MANAGEMENT OF WASTE COMPRESSED GASES AT THE LOS ALAMOS NATIONAL LABORATORY

Dan A. Nickens
Earth Resources Corporation

ABSTRACT

A major program for the management of waste compressed gases was undertaken by the Los Alamos National Laboratory. Excess cylinders accumulated over years of operation were collected and sampled. The cylinders were disposed of through off-site disposal facilities, recycling and reuse. The procedures employed by this program provide a standard for similar projects at other facilities.

INTRODUCTION

The Los Alamos National Laboratory is a research facility operated by the University of California for the Department of Energy. Since its inception in 1942, the laboratory has handled a variety of hazardous materials, including compressed gases. In 1990 a facility wide program was undertaken to manage compressed gases considered as excess to their user's requirements.

The objective of the program was to identify and properly manage cylinders containing compressed gases. The need for this service was originally identified by the Waste Management Group (HSE-7). This group had accumulated approximately four hundred waste compressed gas cylinders at a secure storage location.

The cylinders of concern were those owned by the laboratory. Cylinders which were leased by the laboratory could, in many cases, be returned directly to the vendor.

Historically, compressed gas users at the laboratory had purchased cylinders for their use. Under waste regulations, the laboratory became responsible for disposition of the waste gases.

In recent years it has become very difficult to manage regulated compressed gases. Environmental regulations have restricted past practices such as venting or on-site treatment. Unfortunately, there are very few commercial disposal facilities with appropriate permits and capability for handling waste compressed gases.

Rather than adopt a piece meal approach, HSE-7 decided to attack the entirety of the problem. A contract was let for a single source outlet to collect, sample, identify and dispose of these materials. Concurrently, notices were published to the technical groups at the laboratory advising users of the collection program. Health and safety considerations were of paramount concern in development of an acceptable program. Management of waste compressed gases pose special hazards which are peculiar to these materials. The potential hazards include all those which are associated with other chemical and radiological wastes. Additionally, there are hazards associated with the energy of compression and mobility of the materials when released.

A preliminary listing of the gases believed to be present at the storage location indicated the potential range of hazards. These gases included extremely toxic gases (such as arsine and nickel carbonyl), reactive gases (fluorine and chlorine trifluoride), unstable gases (tetrafluorohydrazine), pyrophoric gases (silane), radioactive gases (tritium), and corrosives (hydrogen fluoride and hydrogen chloride).

Most of the cylinders were in good condition. A significant number, however, were in a deteriorated condition. Some were in non-standard containers which did not meet regulatory criteria.

A preliminary concern for proper management of the cylinders was identification of the contents. Environmental and transportation regulations mandated that the cylinder contents be positively identified. For most of the cylinders, this meant sampling and identification of the contents.

Facilities were established on a remote area of the laboratory for processing of the cylinders. Sampling and analysis of the gases began in August of 1990.

PROCESSING FACILITIES

Specialized facilities were established for processing of the cylinders. These facilities included a vapor containment structure, cylinder sampling equipment, and an on-site laboratory. These were located in an isolated, secure area to provide additional protection against accidental releases.

The vapor containment structure was central to the processing effort. This structure consisted of a large temporary building (approximately 30' by 100', 15' in height). Cylinders were staged inside of the structure for processing.

Activities within the structure were monitored by several cameras.

The structure included several emergency treatment systems. A liquid impinging scrubber, activated carbon scrubber, and molecular sieve adsorbent canister were provided to treat the atmosphere inside of the structure in the event of a release. The vapor containment structure was sealed in order to capture and contain accidental releases.

Incorporated into the vapor containment structure was a valve sampling room. In this area those cylinders in good condition with operable valves were remotely sampled.

The valve sampling setup was similar to that shown on Fig. 1. The cylinders were placed into a containment chamber and attached to a remotely operated valve actuation mechanism. The containment chamber was attached to an emergency treatment system for use in the event of cylinder or valve failure and gas release.

For sampling operations personnel were isolated from the sampling chamber by a steel barrier. The operation could be monitored from a sampling panel through video monitors and pressure transducers.

