Conducting School Chemical Cleanouts

A Training for the Nebraska SC3 Program Dave Waddell Waddell Environmental LLC Project Manager - Rehab the Lab

Goal 1. Keep you out of trouble



Goal 2. Keep You Awake



Goal 3. Keep it light



Legacy Chemicals What's the Issue?

- October 1957 Sputnik launched
- The U.S. panics
- By 1960: \$4,000,000,000 in grants to schools for science
- Schools buy hazardous science lab chemicals by the case
- They're still there!



High Risk Chemicals in Schools

Peroxide Forming Chemicals & Explosives

Potassium, Ether, Dioxane, Tetrahydrofuran, Picric Acid, Sodium Azide, Perchloric Acid, Di- and Tri-nitro Organics

Water and Air Reactives

Potassium, Sodium, Lithium, Calcium Carbide, White
 Phosphorus, Lithium Aluminum Hydride, Sodium Dithionite

Corrosives

- Hydrofluoric Acid, Perchloric Acid, Bromine, Nitric Acid
- Carcinogens and Severe Toxins
- Arsenic, Cadmium, Chloroform, Formaldehyde, Potassium Dichromate, Mercury & Cyanide compounds, Phenol

High Hazard Chemicals

Explosives

Water and Air Reactives
High Hazard Corrosives
Poisons via inhalation and touch

Explosive Chemicals

- Peroxide-formers
- Nitro organics
- Organic peroxides
- Contaminated compounds (unfortunate mixtures)





Nitro Organics

- Tri<u>nitro</u>tolu<u>ene</u> (TNT)
- 2,4-Dinitrophenol
- Trinitrophenol (Picric Acid)
- Metal <u>Picr</u>ates



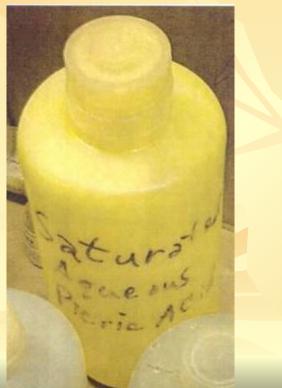


Picric Acid – Trinitrophenol (Constituent of Bouin's Fluid)

Shock-sensitive high explosive when dry or especially in contact with metals (like the cap below)
Found in medical labs (stains brain cells) and schools









Hand-written word "Nitro" In middle school

GLYCERINE

FOR MANUFACTURING USE ONLY

Reported By

WASHINGTON

COMPA

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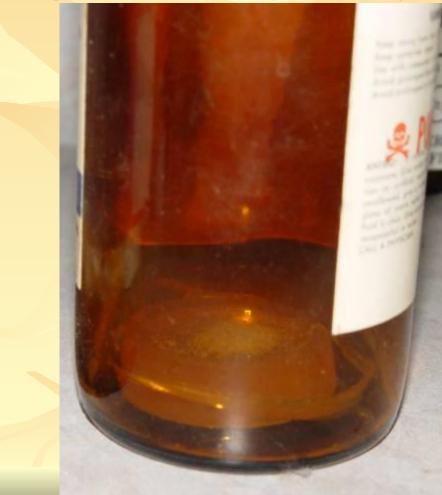
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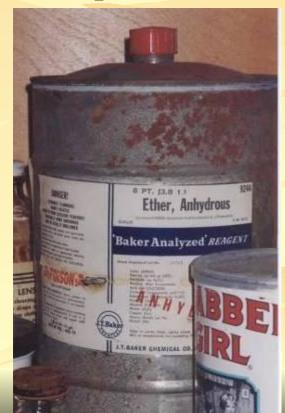
Collodion = ether + nitrocellulose high haz when dry



Peroxidizable Solvents

- Peroxides form in reaction with oxygen (auto-oxidation)
- Can test solvents for peroxides, if >100 ppm = peroxidized
 Need to label them with date opened

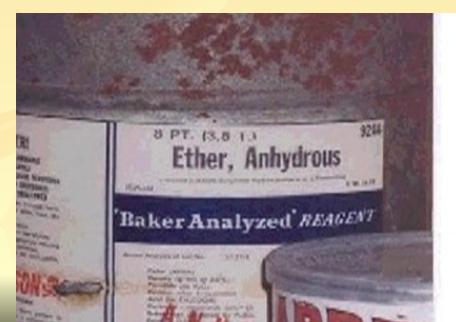






Some Peroxidizable Solvents I've Seen

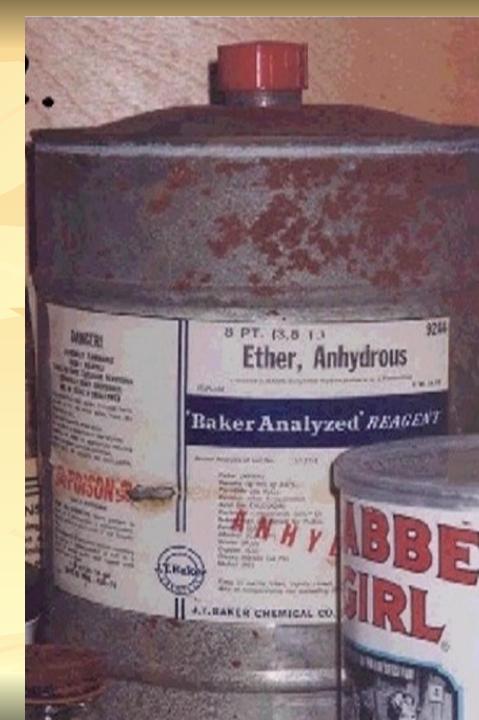
- Peroxides w/o concentration
 - Isopropyl Ether
 - Potassium Amide
 - Potassium Metal
 - Sodium Amide



