MANAGEMENT OF MIXED WASTE GAS CYLINDERS AT LOS ALAMOS NATIONAL LABORATORY

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ABSTRACT

Proper management of mixed waste gas cylinders located at the Los Alamos National Laboratory required the identification and possible recontainerization of the contents prior to recycling or transportation and off-site disposal. Chem-Nuclear Environmental Services, Inc. (CNES) was charged with this task. This paper discusses the entire process step-by-step from collection of the cylinders from various sites at Los Alamos through to final disposition.

PROJECT OBJECTIVE AND WORK TASKS

Over a number of years, Los Alamos National Laboratory (LANL) accumulated approximately 3000 compressed gas cylinders located at various LANL sites. Proper management of these cylinders required the identification and possible recontainerization of the contents prior to recycling or transportation and off-site disposal. Cylinder contents ranged from inert gases to gases containing hazardous substances as defined under OSHA 29 CFR 1910.120(a)(3). Many of the cylinders had been exposed to weather for extended periods of time, causing some to be of questionable integrity due to corrosion. The inventory also included cylinders which were not DOT-rated.

Chemical Waste Management, Inc. (CWM) was selected by LANL to identify and dispose of the cylinders. CWM chose only one subcontractor, Earth Resources Corp. (ERC), to assist with this work. CWM-Tech Services Division provided the support for cylinder transportation and off-site disposal. Chem-Nuclear Environmental Services, Inc. (CNES), the federal services division of CWM, provided overall project management and health physics support including radiological screening for all gas samples. ERC supported cylinder inspection and content identification.

Procedures for the project were designed to: 1) provide for the safety of all personnel working at the site, 2) provide for the safety of all off-site personnel and the surrounding community during project operations, and 3) minimize the potential for environmental damage caused by project operations.

The objective of the CNES Los Alamos Gas Cylinder Project Team was to identify and recontainerize, if necessary, the cylinder contents and either recycle or dispose of the gases off-site at a permitted treatment, storage, and disposal facility. The following primary tasks for the project were set:

1) mobilization and set-up,

2) cylinder inspection and classification,

3) on-site cylinder transport and storage,

4) sampling and analysis of cylinder contents and possible recontainerization,

5) off-site cylinder transportation and disposal, and

6) demobilization at completion of the project.

MOBILIZATION AND SET-UP

No cylinder processing activities occurred until after the mobilization of personnel and equipment set-up were completed. Crucial equipment required for site operations included the following:

1) Cylinder Recovery Vessel and associated equipment,

2) Valve Sampling Trailer,

3) Vapor Containment Structure,

4) On-site Laboratory, and

5) Support Trailers (control, office, & decon).

The site was located on a flat, cleared area. The Vapor Containment Structure was set-up around the Cylinder Recovery Vessel trailer and the Valve Sampling Trailer. Sampling operations were performed in the Cylinder Recovery Vessel and Valve Sampling Trailer. Cylinders were stored in the Vapor Containment Structure prior to sampling. The purpose of the structure was to contain gases from possible leaking cylinders prior to sampling and/or recontainerization.

The CNES Project Team established control zones (Exclusion, Contamination Reduction, and Support Zone) to restrict access to the work area during operations.

CYLINDER INSPECTION

After mobilization was completed, the first phase of the cylinder project operations, the in-situ, visual inspection of each cylinder, was performed. The purpose of this inspection was to categorize the cylinders for segregation based on cylinder condition and the identifiability of the contents.

If available from Los Alamos, CNES obtained historical records for each cylinder indicating the purchase, storage and use of the cylinder, and whether or not the cylinder had been used in a common manifold with other gases which could have resulted in cross-contamination. Upon receipt of appropriate documentation from LANL, the CNES Project Team segregated those cylinders which were clearly identified, DOT-rated containers with standard, operable valves and were in good condition. Upon certification of cylinder contents by LANL, CNES evaluated the cylinder for on-site recycling or off-site disposal.

The inspection also compared external cylinder markings with cylinder and valve types to allow correlation of the cylinder body with its contents. The cylinder condition was also evaluated for stability during handling and transportation to the processing facility.

Categorization of the cylinders for sampling technique was largely a matter of judgment based on the likelihood of valve operation and cylinder integrity. An operable valve was mandatory for disposal. Further, the cylinder had to be safe for transportation and had to meet on-site transportation requirements. General criteria for such categorization included the following:

1) extent of corrosion (i.e. percent of cylinder affected and severity of affected areas),

2) general appearance of valve as seen through cap (i.e., corrosion of valve or other damage),

3) type of cylinder and valve, and

4) preliminary identification of contents.

Cylinders in good condition and transportable were selected for valve sampling operations. Others were staged for processing in the Cylinder Recovery Vessel. After cylinder inspection was completed, the CNES Team labeled each cylinder according to LANL transportation requirements. Based on visual inspection, each cylinder was classified to determine the handling, transportation, sampling, and possible recontainerization requirements for each cylinder.