Cylinders in poor condition or with inoperable valves were sampled using the patented Cylinder Recovery Vessel (or "CRV"). The CRV was specifically designed to remotely access cylinder contents in a inert, contained environment. Central to the CRV system is an ASME-rated pressure vessel. This is connected to vacuum and compressor systems. The entire unit is housed in a steel containment chamber. Figure

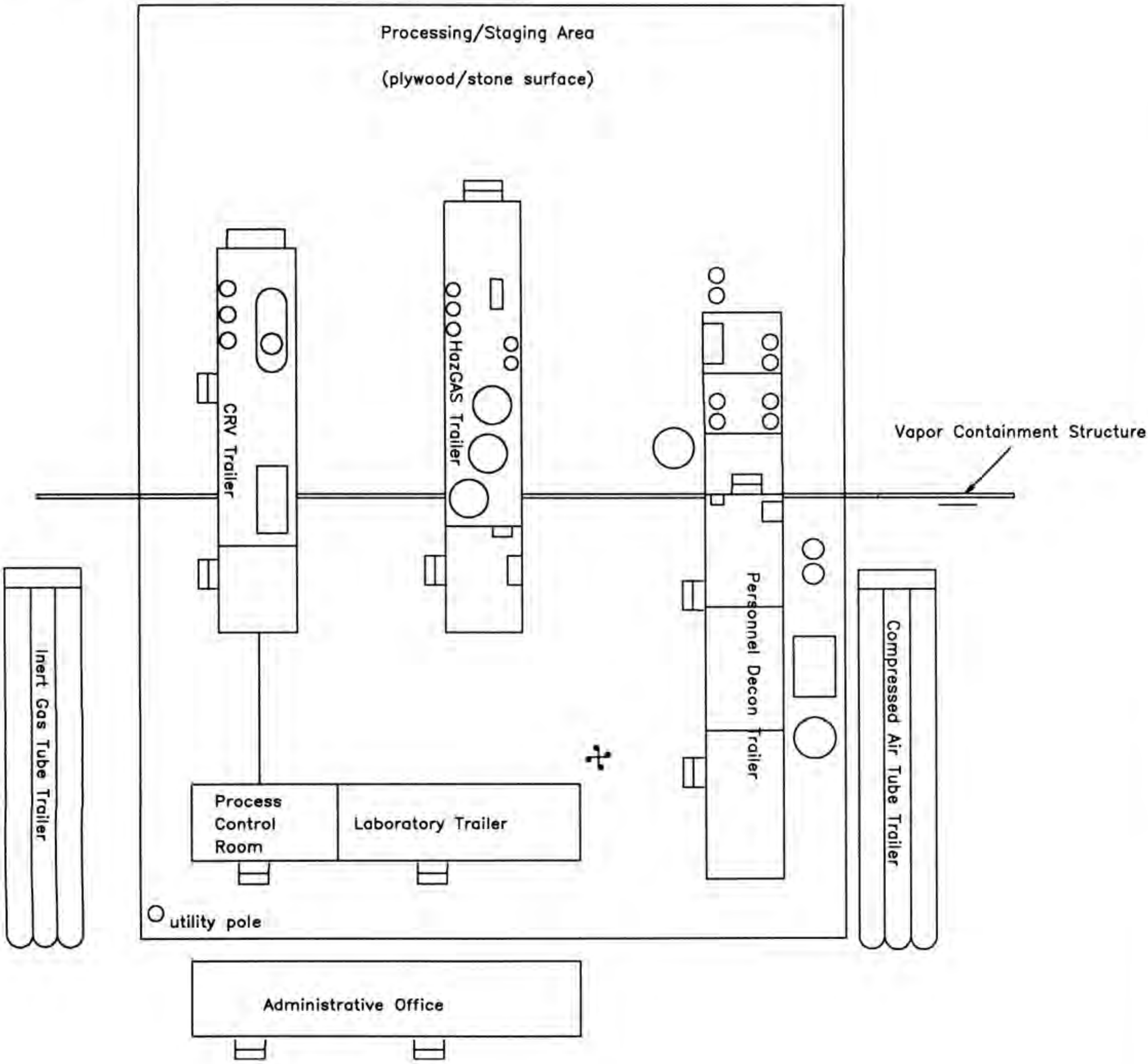

Fig. 1. Site layout.