Peroxides if concentrated by evaporation & distillation

- Acetaldehyde
- Benzyl Alcohol
- Cyclohexene
- Diethyl Ether (Ethyl Ether)
- Dioxane
- Methyl Isobutyl Ketone
- Tetrahydrofuran
- Vinyl Ether

Isopropyl and Ethyl Ethers = Peroxide formers



Isopropyl ether crystals from bottle in preceding photo - exposed to sunlight

Exploding isopropyl ether peroxide crystals (auto detonated)

A Note on Petroleum Ether

- Very common solvent
- NOT explosive
- NOT a true ether
- More like paint thinner



Potassium Metal Peroxide Former & Water Reactive







Potassium Metal (K₂) – Color Key

- Silver Potassium metal -Water Reactive
- White P. Hydroxide corrosive & H2O reactive
- Yellow/Orange P. Superoxide
 - Water reactive, corrosive, unstable
- Red P. Ozonide Highly reactive, explosive



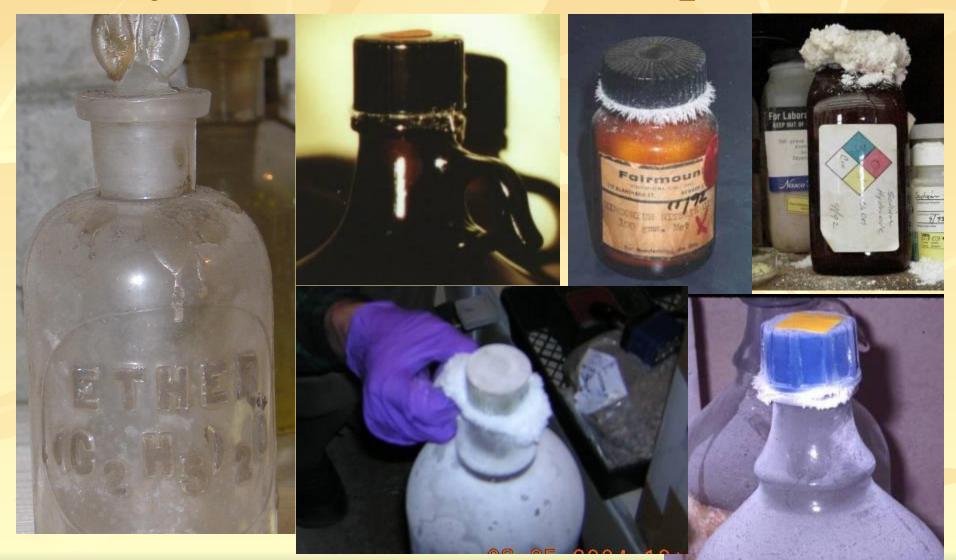
Identifying Potential Explosives the wrong way! What happens when peroxidized ether is distilled

ALUE .

ID-ing Potential Chem Explosives

- Most will be stored in the flammables cabinet
- Never touch the cap of an unexamined bottle
- Carefully move bottles to see labels
- Crystals on acid bottle is normal, crystals on brown glass bottle may be explosive peroxides
- Look on Chemical List for words "Explosive" "Explodes" "Bomb squad"

Crystals on Bottles – Explosive?



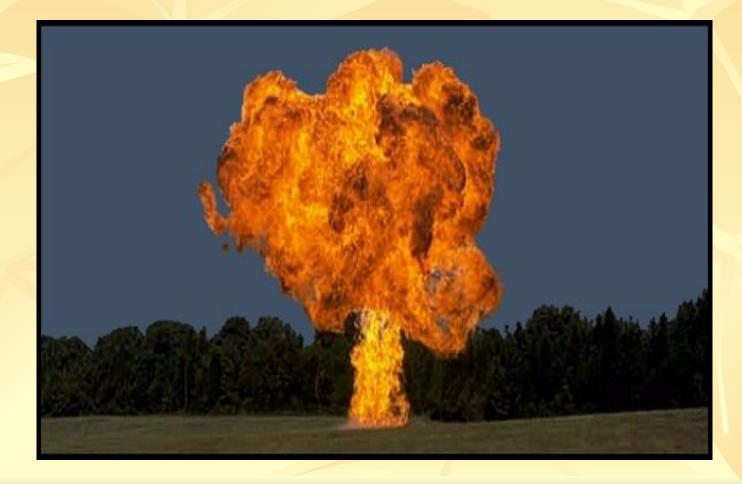
Explosive Crystals?, Nope,

Avaronet

Tetrahydrofuran

Highly explosive peroxide crystals. Crystals on acid bottle, no big deal. Crystals on solvent cap, assume explosive & don't touch!!!

