Bomb-pulse chlorine-36 at the proposed yucca mountain repository horizon: an investigation of previous conflicting results and collection of new data

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Document Title: Bomb-pulse chlorine-36 at the proposed yucca mountain repository horizon: an investigation of previous conflicting results and collection of new data

Identify applicable affected page, section, paragraph, attachment, exhibit, table, figure, or other:
Change 1.0 Scope, objectives and subtasks as indicated below.

Pg 4; end of 1st paragraph (line 4) Add the following new paragraph:

Samples of soil collected from surface plots near Yucca Mountain thought to contain bomb-pulse Cl-36 may be collected and analyzed as a “control” to “validate” the Cl-36 analytical/chemical procedure (i.e., it is expected that some of these samples should contain relatively high concentrations or “hits” of Cl-36). The location of these site(s) will be chosen by the principal investigator but will likely be based on previous Cl-36 work. In addition, the principal investigator has the discretion to include other opportunistic samples, such as water recently found infiltrating the south ramp, which may facilitate reaching the objectives stated earlier.

Approved by:

Pt: [Redacted] Date: 3-23-05
(Signature)
Print name: James Cizdziel

QA Manager: [Redacted] Date: 3-24-05
(Signature)
Print name: Amy Smieciinski

QA Manager evaluated acceptability, that it does not violate quality requirements, and for impacts to other procedures; signature above documents this evaluation as successfully completed.

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Task Title: BOMB-PULSE CHLORINE-36 AT THE PROPOSED YUCCA MOUNTAIN REPOSITORY HORIZON: AN INVESTIGATION OF PREVIOUS CONFLICTING RESULTS AND COLLECTION OF NEW DATA

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1.0 SCOPE, OBJECTIVES and SUBTASKS

Previous studies by scientists at Los Alamos National Laboratory (LANL) and the United States Geological Survey (USGS) quantified $^{36}\text{Cl}/\text{Cl}$ to test for the presence of fast pathways at the proposed Yucca Mountain high-level nuclear waste repository. The goal of these studies was to determine whether or not fluids containing bomb-pulse $^{36}\text{Cl}/\text{Cl}$ traveled along fast travel pathways and reached the repository horizon, however, the two groups followed somewhat different procedures and produced conflicting results. The objective of this study is to attempt to determine the cause of the conflicting results and to obtain additional data to determine whether or not there are bomb-pulse isotopes at the repository horizon.

The chloride anion is one of the best and most widely used hydrological tracers. It is also widely distributed in nature and is found in all natural waters and rock formations. One of the isotopes of chlorine, $^{36}\text{Cl}$, is radioactive with a half-life of 301,000 years and can be used to date groundwater with ages up to one million years. Chlorine-36 is produced naturally in the atmosphere and the sub-surface and has a relatively consistent and small background. It is also artificially produced in nuclear reactions, and the amount of $^{36}\text{Cl}$ in the atmosphere increased significantly while above-ground tests of thermonuclear weapons were being conducted in the late 1950’s and early 1960’s. This pulse of $^{36}\text{Cl}$ can be used to trace and date young groundwater.