2 shows principal system components. The unit is remotely operated from a control station.

The CRV allows samples of cylinder contents to be obtained remotely. Following identification, the gas is transferred into a new cylinder.

An on-site laboratory was located adjacent to the vapor containment site. The laboratory was equipped for radiological analyses and chemical identification.

Chemical analysis of cylinder contents was accomplished using a combination of techniques. The primary instrumentation used was a Fourier Transform Infrared Spectrometer (FTIR) and Mass Spectrometer (MS).

Following identification using these techniques, a small sample of the gas was dissolved in a compatible solvent. The solvent was placed in a liquid scintillation counter for detection of low levels of radioactive materials.

Other facilities at the site included an office trailer and personnel staging trailer.

INSPECTION AND TRANSPORTATION

The initial task required in the management process was inspection of the cylinders. The purpose of the inspection was to categorize each cylinder based on condition and suspected contents. This task was assigned to a Cylinder Inspection

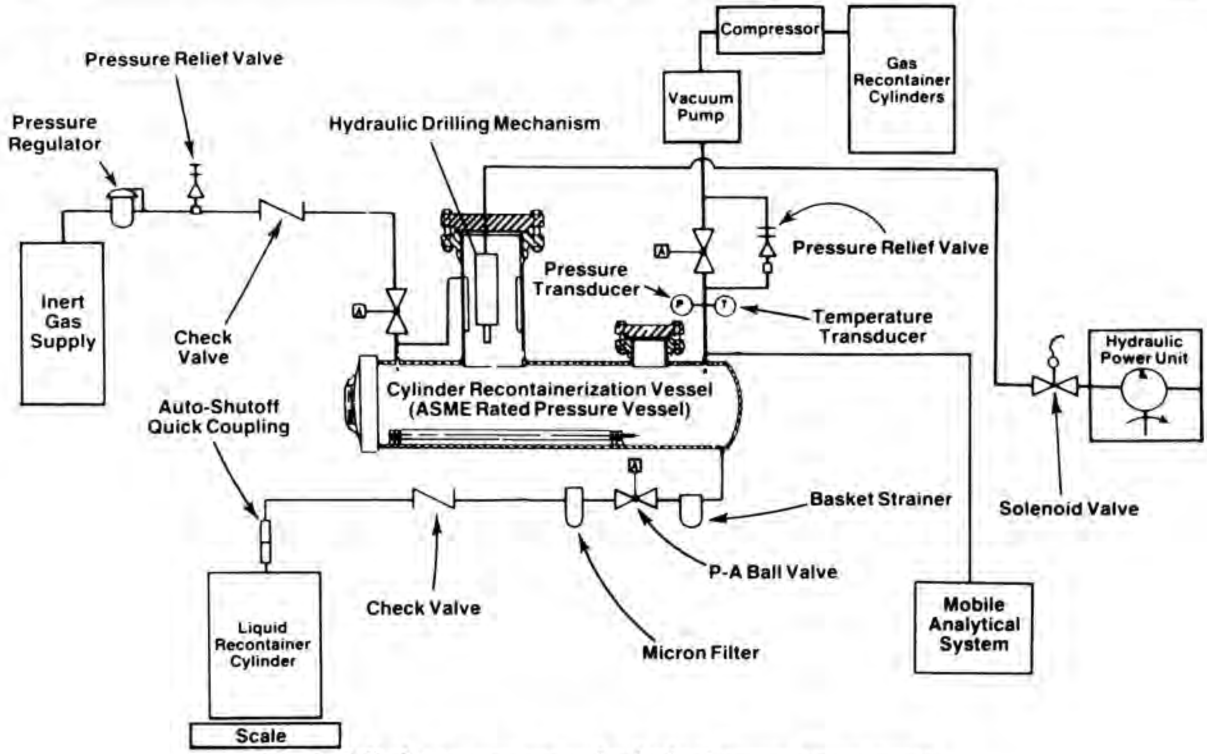

Fig. 2. Cylinder recovery vessel principal system components.