Three 5 gal. containers of peroxidized Tetrahydrofuran



What's in a name? May be clues to a compound's nature

- Dinitro-, Trinitro- = explosive if organic
- Nitrate, chlorate, bromate = oxidizer
- Per = oxidizer <u>if inorganic</u>
 - <u>Per</u>chlorate, <u>per</u>manganate, <u>per</u>oxide, <u>per</u>sulfate, <u>per</u>borate
- Chromate, Dichromate = toxic, oxidizer
- Sulfide, cyanide = poison gas if acidified
 - Note, cyanates aren't cyanides, lower risk

High Hazard Chemicals

- Explosives
- Water and Air Reactives
- High Hazard Corrosives
- Poisons via inhalation and touch

Water and Air Reactives

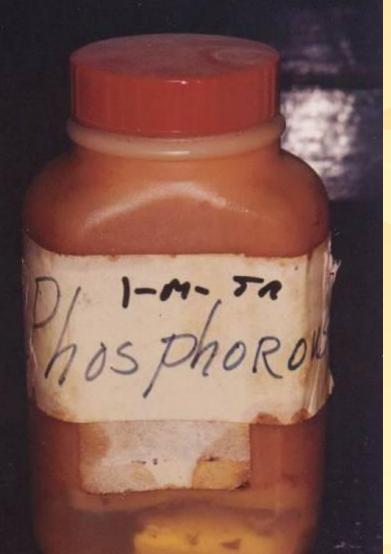
- Air reactive = Phosphorus
- Highly water reactive
 - Lithium metal (less than other three)
 - Sodium metal
 - Potassium metal
 - Calcium carbide (miner's lamp)
- Moderately water reactive
 - Calcium metal
 - Magnesium metal

White Phosphorus

- Pyrophoric (air reactive)
- Stored under water
- If water drops below sticks
- Spontaneously ignites in air



Yellow Phosphorus – air reactive





6616

1/4 LB.

CAUTION: Federal law prohibit dispensing without prescription. AALLINCKRODT CHEMICAL WORKS ST. LOUIS • NEW YORK • MONTEEAL POISON

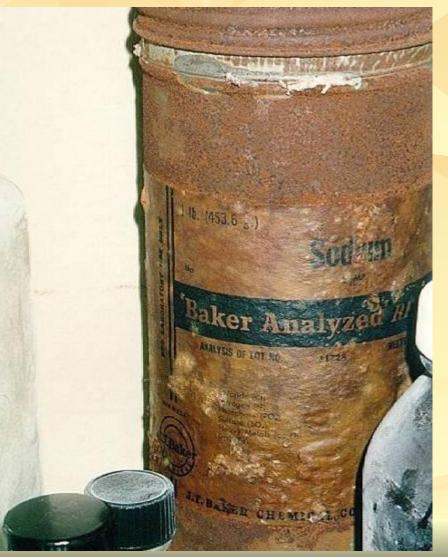
Red Phosphorus

- It's on the side of safety match boxes
- Poisonous
- Not pyrophoric
- Flammable solid





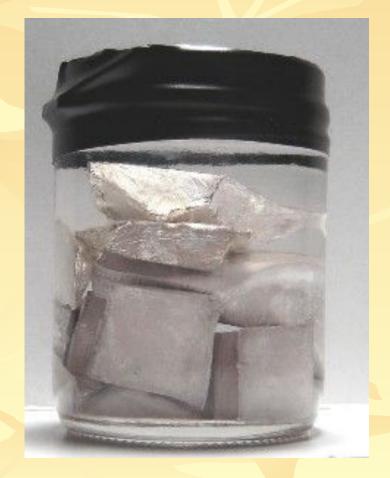
Sodium Metal highly water reactive





Sodium – Safe Amount in Storage

- Flinn Scientific is chemical supplier for many schools
 Good safety record
 They sell sodium and potassium in small can with 5 pieces
- Safest way to buy and store these



Calcium Carbide reacts with water to make acetylene (welding) gas





High Hazard Chemicals

- Explosives
- Water and Air Reactives

High Hazard Corrosives

Poisons via inhalation and touch

Perchloric Acid

Highly corrosive Reacts violently w/ solvents Incompatible with metals Forms explosive salts Oxidizes organic materials like wood Shelves are made of wood and metal



Chemical Clues in Acid Cabinet

- Note plastic bottle
- Note white flakes on adjacent bottle
- What's going on here?



Hydrofluoric Acid

Anesthetic: acid doesn't burn on contact

- Deep tissue and bone disintegration
- Extreme pain, can cause gangrene, amputation
- Highly corrosive, dissolves glass
- Used in Art & Chem classes for glass etching



Hydrofluoric (HF) Acid Spill 1995 Tech spilled 200 mls of HF on both thighs. Burns to 9% of his body, despite washing his legs No calcium gluconate gel was applied Contaminated clothing not removed during rinse Right leg was amputated 7 days after the incident. Died from multi-organ failure 8 days later.



High Hazard Chemicals

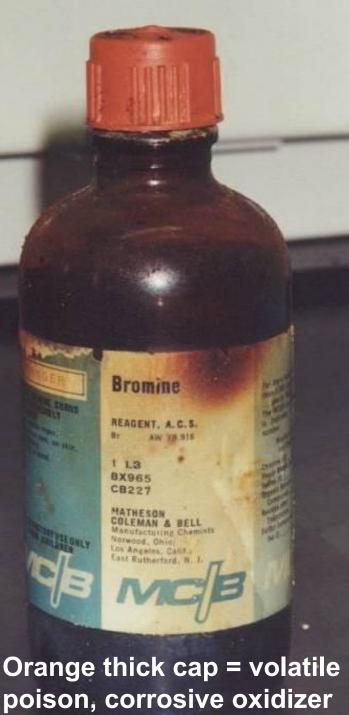
- Explosives
- Water and Air Reactives
- High Hazard Corrosives
- Poisons via inhalation and touch