Yucca Mountain, the site for the proposed high-level nuclear waste repository, is located in tuff that contains fractures that vary in size and extent. These fracturing patterns have been considered in the conceptual model for fast pathways that could transmit recharge water from the surface into the repository horizon. The main motivation for the previous studies was to use bomb-pulse $^{36}\text{Cl}$, which appears to be an excellent tracer, to test for the presence of fast pathways. Ratios of $^{36}\text{Cl}/\text{Cl}$ greater than $1250 \times 10^{-15}$ in material coating rock sample surfaces (e.g., salts left behind from fracture flow) was interpreted to indicate the passage of bomb-pulse water less than 40 to 50 years old (Fabryka-Martin et al. 1997). Experiments conducted by the USGS and LANL yielded widely varying results. The $^{36}\text{Cl}/\text{Cl}$ ratios of Niche #1 core crushed and leached as part of the USGS study ranged between $226 \times 10^{-15}$ and $717 \times 10^{-15}$ and can be interpreted as containing no bomb-pulse $^{36}\text{Cl}$. However, $^{36}\text{Cl}/\text{Cl}$ ratios for core from the same boreholes crushed and leached at LANL ranged from $1016 \times 10^{-15}$ and $8558 \times 10^{-15}$, which can be interpreted to support the presence of bomb-pulse $^{36}\text{Cl}$. The differences in the results may be due to differences in the procedures used by the two groups, but initial attempts to determine the causes of the discrepancies (Chlorine-36 Validation Studies at Yucca Mountain, Nevada) were unsuccessful (TDR-NBS-HS-000017 Rev 00A). A number of “environmental factors” at the two laboratories have also been suggested as possible reasons for the differences. Chloride may be introduced into the leachate solution from sample surface coatings and pores and by dissolution from the rock matrix. The possibility also exists that chloride can be introduced into the samples during the preparation procedures. It should be noted that previous work by the USGS, LANL and Lawrence Livermore National Laboratory (LLNL) followed OCRWM-approved procedures.

We will conduct experiments to quantify $^{36}\text{Cl}/\text{Cl}$, $^{99}\text{Tc}$, and $^{129}I/^{127}I$ in select archived samples from the LANL and USGS studies (if available) and in rocks we collect from Yucca Mountain. The experimental design will consider lessons learned from previous studies. The
experiments will be designed to optimize our chances to identify bomb-pulse $^{36}\text{Cl}$, if one is present, and to aid in the identification of the causes that produced conflicting results in the previous studies. Results of $^{36}\text{Cl}/\text{Cl}$, $^{99}\text{Tc}$ and $^{129}\text{I}/^{127}\text{I}$ analyses will provide evidence as to whether or not young bomb-pulse water has infiltrated the repository site.

This work is subject to the University and Community College System of Nevada (UCCSN) Quality Assurance (QA) Program requirements. This Scientific Investigation Plan (SIP) represents, in part, an independent confirmatory study of previously gathered information.

### 2.0 APPROACH

**Samples:**

Archived samples from the USGS and LANL will be re-analyzed to the extent those samples are available. Samples will be selected based on location, lithology, and previous $^{36}\text{Cl}/\text{Cl}$ results. We propose to collect 50 to 100 new samples from locations in the Exploratory Studies Facility (ESF). Sample sites will be chosen based on previous results, lithology, and proximity to structures or features that indicate the potential for fast pathways. Samples will be collected from core produced by dry drilling or from material excavated from the walls of the ESF. Samples will be collected at least 1 meter deeper than rock exposed in the tunnel walls. DOE will provide equipment and manpower to drill or excavate for sample material. All sample collection for this project will be done in accordance with QAP-8.0 and QAP-8.1. Sample collection will be documented and described in a Scientific Notebook and samples will be stored at the SMF. Samples will be transferred using chain-of-custody procedures.

These sample materials will be used in leaching experiments, Br/Cl determinations, and inductively coupled plasma-mass spectrometry (ICP-MS) studies that will indicate optimum leaching procedures and will aid in selecting samples for $^{36}\text{Cl}/\text{Cl}$, $^{99}\text{Tc}$, and $^{129}\text{I}/^{127}\text{I}$ analyses. Based on the above number and including duplicates, spikes, reference samples and blanks approximately 200 measurements for $^{36}\text{Cl}/\text{Cl}$ will be made by accelerator mass spectrometry (AMS). AMS measurements will be made at the Purdue Rare Isotope Measurement Laboratory (PRIME) or LLNL. PRIME is expected to conduct most of the measurements whereas LLNL may be used to analyze a few splits for corroboration of PRIME results.

