02497

LA-UR-10-?????

Approved for public release; distribution is unlimited.

Title: Chemical Hazard Evaluation of Material Disposal Area (MDA) B Closure Project

Author(s): *J. C. Laul, C, William
*Safety Basis- Technical Services (SB-TS)
TA-21 Closure Project
Los Alamos National Laboratory
MS K 561, P. O. Box 1663
Los Alamos, NM 87545

Intended for: 2010 Safety Analysis Workshop, Knoxville, Tennessee
April 24-29, 2010

Los Alamos
NATIONAL LABORATORY
EST. 1943

Form 836 (7/06)

Chemical Hazard Evaluation of Material Disposal Area (MDA) B Closure Project

J.C. Laul and C. William*
Safety Basis –Technical Services
*TA-21 Closure Project
Los Alamos National Laboratory
jclaul@lanl.gov

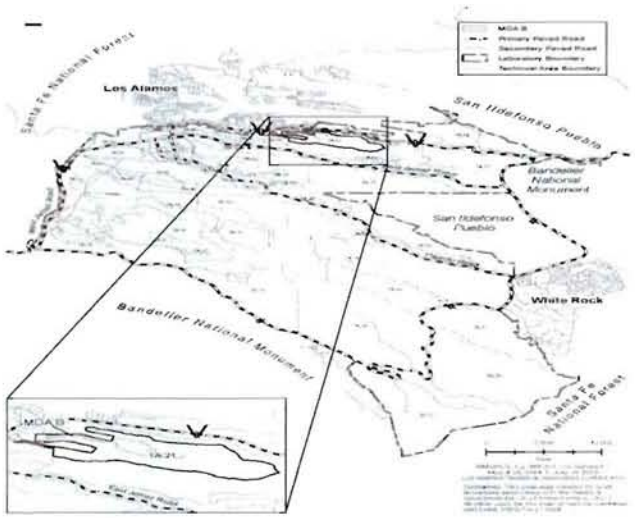
505-665-9791

LA-UR-10-?????

Purpose : TA-21, MDA-B (NES)

- Perform Chemical Hazard Categorization (CHC) of 170 chemicals disposed during 1944 to 1948 in "contaminated dump" landfill.
- Evaluate site history and properties of chemicals, which is very important in CHC.
- Perform Chemical Hazard Evaluation (CHE) of chemicals of concern; peroxide and beryllium.
- Public site boundary is only 20 m, which is a major concern for chemicals such as peroxide (explosion) & beryllium (chronic beryllium disease, CBD).
- These can be prevented or mitigated using EC and SMP to protect the involved workers, workers, and public.

Site Location and History



Los Alamos NNSA April, 2010

3

Site History: TA-21 MDA (B)

- Consists of shallow pits and/or trenches
- Length -1950 ft, Width – 75 to 300 ft
- Area 24,400 sq m or 6.03 acre
- Cover consists of soil, gravel, local asphalt (4-6 inches) and overburden (3- 5 ft)
- Closet distance to the public is 20 m (66 ft)
- Radionuclides – Tritium, Pu-239, uranium, Cs-137, etc, and various chemicals from process waste were disposed in 1940s by the experimental nuclear weapons and science programs.
- MDA-B was initially categorized as HC-3. Using segmentation approach, per DOE-STD-1027, the site was re-categorized as "Less than HC-3" or Radiological.

Los Alamos NNSA April , 2010

4

MDA (B): 170 Chemicals History and Hazards

- Chemicals: compounds, products or chemical reagents, spent or waste chemicals, non-flammable oils, mineral oils
- Some chemicals represented 6 months supply and many were in small quantities (1, 2, 5 lbs).
- Small volume of waste chemicals were disposed.
- Glassware and equipment that contained chemical wash rinses and chemical residues or wastes were disposed.
- Residual chemicals could be cleaning solutions , acids, bases, and experimental solvents at bench scale.
- Disposal of 55-gal drums was rare in 1940s. Unopened chemicals and valuable chemicals were not disposed.
- Based on historical record and best engineering judgment, expected disposal was at best 5% of the chemical inventory.

MDA (B): Chemicals History and Hazards

- Three major fires: each for about two hrs
  - 1946 due to chemical reactions
  - 1947 due to trash (papers, rubber gloves, etc)
  - 1948 due to combustion of mixed chemicals
- These fires produced intense heat and propagated heat within landfill
  - Some chemicals converted to oxide form (stable).
  - Some chemicals degraded or evaporated due to their low BP (e.g., organics – acetone, benzene, ether, toluene, etc).
  - Many chemicals degraded over 60 yrs because of limited shelf-lives.