Skin Contact Toxins



Bromine

Evaporates at room temp
Highly corrosive
Powerful oxidizer



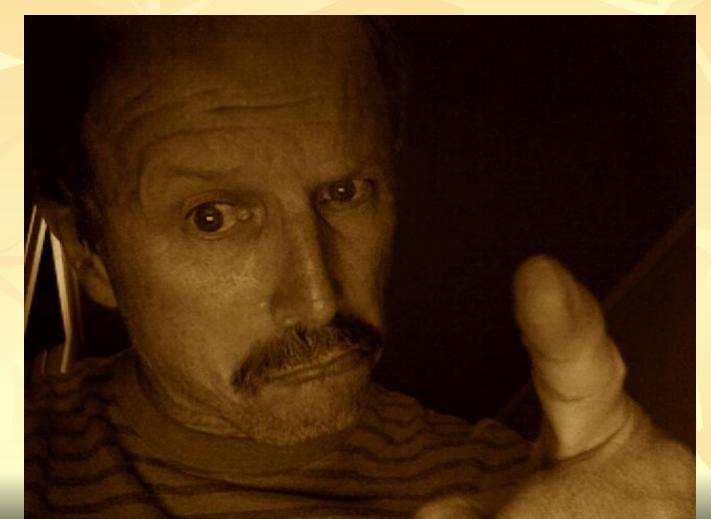


OK, we can see the need

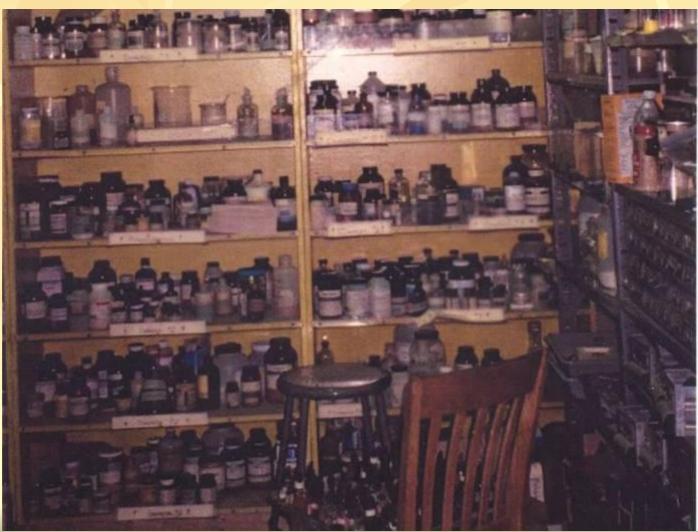
 Now let's fix it
 Nebraska School Chemical Cleanout Campaign can help



Become A Chemical Investigator Take a critical in-depth look around. Just like me, be ruthless!



Where do we start snooping?Act like this is a brand new school for you



Assessing Chem Mgmt Practices

Numerous issues to assess:

- High-risk chemicals on site?
- Excessive amounts of chemicals on site?
- Degraded chemicals and containers?
- Spill plan & clean-up materials?
- Proper storage & disposal of haz chemicals?
- Teachers trained in chemical hygiene?

What are the Challenges?

- Finding time to inventory your stocks
- Staying safe and prepared
- Identifying ones to go
- Finding space to safely store the ones you need
- Finding \$\$\$ to dispose of unneeded chemicals



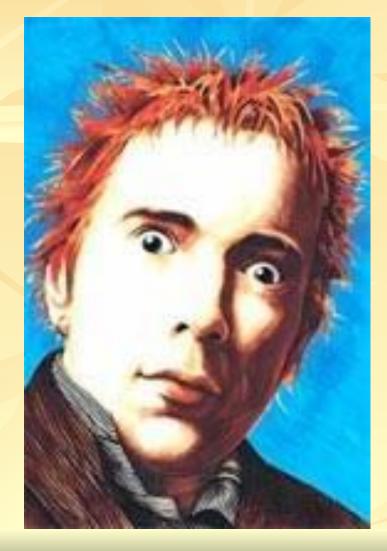
Pause before you begin

Before you enter the room
Assess the risks

Assess your safety options
Best if you're not alone



Be Alert As You Enter



Keep eyes open & wits about you Pause before opening doors or moving bottles Look for chemical and physical hazards

Rusty Hinges?

Leaking acidsLeaking iodine



Is this the only eye wash? better not be...



Site Audits Take a Long Time to Complete You need to look at <u>Every</u> bottle

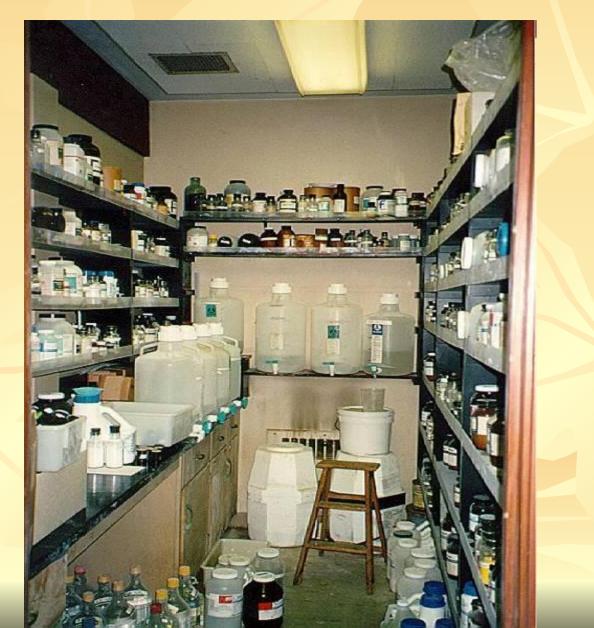




Look Everywhere!