Select splits of samples and aliquots of leachates prepared in our Las Vegas laboratory will be taken to LANL in New Mexico and the USGS Laboratory in Colorado and stored and manipulated there similar to previous studies (as much as physically possible; the laboratory at LANL is no longer available and the hood has been used to expulse Cl gas for other experiments) and then analyzed for $^{36}\text{Cl}/\text{Cl}$. These samples will in essence be trip blanks and will help determine if there are environmental conditions during travel or at the LANL and USGS locations that may influence $^{36}\text{Cl}/\text{Cl}$ ratios. Another group of the same samples will stay in Las Vegas until ready for analysis by PRIME.

**Petrology and Chemical Analyses:**

Fracture surfaces and polished sections of samples will be imaged for Cl and other elements using a JEOL JSM-5600 Scanning Electron Microscope (SEM) and JEOL-8900 Electron Probe Microanalyzer, respectively. These analyses will improve our understanding of sinks for Cl on fracture surfaces and within the tuffs, and will aid in identifying sample material
for leaching studies. These analyses will also aid in determining appropriate leach times, and will help identify leached minerals in the rock matrix in experiments described below.

Leaching Studies:

A number of leaching studies are planned, including some to verify previous results of LANL and the USGS according to their procedures. If available, archived samples from both the LANL and USGS studies will also be analyzed using their methods. These experiments will answer questions about the applicability of the methods used by both laboratories. A series of time dependent leaching experiments will also be conducted, and leachates produced under different leach times will be analyzed for Br/Cl ratios and trace, minor, and major element concentrations using ICP-MS and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) or atomic absorption spectrometry (AA) analyses.

Bromide/Chloride ratios:

Leachates produced over a range of leaching times will be measured for Br/Cl ratios to determine when significant contributions of rock matrix Cl are made to the $^{36}$Cl/Cl ratio measurements. Ion chromatography (IC) will be used to make these measurements.

ICP-MS Experiments:

ICP-MS measurements for trace elements will be made on the leachates from the Br/Cl experiments. The major cations will be analyzed by ICP-AES, ICP-MS or AA. The data will be compared with the Br/Cl ratios to evaluate the degree to which matrix elements are leached under the conditions used by LANL and USGS.

Technetium-99 ($t_{1/2} = 2 \times 10^5$ years):

Technetium-99 is present in the environment primarily because of the atmospheric testing of nuclear weapons during the 1950s and early 1960s. It is present in aqueous solution as the pertechnetate anion, making it a good groundwater tracer. If $^{99}$Tc is found in the subsurface, it would be an indicator of the bomb-pulse, and thus associated with waters that are less than 40 to 50 years old. Technetium can be analyzed by ICP-MS with detection limits in the sub-part-per-trillion (ppt) range. We propose to analyze a number of rock and soil leachates by ICP-MS for $^{99}$Tc. Appearance of this isotope should coincide with elevated $^{36}$Cl/Cl ratios, indicative of bomb-pulse waters.

Iodine129/127:

Iodide, like chloride, is an excellent groundwater tracer and has an isotope $^{129}$I ($t_{1/2} = 1.7 \times 10^7$ years) that, like $^{36}$Cl, was enriched over background during atmospheric testing. Iodide can be analyzed by ICP-MS at ppt concentrations. Moreover, this heavier radioactive isotope can be determined in the presence of at least a $10^{12}$ excess of stable iodine, $^{127}$I, which constitutes 100% of the natural element. This mass discrimination is necessary in order to accurately measure the $^{129}$I/$^{127}$I ratio, which has a background value of about $10^{-12}$ and a bomb-pulse value of about $10^{-10}$, based on data reported for ocean surface waters remote from nuclear installations. We propose utilizing the ICP-MS to determine the $^{129}$I/$^{127}$I ratios in the same leachates, or leachates from replicate rock samples, used for $^{36}$Cl/Cl and $^{99}$Tc measurements. Thus, elevated ratios of $^{36}$Cl/Cl and $^{129}$I/$^{127}$I, and the presence of $^{99}$Tc, would provide irrefutable evidence for the presence of
young (bomb-pulse) water, although the absence of elevated $^{129}\text{I}/^{127}\text{I}$ and $^{99}\text{Tc}$ would not necessarily contradict the presence of bomb-pulse $^{36}\text{Cl}$.