TABLE I

Representative Gases Identified At Los Alamos National Laboratory

Acetylene	Krypton
Arsine	Methyl Bromide
Boron Trichloride	Methyl Mercaptan
Bromotrifluoromethane	Molibdium Hexaflouride
Butane	Monoethylamine
C_{13} - Methane	Neon
Carbonyl Sulfide	Nitrogen 14 & 15
Cyanogen	Nitrosyl Chloride
Dibromodifluoromethane	Nitrous Oxide
Dichloro Silane	Octafluoropropane
Ethane	Oxygen Difluoride
Ethyl Chloride	Oxygen - 16 & 17
Ethylene	Phosgene
Flourine	Phospines
Fluoroform	Silane
Hydrogen Bromide	Silicon Tetraflouride
Hydrogen Chloride	Sulfur Dioxide
Hydrogen Deuterium	Sulfur Tetraflouride
Hydrogen Flouride	Trichlorofluoromethane
Hydrogen Sulfide	Zenon
Isobutane	

Team consisting of a Cylinder Specialist, a Health Physics Technician and an Emergency Coordinator.

Categorization of the cylinders was based on external characteristics and information supplied by the users. The four general categories used were: (1) "Unrestricted" - Standard DOT containers in good condition whose contents have been certified by the user; (2) "Restricted" - Labeled cylinders in good condition; (3) "Unknown" - Cylinders which are suitable for transportation but with no indication of contents; and, (4) "Unstable" - Cylinders in poor condition or with unstable contents.

Contents of unrestricted cylinders were identified based upon certifications of the users. To be acceptable for certification, several criteria has to be met, including: (1) the user had to have personal knowledge to its contents; (2) the purchase and usage history of the cylinder had to be documented; (3) the cylinder could not have been used in applications with other commonly manifolded gases; and the cylinder must not have been connected to a process in a manner in which it could become contaminated.

Initially only a few cylinders were certified. As a cost saving measure, a laboratory task team was organized to work with the users to document cylinder contents. In the latter stages of the project a significant percentage of the cylinders were accepted under this classification.

If the cylinder configuration and labeling was consistent with its certified contents, the cylinder was taken directly to a storage area for direct disposition. Based on inconsistencies between labeling and analyses, however, the Laboratory agreed to sample a representative number of the certified cylinders.

In addition to visual classification of the cylinder condition, the exterior was scanned for evidence of radioactivity. The Health Physicist completed a radiation survey and obtained a surface swipe for analysis.

Because the facilities at Los Alamos are spread out over a large area, the cylinders had to be collected and moved to the processing facility. Fortunately the transportation routes did not extend outside of Laboratory controlled areas. Regulatory prohibitions would have prevented transportation of unidentified gases over public roadways.

Transportation was accomplished using a specially modified truck. An emergency response crew accompanied the truck throughout the short trip to the processing facility.

SAMPLING AND ANALYSIS

More than fifteen hundred (1,500) cylinders were sampled during the course of the one year program. The variety of cylinder types and gases encountered posed significant challenges for both sample collection and analysis.

Of those sampled, most were accessible through the cylinder valve. A total of 1,316 cylinders (84% of the number sampled) were processed in this manner. Approximately two to three percent of the attempts to sample in this manner were unsuccessful due to valve failure.

The valve sampling system provided a mechanism for sampling all standard valves (those designated by the Compressed Gas Association, (CGA)). Because of the higher potential for failure, those cylinders with petcock valves (discontinued CGA 110 type), were not sampled in this manner. Cylinders with multiple valves were also excluded since this configuration could have resulted from failure of the primary valve.

In some cases cylinder valves were found to be leaking upon removal of the dust cap protecting the connecting threads. Because the caps were removed by workers using totally encapsulating suits with supplied air, there was no exposure to hazardous gases. Further, sampling was completed inside of the vapor containment structure which contained any release to the environment.

Failure of the cylinder valve to open was a typical problem. Although applying the maximum recommended torque, some valves would not actuate. Even where the valve handle rotated, there were cylinders where the contents could not be accessed. Because of the obvious safety concerns, an important part of the sampling operation was verifying that there was free access through the valve to the interior of each cylinder.