In the Stockroom



In the Cabinets







On Shelves







In and Under the Hood



In Drawers







In the Refrigerator in the Lab



And the One in the Break Room



By the Sink



By the Other Sink



Under the Sink



On the Benches



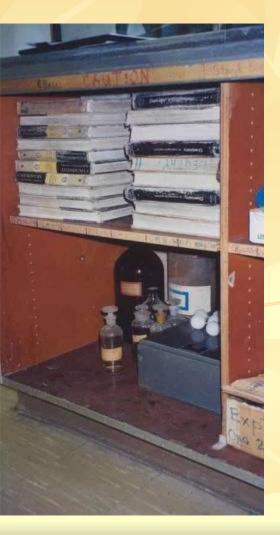
On the Carts







In Bookcases by students





Potassium CYANIDE!!!

Chem III

Hassion Change

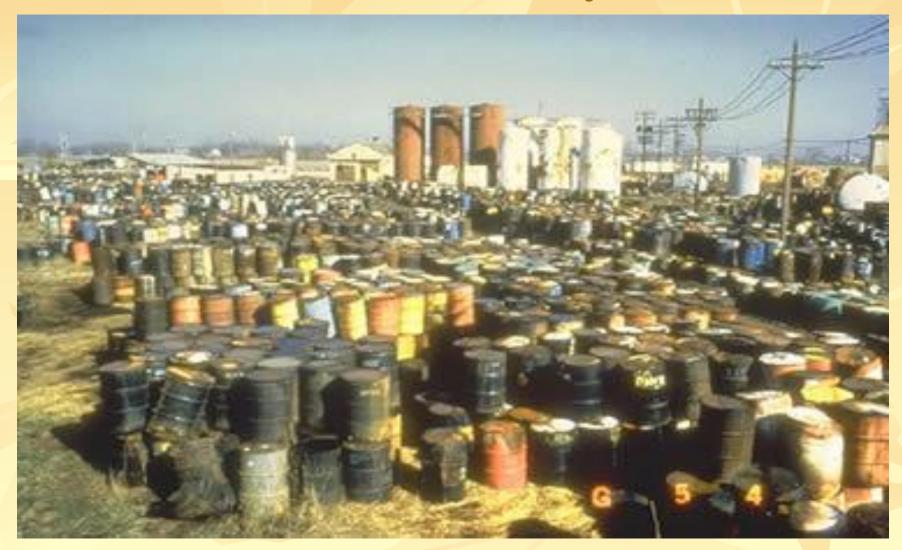
Look High



Look Low



Check the Backyard



just kidding... this isn't a school

How to track your inventory

- Compound name
- Number of containers
- Capacity of containers
 - Don't track amount in the containers
 - It'll be full again at some time (or gone)
- When a container is emptied, save it
- Don't adjust inventory if it will be refilled

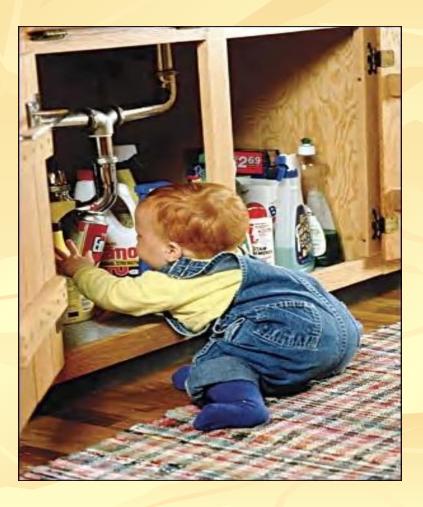
School Chemicals Database Info on 975 Chemical Compounds

Search: Search grid fields here	Go Clear				Expo
		123456789	10 >> (View	All) Ya	ou are viewing pa
Chemical Name	Acute Exposure Hazard	Chronic Exposure Hazard	Environmental Toxicity	Hazard Rank	Minimum Grade Level Restrictions
Abscisic Acid	No acute toxicity data reported	No confirmed human disease- related or reproductive hazard data reported	No fish toxicity data	1	Elementary demonstrations only
Acetal	Explosive. Peroxide forming compound. Flammable. Slightly toxic by ingestion & skin contact. Irritant.	No confirmed human disease- related or reproductive hazard data reported	No fish toxicity data	5	Ban Candidate
Acetaldehyde	Explosion risk from peroxide formation. Flammable. Slightly toxic by inhalation, ingestion and skin contact. Irritant to eyes.	Liver function impairment	Toxic to fish	5	Ban Candidate
Acetamide	Slightly toxic by ingestion	No confirmed human disease-	Non-toxic to fish	2	Junior High

Found at the King County Rehab the Lab website http://lhwmp.org/HWApp/projects/schools/ChemList.aspx

Acetanilide	Slightly toxic by ingestion. Irritant	No confirmed human disease- related or reproductive hazard data reported	No fish toxicity data
Acetic Acid (<1 Molar)	Irritant. No acute toxicity data reported at this dilute concentration.	No confirmed human disease- related or reproductive hazard data reported	Non-toxic to fish
Acetic Acid (>6 Molar)	Combustible liquid and vapor. Corrosive. Toxic by skin contact. Slightly toxic by ingestion.	Chronic lung	Non-toxic to fish
Acetic Acid (1 Molar to 6 Molar)	Corrosive. Slightly toxic by skin contact and ingestion.		Non-toxic to fish

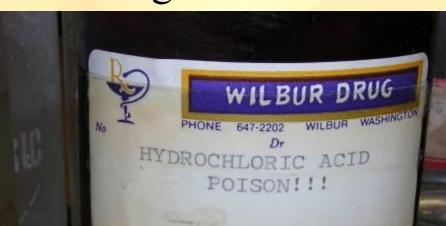
Deciding What Needs to Go



Dispose of Chemicals that are really:

- Dangerous
- Decrepit
- Excessive
- Useless
- Incognito







Haz Rankings Link to Grade Levels

• Hazard Rank $\mathbf{0}$ = safe for all grades 26 chemicals, e.g. Vinegar, Sugar, Starch Hazard Rank 1 = elementary demos & above 19 chemicals e.g. mineral oil, rubbing alcohol Hazard Rank 2 = junior high & above • e.g. cobalt nitrate, ethanol, gram's iodine stain Hazard Rank 3 = high school & above • e.g. concentrated acids & bases, hexane

Haz Rankings Link to Grade Levels

Hazard Rank 4 = advanced placement chem

- 119 chemicals with limited utility & high hazards
- Requires chemical hygiene plan & approval
- e.g. Formalin, lead chloride, bromine water
- Hazard Rank 5 = ban candidates
 - 201 chemicals w/ no reported usefulness, high hazards and easy exposure routes
 - e.g. Arsenic, pure cyanide, mercury, explosives

Let's walk through the process

- Find & inspect all chemical storage areas
- Are there other areas with stored chemicals?
- Identify the highest risk chemicals
 - Hazard level 4 & 5 in the database
- Ensure incompatible chemicals are segregated
- Mark those that need to be disposed
 - Right side good, left side bad on shelves
 - Signage clearly indicating this

Chemical Assessment Safety First

Teacher gave me these gloves to clean up a small chemical spill at their high school.

Familiarity breeds contempt – and children. – Mark Twain

Where's the goggles, gloves, lab coat?

Nitrile gloves are supple & chemical resistant.

> Change immediately if visually contaminated!



Protective clothing

- Safety glasses
- Gloves
- Funky clothes
 - Stockrooms are dusty
- Splash resistant goggles
 Chemical resistant clothes & shoes



Start with the Flammables

- Safely stored?
- No incompatibles?
- Well labeled?Name & hazard
 - INAILLE & Hazalu
- Only those you need?
- If I see scorch marks, I ask "what happened?"



Flammables must be in cabinets Limit is one gallon in classroom



Check Flammables Cabinet Carefully

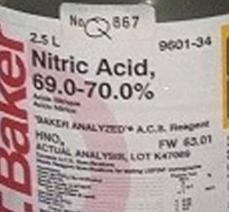
Do the chemicals match the curriculum? Peroxidizable solvents will generally be here Never handle bottles by cap Take your time!



Move <u>glacial</u> acetic acid and formic acid to the flammables cabinet

321

Mix these, could get flaming acid



Acetic Acid, Glacial

Assessing the corrosives



Acids & bases, common yet very dangerous







Safety glasses inadequate by corrosives



Sodium hydroxide burns eyes!!



Corrosives near? Wear Goggles!!!



Curses!

Foggy Goggles!



Acids & Hydroxides = incompatible

- Acids rust metal
- Acids need to be in locked non-metal cabinet
 - SciMatCo makes a great one
- Liquid bases need to be in locked cabinet
- All hydroxide liquids are corrosive bases
 - Bases don't corrode metal much
- They react with each other generating heat and corrosive vapors

Know your corrosive cap colors



ACIDS

- Red Nitric acid
 - Yellow Sulfuric
- Blue Hydrochloric
- Brown Acetic
- Black Phosphoric

BASES

 Green – Ammonium hydroxide

Metal Acid Cabinets Serious risk of shelf collapsing



Rusting shelf clips could lead to collapse and acid release



Leaking Nitric Acid and Ammonium Hydroxide

HNO3

Ammonium chloride crystals (ammonium hydroxide and hydrochloric acid)

00800

BEAGENT GRADE

CORCO

fiel

EAGENT GRADE

SULFUR

COBCO

VDROCHLORIC

Nitric Acid Number One problem acid

Eats its cap in 7 – 10 years
Extremely corrosive
Powerful oxidizer
Check all red caps for integrity



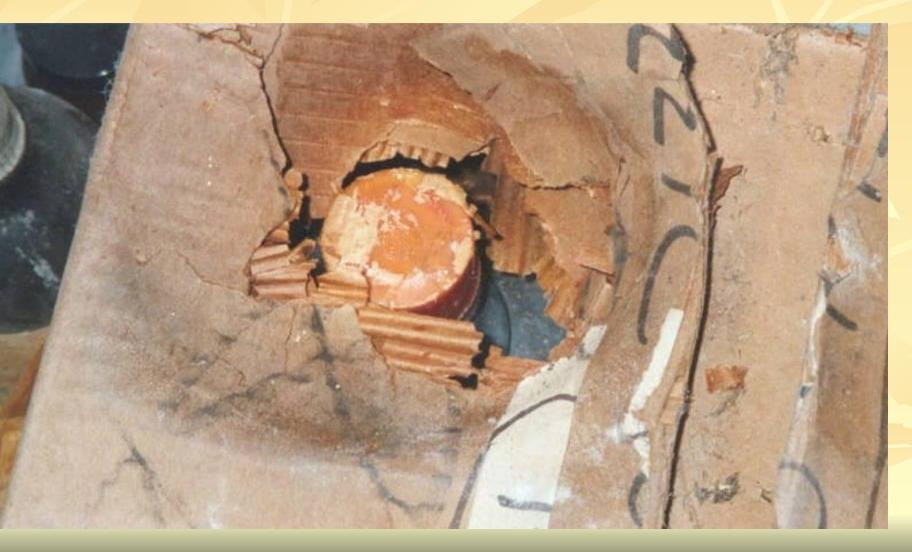








Nitric acid, oxidizer and corrosive. Fumes ate through plastic cap then oxidized cardboard box. Extreme fire risk! Six pounds of cyanide right above it. Earthquake could mean gas chamber for 500 students