Note: Experiments using radioactive material will be conducted in UNLV MSM 167 Radiation Laboratory and personnel conducting the work will be UNLV rad trained.

Contamination Control:

Samples will be handled using gloved hands and sealed and in labeled plastic bags. Sample processing (crushing) will be conducted in large plastic bag or other environment to minimize contamination. Equipment that comes in contact with the samples will be cleaned and rinsed in deionized water prior to use. Samples will be leached in a HEPA-filtered environment and leachates stored in sealed and labeled plastic bottles. Blanks will be collected when feasible to monitor contamination during processing and analyses.

Meetings:

Attempts will be made to hold quarterly meetings in Las Vegas to review current and future activities, discuss preliminary results and provide a forum for interested parties. We will invite scientists from the DOE, LANL, USGS and UCCSN QA task to participate.

3.0 SCHEDULE OF WORK

The following is the proposed sequence of work for this study. Since this work is dependent on cooperation with other entities some of the timing may change. However, most of the proposed activities are independent of each other so no impact on the outcome is expected.

The investigators will receive the appropriate training from the Yucca Mountain Project (to access the Nevada Test Site and ESF) and UCCSN QA Office. PRIME and possibly LLNL will be qualified as a supplier prior to conducting AMS measurements. Investigators will also consult with previous investigators from the USGS and LANL to discuss their procedures and availability of archived rock samples. Concurrently we will be developing ICP-MS procedures for $^{99}\text{Tc}$ and $^{129}\text{I}/^{127}\text{I}$. When we have obtained rock samples (archived and new) we will start evaluating leaching procedures. After leaching, samples will be analyzed for trace elements by ICP-MS in accordance with IPLV-009, bromide and chloride in accordance with IPLV-008 and major cations in accordance with IPLV-011. New IPLVs will be written for ICP-MS analyses for $^{99}\text{Tc}$ and $^{129}\text{I}/^{127}\text{I}$. Concurrent with leaching experiments, samples will be examined using the SEM and electron microprobe. The SEM will produce images that qualitatively indicate the spatial distribution of elements on a sample surface. Preparation of polished sections of the rock will be documented in a Scientific Notebook. Quantitative electron microprobe analyses will be collected in accordance with IPLV-015 and –019. A new IPLV will be written for electron microprobe standard verification.

Data will be submitted after a technical and QA reviews. The final report will be submitted within 60 days after the end of the project. Quarterly reports will be submitted during the course of the investigation. Finally, meetings will be held on quarterly basis (as discussed above).
4.0 INTERFACE CONTROLS

External Interfaces:
  Yucca Mountain Cooperative Agreement Contact: Institutional Affairs Office (DOE).
  DOE Technical Task Representative: Drew Coleman
  USGS: Jim Paces
  LANL: Robert Roback
  LLNL: Robert Finkel
  SMF: Chris Lewis

Internal Interfaces:
  Principal Investigator: Klaus Stetzenbach
  Investigators: James Cizdziel, Vernon Hodge, Jean Cline, Fred Phillips
  Analysts: James Cizdziel, Anna Draa, Caixia Guo, Kaz Lindley, Tatjana Jankovic

Meetings will be held with USGS and LANL to learn first hand about their work and procedures, to observe laboratory conditions, and gain input from previous investigators.

5.0 EQUIPMENT AND INSTRUMENTATION

The specific equipment used for each measurement will be documented in the scientific notebook or other QA record. Documentation will include the instrument manufacturer, model, and serial number as well as all applicable instrument manuals. The calibration, accuracy, and precision requirements for all equipment are to be described in the corresponding IP. Analytical instruments will be calibrated before each use (where applicable). All measurement and test equipment will be stored in a locked laboratory to prevent loss and tampering.