CNES used the following nomenclature and criteria for detailed cylinder classification:

1) Unrestricted cylinders were in stable condition and suitable for handling and transportation. These were properly labeled, DOT-rated containers. The contents of these cylinders were certified by LANL. Unrestricted cylinders were not required to be sampled.

2) The Restricted classification of cylinders applied to those cylinders which were suitable for transportation and had external markings indicating stable contents. These containers were not necessarily DOT-rated containers. The major difference between this classification and the Unrestricted classification was the certification of contents by LANL.

3) Unknown cylinders were those which appeared to be suitable for transportation, but the contents were not readily identifiable.

4) Unstable cylinders were those whose poor condition may have rendered them unsafe to handle using standard techniques. This condition may have resulted from extreme corrosion, damage to the cylinder shell, valve integrity, or unstable contents (i.e. unstable hydrogen cyanide). Upon identification of any cylinder of this type, the immediate area was isolated from the remaining work area.

CYLINDER TRANSPORTATION AND DISPOSITION

CNES personnel followed various procedures and protocols outlining the regulations and coordination procedures for safely transporting the cylinders from the sites to the central processing area. The protocols included predeparture preparation, cylinder recovery, departure from the pickup location, and emergency response.

Radioactive cylinders were handled separately from the other containers. These cylinders were collected as a group and transported in accordance with applicable LANL regulations to the central processing area. Cylinders were then transported on an open flatbed truck and segregated for transportation according to general classification (flammable, corrosive, poison, etc.).

Cylinders were delivered to the cylinder staging area at the central processing facility. Processing consisted of: (1) loading cylinders onto the flatbed at the generating facility; (2) transporting to the processing facility; (3) temporary holding at the facility during processing; and (4) sampling, identification, and recontainerization (if required). At the end of each work day, cylinders sampled and/or recontainerized were removed from the processing facility and transported to another holding area prior to disposition. This holding area is a permitted RCRA storage facility. Mixed waste was stored at the interim status storage facility.

If the cylinder contents were acceptable for disposal at an off-site facility, the cylinder was packaged with other acceptable cylinders. The CNES Team then completed the proper shipping documentation. The current off-site facility can accept gas cylinders in the following classifications only: 1) Nonflammables; 2) Flammables; and 3) Freons. This facility is currently modifying its incinerator to accept cylinders in the following additional classifications: 1) Corrosives, 2) Toxics, 3) Pyrophorics, 4) Poisons, and 5) Poison

A. Radioactive or mixed gases will remain in storage at LANL until disposal facilities or treatment technologies are permitted. The metal from the cylinder carcasses was certified clean and properly recycled. Cylinder shells containing P-listed gases were triple-flushed prior to recycling/landfilling. Flush-water was appropriately handled as hazardous waste. The off-site facility provided certification of proper disposal to LANL/CWM.

CYLINDER SAMPLING

The CNES Project Team began cylinder sampling operations after the cylinders had been inspected, transported, and staged at the cylinder processing facility. Prior to sampling, the CNES Team reviewed chemical information pertaining to any suspect contents. Personnel were briefed on appropriate emergency actions to be implemented should an incident occur.

Valve Sampling

Valve sampling was completed in the Valve Sampling Chamber inside the Valve Sampling Trailer. The chamber provided a containment system in the event of cylinder or valve failure during sampling operations. The chamber was constructed of 1/2" steel plate with dimensions of approximately 30" X 30" by 6.5' in height. A lexan observation window was incorporated into the door so that operations could be monitored by a remote video system.

An emergency scrubber system consisting of molecular sieve and carbon adsorption units was attached to the sampling chamber. The air from the chamber was circulated through the dry scrubbers and back into the chamber.

The sampling room containing the chamber was isolated from personnel by a 1/4" thick steel barrier. The sampling control panel was located in the outer room. A secondary valve was attached to the target cylinder, providing a backup means of closing the cylinder should the primary cylinder valve fail. Immediately upon detection, leaks could be stopped or restricted. CNES personnel could detect cylinder leaks through the sample port in the chamber using portable instrumentation (Total Organics Monitor, Combustible Gas Monitor, etc.) or by observation through the installed closed-circuit television.

Each cylinder was moved individually into the chamber. The cylinder to be sampled was taken to a station immediately inside the sampling chamber and secured to the cap removal station. At this point, the cylinder cap was removed using chain wrenches attached to the body of the cylinder and the cap. The cap or the neck ring area (not part of the cylinder structure) was tapped with a non-sparking hammer to loosen any rusted threads. If the cap could not be removed without excessive force, as an option, the cap was cut off from the cylinder prior to valve sampling.