Sodium hydroxide rounded white crystals all over the place



Dry Chemicals Shelves General Housekeeping is a Clue

- Look for mercury & mercury compounds
- Generally safety glasses are acceptable here
- Look for gas cylinders
- Look for ancient chemicals

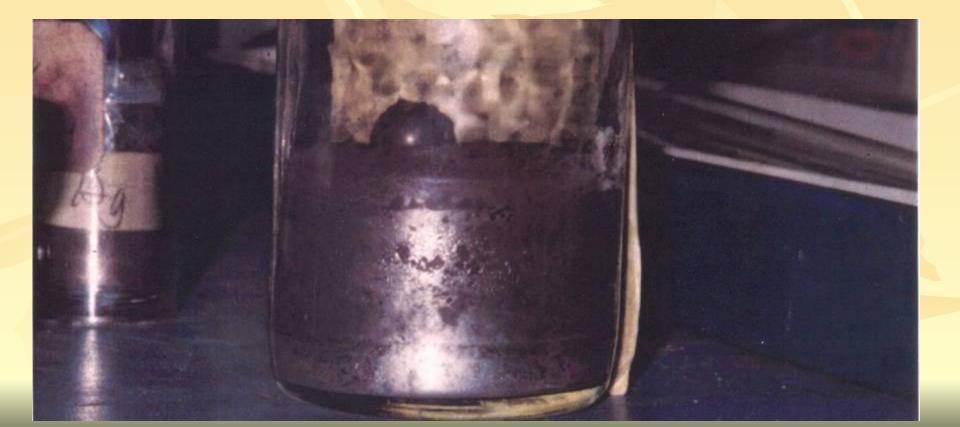


Chlorine!

NWWO

The "Box O Gases"

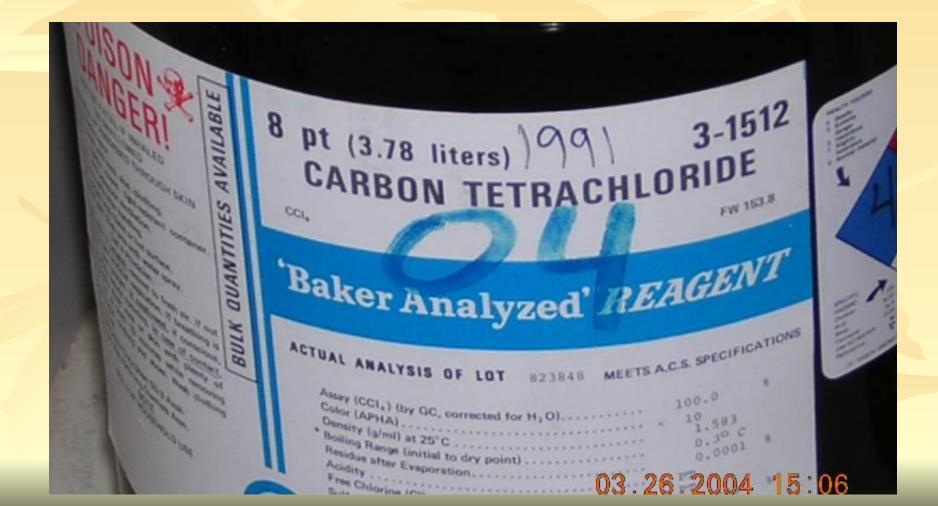
What I Ask When I See This #1
For mercury, cadmium, arsenic compounds
Do you use this compound?
Could you drop this demo?



What I Ask When I See This #2 Do you teach organic chemistry here? If not, many of the higher hazard solvents can go



What I Ask When I See This #3 Are you using this compound? Why?



What I Ask When I See This #4 How much lead nitrate a year do you use? 454 grams per pound, how many years supply is it?



What's Wrong With This Picture?



- Flammable liquid in standard freezer
- Oxidizer by flammable liquid
- Cold inhibits the preservative, so speeds formation of peroxides
- Chloroform reacts with light to form phosgene gas, a chemical warfare agent



Spill Response

- Are you prepared? Typically no.
- What could spill?
 - Corrosive acids & bases, flammables, mercury, etc.
- Do you have written plan?
- Do you do hands-on training?

Suggested Spill Supplies

Personal Protective Equipment

- Gloves, goggles, sturdy shoes, lab coat/apron
- Acids
 - Kitty litter, 4 lbs. sodium carbonate, pH paper test
- Bases
 - Kitty litter, 2 lbs. citric acid, pH paper test
- Solvents
 - Kitty litter/absorbent pads

Small broom, dustpan, collection container with lid

Chemical Storage Recommendations

- Segregated storage system most in use is from Flinn Scientific, Inc.
- Schools don't have the shelves to fully do it
- I simplified and consolidated it to make it work in the limited space you have
 - Storage scheme is included in your CD

Problem? Bottle as structural support



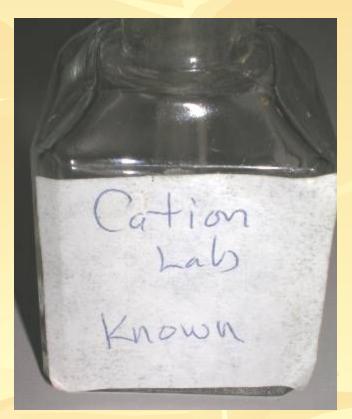
Good cupboards, good shelving, but still storing on counter.