The Harry Reid Center for Environmental Studies (HRC) at the University of Nevada, Las Vegas, has a Dionex IC for analyzing anions (Br⁻ and Cl⁻), ICP-AES or AA for major cations, and three ICP-MS’s for the measurement of trace elements. One of these ICP-MS instruments, a high-resolution multi-collector instrument, will be used for the ¹²⁹I/¹²⁷I measurements. Other equipment that may be used includes analytical balances and pipettors. Balances and pipettors will be calibrated annually by Bechtel, an outside qualified source.

The UNLV Geoscience Department has a modern micro-imaging laboratory that includes a JEOL-8900 Electron Probe Microanalyzer and JEOL JSM-5600 Scanning Electron Microscope (SEM). These instruments will primarily provide images that qualitatively indicate the distribution of elements on sample surfaces and polished sections. The electron microprobe may provide quantitative Cl analyses for some samples.

The AMS that will be used for the qualified ³⁶Cl measurements is located at PRIME. PRIME will be qualified as a supplier prior to conducting measurements. LLNL may be making corroborative AMS measurements, or may also be qualified as a supplier.

6.0 STANDARDS and QUALITY CONTROL

For AMS measurements, backgrounds are determined by analysis of “machine blanks” and “chemistry blanks”. The former are samples that are known to have negligible radionuclide
content whereas the later are samples prepared to assess contamination from reagents and sample preparation steps. Blanks will run every 10 unknown samples. Chemistry blanks will be run as unknowns and the machine blank will be subtracted from the result. No formal decision has been made as to the numbers and frequencies of other QC samples, but accuracy and precision will be assessed for sample preparation and analysis and documented in the scientific notebook or other QA record and addressed in the final technical report. Preparation of samples, including QC samples, will be coordinated with PRIME prior to the leaching of the samples.

For techniques other than AMS, determination of precision and accuracy of the analytical measurements are described in each corresponding procedure. Precision will be addressed through the use of field and/or laboratory replicates. Accuracy will be evaluated using initial and continuing calibration verifications. All standards used must come from NIST, a qualified supplier, or the basis of acceptance reviewed and approved by the QA Manager in accordance with QAP-12.0 “Control of Measuring and Test Equipment,” before standards are used for quality affecting work.

7.0 SOFTWARE and MODELS

No software will be developed in this study. The software packages used in this study include 1) The analytical instrumentation software used for data acquisition, and 2) Spreadsheet software such as Quattro Pro or Excel for data reduction. Any macros used in Excel, etc. will be qualified and documented. Use of the analytical instrumentation data acquisition and spreadsheet software will be documented or referenced, along with the specific version used, in the instrument scientific notebook or other QA record. Control of electronic data is addressed in each IPLV that involves electronic data management, primarily instrument system IPLVs. No models will be developed for or used during this study.

8.0 PROCUREMENTS and SUBCONTRACTS

Calibration standards will be purchased directly from NIST or qualified vendors. The basis for acceptance of any standards that are not available from a qualified supplier will be documented in the scientific notebook. Polished sections will be prepared by Mark Mercer of Petrographic Services. Section preparation will be documented in the scientific notebook. LLNL and PRIME will be subcontracted for the various $^{36}$Cl analyses. Balances and pipettors will be calibrated annually by a qualified supplier.

9.0 IMPLEMENTING PROCEDURES and SCIENTIFIC NOTEBOOKS

Scientific notebooks will be maintained at the HRC and in Geoscience and will document measurements made in the respective departments. Each notebook will describe the IP(s) associated with the measurements. The IPs to be used for this task are listed below.

Existing IPs:

IPLV-001, “Rock Crushing”
IPLV-003, “Analytical and Top Loading Balance Use”.