As expected, an incredible variety of gases were identified. Table I shows some of the gases and their characteristics.

Analytical results proved the prudence of the sampling program. At the mid point of the project, a survey showed more than forty five percent (45%) of labeled cylinders contained different or additional constituent gases. Ten percent (10%) increased in hazard classification based on sampling results.

Several extremely hazardous cases illustrate the problem posed by inadequate labeling of cylinders. An oxygen cylinder with standard medical post valve was found to contain radioactive tritium. Some cylinders configured for inert gases contained either poisonous or reactive gases.

Many of the cylinders and valves failed to follow standards of the Compressed Gas Association. For example, the CGA 540 oxygen valve was frequently found on cylinders containing a variety of other gases.

By the conclusion of the project, a total of two hundred and sixty-two (262) cylinders were processed through the Cylinder Recovery Vessel. Because of the relatively slow processing rate, CRV operations extended beyond valve sampling by several months.

Without the capabilities of the CRV, more than sixteen percent (16%) of the cylinders could not have been handled. Only the CRV was capable of managing the extremely powerful oxidizing gases commonly used at Los Alamos. The unique ability to manage these gases in a remote, contained process was crucial to the success of the project.

DISPOSITION OF WASTE GASES

The ultimate goal of the project was safe disposition of the compressed gases. The effort to dispose of the gases has initially met with mixed results.

Some of the cylinders were found to contain air or inert gases at atmospheric pressure. Where the cylinders were not reusable, they were decommissioned and disposed of in a landfill. Many of the cylinders were reclaimed by the gas plant at the laboratory for reuse.

Gases which were typically used by the laboratory were likewise recycled by the gas plant. These were generally common, innocuous gases such as nitrogen or argon.

Originally a permitted hazardous waste incinerator was slated for disposal of waste gases. Developmental and operation difficulties, however, delayed the facility in accepting most of the gases except for freons and inert gases.

A specialty gas manufacturer was approved for purchase and recycling of cylinders. This option is viable for any commercially available gas, except radioactive gases.

There is currently no identified outlet for radioactive gases.

HEALTH, SAFETY AND EMERGENCY RESPONSE

The cylinder management program was predicated upon principals of safety and environmental protection. The variety of hazardous gases and condition of cylinders posed significant challenges to these goals.

Engineering controls were instrumental in providing adequate safety for workers. As previously discussed, critical sampling operations were completed remotely.

Direct handling of the cylinders was completed in completely encapsulating, positive pressure suits with supplied air. Only after a cylinder's contents was identified was a lower level of protection authorized. Engineering controls were also in place for preventing accidental releases. All of the sampling apparatus had some manner of secondary containment. Further, the entire operation occurred inside a vapor containment structure. Emergency treatment equipment was available for accidental releases.

The effectiveness of these controls was clearly demonstrated in one of the two safety incidents which occurred in the course of the project. A cylinder which may have contained residual oxygen difluoride was removed from the CRV. When monitoring systems detected an atmospheric contaminant inside of the structure, emergency treatment systems were activated. Exterior monitoring of the structure found no detectable release to the atmosphere.

Personnel who had been working inside the structure in protective equipment were sent to the hospital as a precautionary measure. Examinations showed that there was no evidence of exposure.

One other safety incident of note involved the radiological analyses. During sample preparation, phosgene apparently degassed from a small vial of scintillation fluid. The laboratory was evacuated as a precautionary measure. Although there was no hazardous exposure to personnel, procedures were modified to provide for complete isolation of scintillation fluids.

CONCLUSION

The management of hazardous gases at the Los Alamos National Laboratory was a major step in dealing with problem material which had accumulated over fifty years of operation. The procedures demonstrably accomplished the goals of worker protection and environmental protection.

In August of 1991 the project was suspended for lack of funding. Despite its premature termination, significant progress was made towards identifying the full scope of the problem and acceptable means of managing it.

Procedures for management of these materials were thoroughly tested and evaluated in the course of the project. The lessons learned and success of the operation provide standards for handling compressed gases at other laboratory, governmental and industrial facilities.