C plus or minus 2°C within a glovebox environment is unnecessary because, any mercury or mercury compound that survived the pyro-oxidation process at approximately 850°C for two hours has a low volatility and at 28°C that volatility would be considerably lower, and any further cooling of the sample between the time it was removed from the furnace until it is received by the laboratory would not result in any quantitative preservation of mercury in the sample matrix.

In order to confirm the above position, two outside experts were retained to determine the validity of the premise that further cooling to 4°C for samples from the pyro-oxidation process would not be necessary. The experts concluded that (1) because the vapor pressure of any mercury compound that survived the pyro-oxidation process at 850°C would be quite low at 28°C, and (2) any further reduction in sample holding temperature would not result in any appreciable reduction in loss of mercury or mercury compounds from the sample. Further cooling to 4°C is unnecessary for the preservation of mercury in the pyro-oxidized samples. The attached two draft reports from Drs. Cleveland and Norman provide additional information, thoughts, opinions and conclusions.

Additionally, the Rocky Flats Building 559 laboratory was asked to review its procedures to determine if proper Quality Assurance/Quality Control (QA/QC) procedures were in place for the mercury analyses. The laboratory determined that (1) no laboratory contamination occurred, and (2) the mercury detected in both samples was not anomalous. Also, the laboratory procedure for the mercury analysis was reviewed for possible errors in the addition of reagents. No errors were found.

From the analysis conducted by the off-site experts and process knowledge, sample preservation at 4°C of pyro-oxidized samples for mercury is not necessary to conserve the mercury or mercury compounds in the sample. While the exact mechanism for retention of mercury during the pyro-oxidation process is not known and the form in which the mercury (e.g., an amalgam or an inter-metallic species) is not known, it is likely that any mercury or mercury compounds that remains in the waste matrix during the pyro-oxidation will remain within the waste matrix and will not volatilize off at ambient room temperature or 4°C. Therefore, further cooling of the sample to 4°C will not result in any additional quantitative preservation of mercury in the sample from a pyro-oxidized salt.

- Attachments: (1) *Possible Reasons for Presence of Mercury in Processed DOR Salts - Interim Report*, Jesse M. Cleveland, Ph.D., dated June 27, 1998
(2) *Mercury in DOR Salts Problem - Progress Report*, Arlan D. Norman, Ph.D., Professor of Chemistry, University of Colorado, dated June 29, 1998

Jesse M. Cleveland
2790 Stanford Avenue
Boulder, Colorado 80303

June 27, 1998

MEMO TO: Dave French, Aspen Associates, FAX 642-3352

FROM: Jesse M. Cleveland, Consultant

SUBJECT: Possible Reasons for Presence of Mercury in Processed DOR Salts - Interim Report

Out of 200+ cans of DOR salts that were oxidized/homogenized by holding at 800° C for two hours with stirring, two had finite concentrations of mercury despite the fact that the boiling point of mercury is 356° C. This result is puzzling, but there are possible explanations. First it should be noted that there are only trace amounts of mercury in the samples: 432 ppb in one sample and about 2 ppm in the other.

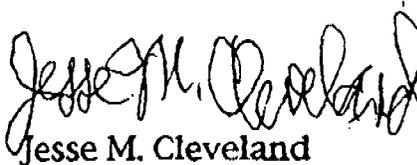
Two questions come to mind: Is the mercury really present, or is it an analytical artifact? If the mercury is indeed present, how could it survive two hours at a temperature almost 350 degrees above its boiling point? Let's address these two questions in reverse order.

The two samples with positive mercury results came from R & D glove boxes - boxes that have been used for salt-scrubbing with zinc and aluminum. The sample with 432 ppb of mercury also had 82 ppm of zinc. Zinc forms strong amalgams with mercury, and these amalgams would be expected to have lower vapor pressures than mercury itself. It is therefore plausible that such amalgams could persist under these conditions, but vapor-pressure data for zinc-mercury amalgams is necessary before this possibility can be evaluated. A literature search is currently underway to attempt to obtain these data. I am hesitant to invoke what is really a reaction between trace elements to explain the presence of mercury, but no better explanations come to mind.

Is the mercury really there? At these low levels, the analytical results could be erroneous, either because of sample contamination or instrumental malfunction. Before an extensive campaign is undertaken to reheat and resample all 200+ cans, I would strongly recommend that only

the two cans with positive mercury results be reheated and resampled. I suggest that both of the resulting samples be thoroughly homogenized and divided into two portions, one being analyzed at Rocky Flats and one at Los Alamos. Further treatment of all the samples would not be indicated unless these samples again indicate the presence of mercury.

Finally I would like to make a brief comment regarding the sampling protocol. These cans were not sampled according to that protocol, in that they were sampled at 28° C rather than 4°, as required by the protocol. Whether this is acceptable is an administrative matter beyond my purview, but from a technical standpoint it is inconceivable that samples that had retained mercury at 800° would lose it at 28°. Hence I see no reason to disqualify these analyses on the basis of this temperature basis alone.



Jesse M. Cleveland



University of Colorado at Boulder

Dr. Arlan Norman
(303) 492-7366
Department of Chemistry and Biochemistry

Campus Box 215
Boulder, CO 80309-0215
U.S.A.