Upon removal of the valve cap, the valve was carefully inspected. To be considered for the remote valve sampling operation, the valve threads must have been in good condition and had an adequate sealing surface. Excessive valve corrosion was cause for rejection of the cylinder for valve sampling. Also, after the cap was removed, CNES personnel performed a thorough radiological survey on the valve area and threading. If the valve region was contaminated, the cylinder was removed and stored at the interim status mixed waste storage facility with other radioactive cylinders to be sampled on a batch basis.

A replacement cap was screwed onto the cylinder. The cylinder was then moved from the cap removal station to the remote valve opening station. The cylinder was attached to the opening stanchion, and the valving mechanism lowered onto and affixed to the valve.

The valve opening mechanism was a pneumatically actuated wrench containing adapters to allow it to fit various types of valves. The mechanism's control was operated from a remote location outside a secondary barrier.

Prior to connecting the cylinder, an inert gas purge was initiated. Once in position, a flow reducer (snubber) was attached to the CGA fittings of the valve during purging. This was, in turn, attached to a secondary valve which could be used should the original valve fail. After attachment to the remote sampling system, all personnel would leave the sampling room.

Sampling was directed from the remote sampling control panel. After all attachments were made, air and inert gas were withdrawn from the system and all lines purged with the inert gas. Prior to attempting to open the valve, a vacuum was stabilized and verified in all components of the sampling system.

At this point, the valve opening mechanism was actuated. Success of the operation was indicated by monitoring pressure in the sampling system. Valve rotation was shown on the video system. After rotation and pressure increase were noted, the valve was closed and the cylinder isolated.

The remote valve opener was constructed to permit maximum application of torque without over-stressing the valve. If this mechanism was incapable of opening the valve, the cylinder was removed and staged with other rejected cylinders to be processed in the Cylinder Recovery Vessel.

Cylinder Recovery Vessel Sampling

After a cylinder was positioned within the Cylinder Recovery Vessel, it was clamped in-place and the vessel hatch was closed. With all personnel evacuated, cylinder processing was performed from a remote location in the Control Trailer. General operational procedures for cylinder processing were as follows: 1) remove air from the vessel and verify integrity of system by monitoring for pressure increase; 2) recharge vessel with argon to slightly greater than atmospheric and monitor pressure for decay; 3) start drill and pierce cylinder; 4) stop drill; 5) record pressure and temperature; 6) sample gases in vessel and analyze; 7) recontainerize, dispose or vent gasses (at LANL direction); 8) induce vacuum in vessel; 9) purge system with argon and containerize or dispose (disposition based on analysis and LANL approval); 10) open vent; 11) monitor atmosphere inside containment chamber for contaminants using portable instrumentation and appropriate Draeger tubes or laboratory analysis; and 12) enter chamber, open vessel and remove empty cylinder and newly recontainerized cylinder (if applicable).

Included in the operation were controls to verify equipment functioning. The CNES Team monitored the entire operation by remote video camera. Pressure and temperature were monitored at numerous points in the process system. These systems allowed the CNES operator to control the process effectively.

After the contents of the cylinder were released into the vessel, a sample was withdrawn through a sampling port extending to the exterior of the vessel. An evacuated sample vessel attached to the port was opened to permit a small volume of the sample to enter. This vessel was removed and taken to the on-site laboratory for immediate analysis. Only after analysis was completed did CNES proceed with further operations.

Most compressed materials could be handled in the gaseous phase. Even compressed liquids were easily volatilized and recontainerized in the vessel through its vacuum system. The vessel system could, however, accommodate liquid withdrawal. To facilitate liquid removal, the vessel was movable through two axes. The target cylinder could be remotely inverted for liquid drainage. When liquids were handled in this fashion, a suitable purge solvent was employed to clean the system (typically freon or a mild caustic). Any hazardous or mixed waste generated from decontamination was collected and removed to a permitted or interim storage area at the end of each day.

Regulated hazardous materials released inside the recovery vessel were recontainerized for disposal or recycling. The vessel contents and contaminated purge gases were transferred to new DOT-rated containers which were labeled and staged immediately upon removal from the vessel trailer.

Controlled venting of the contents was an option suitable for inert or innocuous materials. Typically, these were common components of air. These atmospheric gases included air, argon, carbon dioxide, helium, neon, and nitrogen. The primary hazard associated with these gases was concentration in a confined area. Controlled and monitored venting permitted these gases to be released without further processing.

When the cylinder processing was completed, the open target cylinder was removed from the chamber and inspected to verify that it was empty. The cylinder was removed from the vessel to the outer containment chamber. A loose surface contamination survey of the vessel chamber was performed to ensure that the chamber met the appropriate release requirements.

The cylinder was then cut into halves with a power saw. Any remaining solid residue was removed, containerized and disposed of as required.