Properties of Volatile Chemicals with High VP

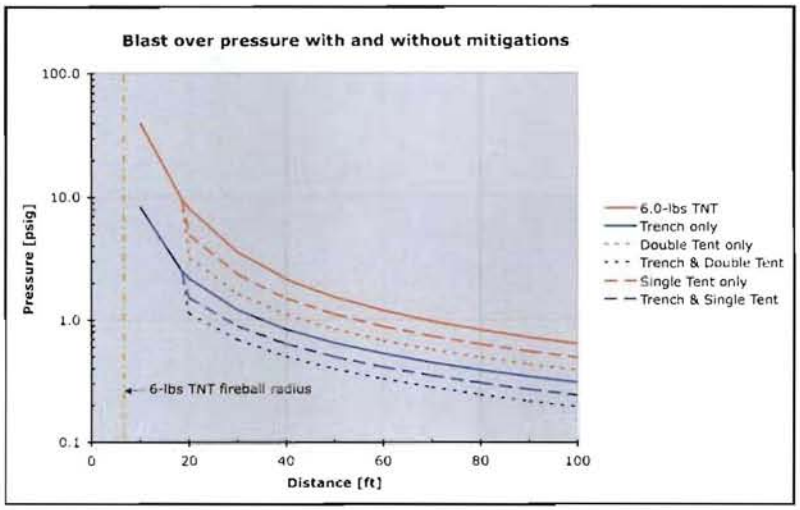
Chemical CAS #	Mol. Wt.	VP mm Hg	BP & Density	Comment
Nickel carbonyl 13463-39-3	135	400 at 26 °C	B.P= 43 °C D=1.32 g/cc	Liquefied gas, flammable, explodes at 60 °C. Reacts in air or water to form nickel oxide
Hydrochloric acid Conc.(42%); 7647-01-0	36.5	709 at 20 °C	B.P= -85 °C D = 1.27 g/cc	Colorless gas or fuming liquid, suffocating odor, soluble in water.
Ammonium-hydroxide (28%) 1336-21-6	35	556 at 21 °C	D = 0.891 g/cc	Liquid and vapor extremely irritating to eyes
Ethyl Ether 60-29-7	74	442 at 20 °C	B.P= 34.5 °C D = 0.715 g/cc	Liquid, volatile, burns, slightly soluble in water, forms peroxide (shock sensitive) with sodium dichromate
Acetone 67-64-1	58	180 at 20 °C	B.P= 56 °C D = 0.792 g/cc	Liquid, volatile, flammable, miscible with water

These chemicals with high VP and low BP have degraded or evaporated during major fires

Shock-Sensitive Chemicals: Ether Peroxide Crystals

- Ether was used in Plutonium and uranium purification.
- Ether has mostly degraded or evaporated during fires.
- Ether forms peroxide crystals with sodium dichromate.
- Peroxide crystals are shock-sensitive and may cause explosion .
- Bounding hazard: Assume 9-L ether bottle; forms 10% peroxide solution with oxygen (15%) from soil; yields 6-lb TNT explosion
- MacAfee et al (2008) calculated that a fragment of size 1/4 in x 1/4 in x 1/2 in with initial velocity of 1 km/s remains hazardous up to about 54 ft.
- Thus, a 60 ft blast zone is a safe distance for workers

Blast Over Pressure with & without Mitigation



Chemical Hazard Categorization (CHC)

- A facility CHC is based on comparison of maximum expected TQs based on PAC-3 (AEGL/ERPG/TEEL-3) levels as function of distance.
- PAC-3 is "the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing life-threatening health effects"
- TQs for about 3200 chemicals are posted on LANL Safety basis website, using PAC-3 Rev 24 values.

Hazard Type	High	Moderate	Low
Chemical	The TQs calculated consequences is > PAC-3 at the nearest site boundary (SB) for public	The TQs calculated consequences is > PAC-3 at 100 m and < SB	The TQs calculated consequences is < PAC-3 at 100 m

MDA (B) Site CHC

- SB for public is only 20 m, 5 times < than 100 m, which is unusual situation
- TQs at 20 m (public) is about 10 times lower than TQs at 100 m for the workers.
- Three chemicals: nickel carbonyl, hydrochloric acid (42%), and ammonium hydroxide (28%) exceed TQs at 20 m, indicating a **High** hazard site. But, these chemicals being highly volatile (high VP, low BP) have mostly degraded or evaporated by three major fires and over 60 yrs duration
- Next step is to compare the inventory with the TQs at 100m. None of the chemicals exceed TQs at 100 m
- Thus, MDA (B) site is a Low Chemical Hazard Site.

Beryllium (Be) Exposure to Workers and Public

Be inventory = 1 lb, screened out. Because of health hazard of sensitization and CBD, it is evaluated in a fire scenario.