TO: Dave French
Aspen Resources, FAX 966-2256

FROM: Arlan D. Norman
Professor of Chemistry; Consultant 

SUBJECT: Mercury in DOR Salts Problem
Progress Report

DATE: 6/29/98

The Problem Outlined/Presented

Some 250 samples of pyrooxidized waste salts have been prepared for disposal. Of these samples, two are reported, based on cold vapor atomic absorption spectroscopy, to contain mercury (Hg) at 432 ppb and 2 ppm levels. The origin or species form (compound vs elemental) of the Hg in these samples is not known. Samples for analysis were collected from the pyrolysis cans at ca. 850 °C, then the samples were cooled over a several hour period to 28 °C. A major question to be resolved is: are the samples "stable" at 28 °C or could further Hg be lost at that temperature, thus necessitating that the samples be cooled even further to 4 °C? Perhaps secondary, but not unrelated issues deal with the origin and form of the Hg in the samples.

My assumption is that the analytical data are reliable and that Hg is in fact in the samples. However, this might be incorrect and perhaps should be discussed further.

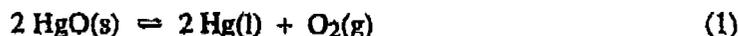
Discussion

Issue 1. I do not see any way that samples that retain Hg at 850 °C under a gas purge, irrespective of the mercury species present, would further lose Hg at 28 °C. I can see no need to cool the samples from 28 °C to 4 °C as required by the EPA handling protocol. If there is mercury present, it must either be effectively immobilized (i) by the solid matrix or (ii) because of some other process, such as amalgamation (see below).

Issue 2. The principal reactions in the pyrooxidation process involve the high temperature carbonate oxidation of Pu, PuCl₃ and PuOCl₃. These are claimed to yield: (from CaCO₃ oxidation), PuO₂, CaCl₂, CaO, C, CO₂ and CO and (from Na₂CO₃ oxidation), PuO₂, NaCl, Na, NaCl, C, CO₂ and CO. Products were characterized based on thermodynamic calculations and experimental observation. The reactions occur in a NaCl/KCl melt at high temperatures. I have not attempted to redo the thermodynamic calculations, but the conclusions appear reasonable. I find it curious that Na is found among products of the oxidation reactions, but perhaps it persists because of a solubility problem, and therefore it shows slowed reactivity in the melt environment. In all reactions there appears to be excess oxidizing capability (carbonate) present throughout the entire pyrolysis process.

In my opinion, if there is mercury in the final pyrooxidized reaction mixture, it would be there as Hg metal. Hg metal is relatively noble, and there appears to be nothing in the reaction

mixture sufficiently strongly oxidizing to oxidize Hg to its ions. Thus, if Hg metal is present in the original DOR salt mixture it would stay as such during the oxidation. If a Hg compound such as HgO, HgCl₂ or Hg₂Cl₂ were present in the original DOR mixture, these compounds would all be decomposed at the high temperature reaction conditions, to Hg metal and the elements, such as e.g. for HgO, which decomposes at > 450 °C as shown in eqn 1. At 800 - 900 °C the equilibrium would be shifted far to the right. Oxygen (O₂) would likely be swept from the



reaction apparatus during pyrolysis; halogens might react to form halide salts.

In all samples for which I have seen elemental analysis data, considerable amounts of Zn were present. In at least one sample, the presence of metallic Zn was noted. Furthermore, in samples where Na₂CO₃ is used as the oxidant, apparently Na can form; thus, Na metal could also be present in the samples of concern. Analytical data I have seen so far do not indicate whether or not Na metal was present. It seems possible that Zn (and also Na) could act as a sink for the immobilization of Hg, through the process of alloying or amalgamation. At the high temperature of the reactor and under stirred conditions, I would expect both the Hg and the Zn to be dispersed in the medium. However, as the medium is cooled, Hg/Zn alloying could occur. It is known that alloying can occur - alloys/metal solutions containing up to 1.9 wt % of Zn in Hg can form. Alloys with high Hg/Zn ratios are possible. There is enough Zn in the systems to alloy the much lesser amounts of Hg present.

However, there are issues of continuing concern with the above amalgam theory. I do not yet know in what temperature ranges the alloys are stable and if it is reasonable that such an alloy would be stable at the temperatures at which the salt melt or materials in the melt solidify. If the alloy can form, I expect that the vapor pressure of Hg above it will be considerably lower than that of pure Hg metal and that the Hg would be effectively immobilized. Vapor pressure data on the Hg alloys have yet to be obtained either from the literature or from an authoritative metallurgy source. However, that amalgamation could be significant in the process appears sufficiently likely that the theory should be more fully explored.

Based on my discussions with personnel who are familiar with or have first hand knowledge of the SALT samples, the most likely source of Hg would seem to be from minor contamination that occurred as samples were handled in the glove box environments. Very low levels of Hg are at issue. It is known that Hg electrical switches were present in the glove boxes - the contamination that would result from breakage of such a switch and the resulting unclaimed residue could easily account for the levels of Hg seen. Other sources such as Hg in glove materials, or traces of Hg in the pyrolysis reagents or pyrolysis apparatus materials seem less likely.

However, I continue to be concerned that the two DOR samples might in fact not contain mercury at all. Perhaps the presence of Hg is the result of an analytical problem/error. Before a massive restudy of the already pyrolyzed DOR samples is undertaken, if that were to be done, it seems vital to reanalyze the problem samples. This resampling and reanalysis should involve not only the Rocky Flats lab but also an independent lab such as that at Los Alamos.