Sample Analysis

CNES performed chemical analysis at the on-site laboratory using two primary instruments: a Fourier Transform Infrared Spectrometer (FTIR) and a Mass Spectrometer (MS). The FTIR provided identification of most gases. Some gases (primarily elemental gases such as oxygen, nitrogen, etc.) could not be detected with the FTIR and required identification by the Mass Spectrometer. In each case, spectra generated were compared with the computer library of more than 13,000 gases. These analyses produced qualitative data from which the CNES Project Team could identify cylinder contents.

Identification of the chemical contents by this method took approximately five to ten minutes. During this time, the sample lines were purged with inert gas and discharged through a dry scrubber. After analysis, the sample cylinder was evacuated and purged.

The chemical analyses were performed prior to the radiological analyses. The FTIR and MS could become contaminated with radioactive isotopes; however, the instruments could be decontaminated to releasable limits. Performing the chemical analyses first prevented chemical reactions during the radiological analyses.

Samples of gas from each cylinder were passed through an absorption system designed to remove particulate matter suspended in the gas and dissolve the gas in solution. The filtered gas was then placed in a vial of liquid scintillation fluid to be counted in a Liquid Scintillation Counter. Levels of detection were dependent upon the sample volume, the radioisotope of interest, and the counting time. With a 45 minute counting time for each sample, the minimum detection limits for various isotopes are identified in Table I. A gas cylinder was considered contaminated if the count rate had a t-distribution number of standard deviations above background. Approximately 0.5% of the gas cylinders sampled exhibited activities greater than this limit. These cylinders were stored at the interim mixed waste storage site.

Gas cylinders which had been selected for disposition at LANL contained gases with different reactive and ab-

TABLE I

Radioactive Isotopes Minimum Detectable Activities

Nuclide	Gas	MDA
H^3	Organic	9.4E-08
H^3	H_2	7.2E-05
H^3	H_2O	6.3E-07
C^{14}	CO_2	2.2E-07
C^{14}	Organic	9.1E-08
P^{32}	Solid	2.4E-07
S^{35}	SO_2	2.6E-06
Kr^{85}	Kr	5.3E-06
I^{129}	Solid	2.4E-07
U^{238}	UF_6	2.4E-07
Pu^{239}	Solid	1.6E-08

sorption properties. CNES selected different liquid scintillation fluids based on the reactive and solubility properties for the gases at LANL. One of the problems the CNES Team encountered during this phase was the reaction between the gas and the scintillator cocktail. This reaction produced a chemiluminescent peak which did not fade after 24 hours as previous data for liquid scintillation counting had indicated. The chemiluminescent peak was most likely produced by a pH change. On the advice of Packard, CNES personnel added 100 μL of acetic acid to each sample exhibiting this peak. The peak would decrease in height after recount. Test specimens were run with H^3 and acetic acid to ensure the tritium peak did not decrease after acetic acid addition.

Another problem encountered with radiological sampling involved color quenching of samples which lowered the counting efficiency for each sample. The radiological sampling system was modified to include piping with teflon lining, reducing this problem. The last problem encountered with the radiological sampling of the gas cylinders was off-gassing of the gas after it had been passed through the liquid scintillation cocktail. The off-gassing encountered in the laboratory occurred while pippetting samples for the Liquid Scintillation Counter and more than likely occurred as a result of temperature increases. To prevent laboratory contamination, preparation of all liquid scintillation samples occurred in a fume hood installed in the laboratory.

SAMPLE AND EMERGENCY TREATMENT SYSTEMS

Three treatment systems were available on-site for emergencies and residual sample gases. The first system was the dry scrubber system used to mitigate the discharge of small volumes associated with the sampling process. The second system consisted of adsorbent canisters which were used to treat gases in the event of a cylinder leak inside the Valve Sampling Chamber, the secondary containment of the Cylinder Recovery Vessel trailer, or the Vapor Containment Structure. The dry adsorbent canister system was used a total of three times during the project to treat gases from leaking cylinders inside the containment structure. No release occurred to the environment as the gas was contained in the structure. The solid hazardous waste contained in the canisters was properly packaged and disposed of by LANL. The third system was a liquid impinging scrubber which was used for the emergency treatment of the excess gases in the event of overloading the adsorbent canisters.

DEMOBILIZATION

Currently this project is still underway. After the completion of the sampling activities, the CNES Project Team will begin demobilization activities. Objectives of demobilization include restoration of site conditions and removal of equipment and personnel.

Very little adhering contaminants will be collected as a result of operations involving compressed gases. Unless non-volatile contaminants are encountered, decontamination requirements for equipment will be minimal. Since the equipment is set-up on a LANL low-level radioactive waste disposal site, CNES will survey all equipment to verify that radioactive contamination levels are below LANL release limits.