	Be-powder/ chips	EPIcode, V 7.0	
MAR ARF ST	1.0 lb 2.35E-5 2.35E-5		
Parameters	Wind speed 1.5 m/s (h=10m); Stability class F; Release ht 0 m; Terrain std; deposition velocity 0.3 cm/s; plume centerline		
Conc.	mg/m^3		
30 X-meter	**5.2E-5 (lofting)**	χ/Q s/m^3, (30 m)	4.4E-3
100	**3.2E-4**	χ/Q s/m^3, (100 m)	2.7E-2
300	4.4E-5	ERPG-3 (mg/m^3)	1.0E-1
500	1.5E-5	ERPG-2 (mg/m^3)	2.5E-2
1.000	3.7E-6	ERPG-1 (mg/m^3)	**1.0E-2**

Beryllium (Be) Exposure to Workers and Public

- Be conc. (mg/m^3) at 100 m and 30 m (20 m, public) are 2 to 3 orders of magnitude lower than the ERPG-1 value of 0.01 mg/m^3, thus no concern for the workers or public.
- EPA 40 CFR 61 has set Be air emission std of 0.01 $\mu g/m^3$, to protect the public (no CBD). This emission limit is averaged over a 30-day TWA, which is equivalent to 28.8 $\mu g/m^3$ in a 15 min TWA.
- Be conc. of 0.052 $\mu g/m^3$ at 20m (public) is 2 to 3 orders of magnitude lower than 28.8 $\mu g/m^3$; implies that public is well protected, and also non-involved workers at 100 m.
- For involved workers, occupational TLV is 2.0 $\mu g/m^3$. But, 10 CFR 850 requires a protection level exposure at 0.2 $\mu g/m^3$ by personal monitoring to further prevent any potential CBD through SMP.

Conclusions :

- MDA- B (NES) is the "contaminated dump," with radionuclides & chemicals from process waste disposed during 1940s. About 170 chemicals disposed might have been products, unused and residual chemicals, spent, waste chemicals, non-flammable oils, mineral oil.
- MDA-B was considered a **High** hazard site. However, based on historical records and best engineering judgment, the expected chemicals disposed are probably at best 5% of the inventory.
- Low inventory coupled with 3 major fires and limited shelf-life over 60 years made it from High to **Low** chemical hazard site. Thus, knowing the site history and physical and chemical properties are very important in characterizing a NES site.
- Public SB is only 20 m, which is a major concern. Peroxide during remediation can cause explosion up to 54 ft. Thus 60 ft blast zone as EC is used to protect the workers.
- Be conc. are 2 -3 orders of magnitude lower than ERPG-1, thus no concern for public and non-involved workers. For involved workers, SMP such as PPE, Be monitoring program and controls are adequate.

Chemical Hazard Evaluation of Material Disposal Area (MDA) B Closure Project

J.C. Laul* and C. William
*Safety Basis-Technical Services, Los Alamos National Laboratory
TA-21 Closure Project, Los Alamos National Laboratory
MS K561, P.O. Box 1663, Los Alamos, NM 87545
jclaul@lanl.gov, 505-665-9791
LA-UR-10-00242

Technical Area -21, Material Disposal Area (MDA) B is a buried waste site, a 1940s landfill known as the "contaminated dump," with radionuclides and chemicals from process waste disposed during 1944 to 1948. The abstract focuses on chemical hazard categorization (CHC) and hazard evaluation of chemicals of concern (e.g., peroxide, beryllium).

About 170 chemicals might have been disposed in the landfill. Chemicals included products, unused chemicals, spent, waste chemicals, non-flammable oils, mineral oil, etc. Storing or disposing chemicals, including valuable chemicals, in landfill was not considered. Glassware and equipment that contained chemical wash rinses and chemical residues or wastes were apparently disposed in MDA B. Residual chemicals might have been cleaning solutions, acids, bases, and experimental solvent at the bench scale. Chemical containers were either partially used reagents, or empty with some residues. Based on historical records and best engineering judgment, the expected chemical contents are probably 1-3 % and at best 5% of the chemical inventory (conservative estimate).

There were three major fires for ~ 2 hrs each in 1946, 1947, and 1948. The fires undoubtedly produced intense heat that propagated within the landfill, where many chemicals could have oxidized, degraded or evaporated due to their low boiling point (organic chemicals – acetone, ether, benzene, toluene). Many chemicals most likely degraded over 60 years because of limited shelf life. Volatile chemicals such as nickel carbonyl, hydrochloric acid, and ammonium hydroxide, with high VP and low FP or BP would have easily degraded or evaporated due to heat in a fire scenario. Thus, over 60 years, their contribution is negligible.

A facility CHC is based on the comparison of expected quantities to TQs based on PAC-3; AEGL/ERPG/ TEEL-3 levels as a function of distance: **Low** hazard if the chemical quantity is < TQ at 100 m; **Moderate** if the quantity is > TQ at 100 m; and **High** if the quantity is > TQ at the site boundary (SB) for the public. The SB is typically higher than 100 m. However, the MBA SB is only 20 m, which presents an unusual situation. The TQs at 20 m for the public are about 9.4 times < TQs at 100 m for the workers. Three chemicals; nickel carbonyl, hydrochloric acid, and ammonium hydroxide exceed TQs at 20 m, which will make MDA-B a **High** hazard facility. However, these chemicals, being volatile have either evaporated or degraded. When compared with the TQs at 100 m, none of the chemicals exceed at 100 m, which makes the MBA B a **Low** hazard chemical site. Thus, knowing the site history and physical and chemical properties are very important in characterizing a disposal site.

Chemicals of concern during the excavation operations are peroxide that can cause potential explosion and beryllium exposure because of its sensitization and CBD properties. These can be prevented or mitigated using EC and SMP to protect the involved workers and public. Details will be presented at the meeting.