IPLV-008, “Measurements of Anions in Water Samples by the Ion Chromatography System.”
IPLV-009, “Measurement of Trace Elements in Water Samples by the Inductively Coupled Plasma Mass Spectroscopy (ICP-MS).”
IPLV-015, “Electron Microprobe Analysis on the JEOL 8900-R”
IPLV-017, “Pipettor Use and Calibration Check.”
IPLV-019, “Carbon Coating Thin Sections for Electron Microprobe Analysis”

IP to be modified:

New IPs:  IPs for the leaching of chloride from rocks and for the determination of $^{99}$Tc and $^{129}$I by ICP-MS. The development of these procedures will be driven by Scientific Investigation Control, QAP 3.0, until the process becomes stable enough for the IP to be written. LLNL, LANL and USGS procedures will be studied for potential use in this work.

10.0 HOLD POINTS

There are no prerequisites or hold points associated with this task. Decision points associated with the analytical measurements are addressed by use of quality controls to indicate when there is an analytical or other problem which needs action described in the IPLVs.

11.0 DATA RECORDING, REDUCTION, AND REPORTING

When possible, data packages consisting of the hard copies of raw data generated from each instrument will be referenced by the analysis date and will be attachments to the scientific notebook. Data recording requirements for each scientific notebook are described in the corresponding IPLV. For the ICPMS results, a summary of data generated from instruments is exported to a spreadsheet (Microsoft Excel) where final data reduction is performed. A hard copy of the spreadsheet containing the reduced data will be included in the data package. For the $^{36}$Cl measurements, data will be transferred from PRIME or LLNL via a report containing details of the analyses, including associated QA information. If transferred electronically, the data will be zipped to document that there was no data corruption in the process. The final verified reduced data for submittal to the TDA will be controlled in accordance with QAP-3.1. If data is obtained that is unqualified, it will be used for corroboration only and no conclusions will rely solely on that data.

12.0 REVIEWS AND VERIFICATIONS

Internal verification of all data will be performed by someone other that the originator to check compliance to the procedures and to verify the accuracy of the data reduction. Internal technical review will be performed and documented on the data, scientific notebooks, all reports, and journal articles (non-deliverables) generated in this task. In addition, QA review will be
conducted on plans, procedures, data, scientific notebooks, and qualified reports. Any report of data generated without full internal verification will be labeled as “preliminary” data. Data review and verification will include the following: check for compliance with criteria described in each procedure and visual inspection and comparison of the data to be submitted to the TDA to that of the reduced data to ensure accuracy. Data will be acceptable when the data review and verification steps are successfully completed.

13.0 RECORDS AND DELIVERABLES

QA records are handled in accordance with QAP 17.0, “Quality Assurance Records.” Records designated as QA records in the UCCSN QAPs and IPLVs listed include but are not limited to:

1) Hard copies and/or electronic media containing raw and reduced data including calibration and QC results.
2) Scientific Notebooks including attachments.
3) Calibration and checks for each balance and pipettor used to collect or produce quality affecting data for this study.
4) Chain of custody forms.
5) Copies of quality affecting deliverables.

Deliverables are submitted to the HRC Administrative Task PI for submittal to DOE in accordance with the cooperative agreement and include but not limited to:

1) Qualified final technical report
2) Qualified reduced data used in technical reports will be submitted to the Technical Data Archive (TDA) in accordance with QAP 3.6, “Submittal of Data to the Technical Data Management System”.

14.0 REFERENCES

1) IPLV-003, “Analytical and Top Loading Balance Use”
2) IPLV-008, “Measurement of Inorganic Anions in Water Samples by the Ion Chromatography System”
4) IPLV-017, “Pipettor Calibration Check”
5) QAP-3.1, “Control of Electronic Data”
6) QAP-3.6, “Submittal of Data to the Technical Data Management System”
7) QAP-8.0, “Identification and Control of Items and Samples”
8) QAP-7.0, “Control of Quality-affecting Procurement and Receipt”
9) QAP-12.0, “Control of Measuring and Test Equipment”
10) QAP-17.0, “Quality Assurance Records”