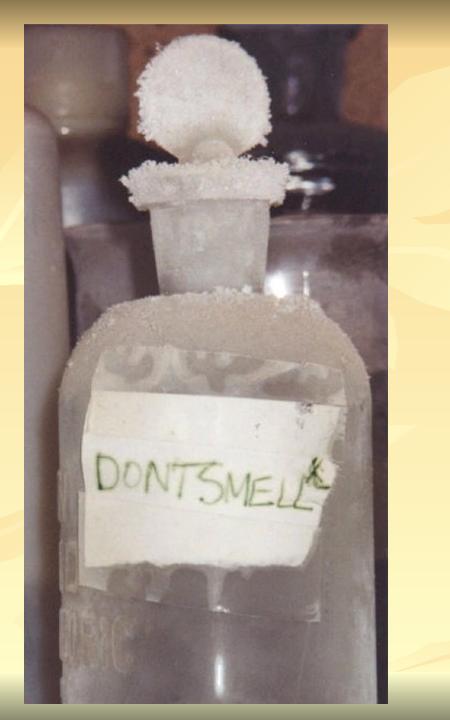


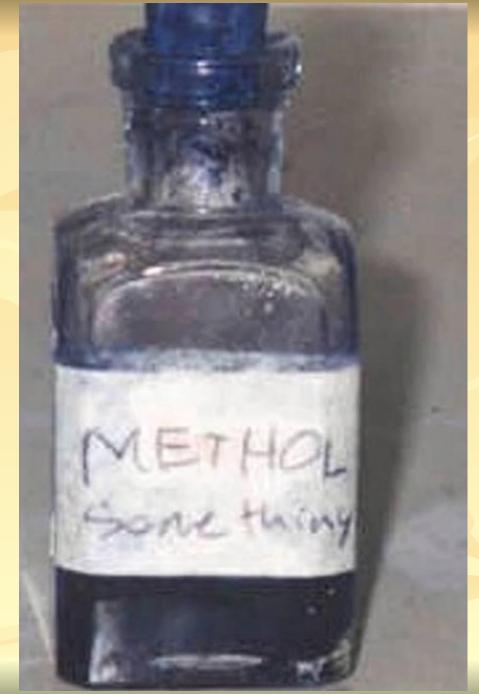
Can You Properly Manage Unknowns?

- Can't respond to spills
- Can't guarantee proper PPE
 Can't dispose of it properly unless you know its hazards
 - Very expensive to test

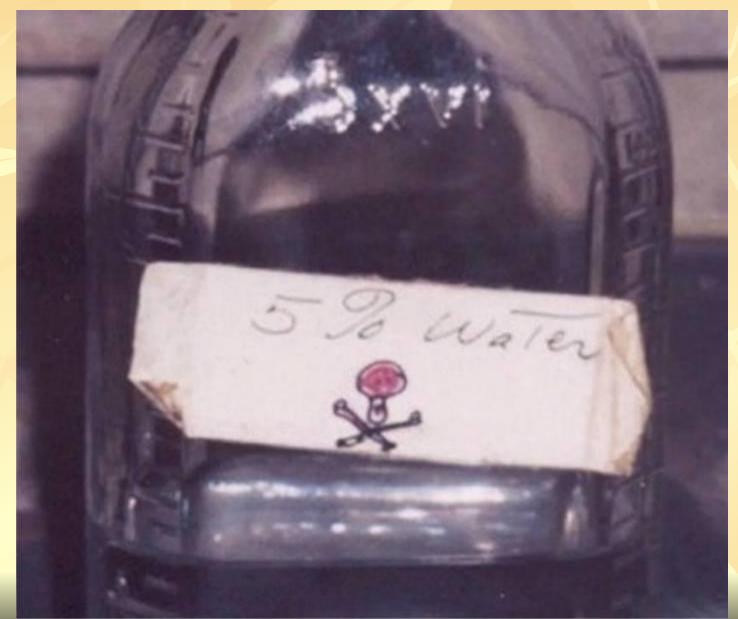








What's the other 95%?

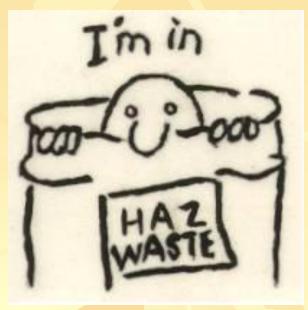


Chemical Waste Disposal



What's Hazardous Waste?

- It's a waste
 - No longer needed or useful
- It's hazardous
 - Is on a list or has hazardous characteristics
- Regulations
 - Resource Conservation & Recovery Act (RCRA) 40CFR
 - Clean Water Act, Clean Air Act, DOT regs

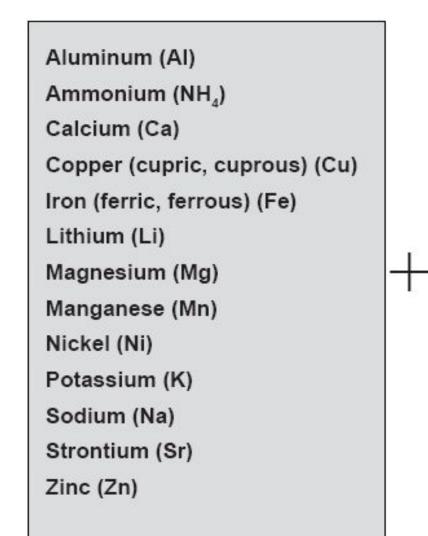


Hazardous Waste Characteristics

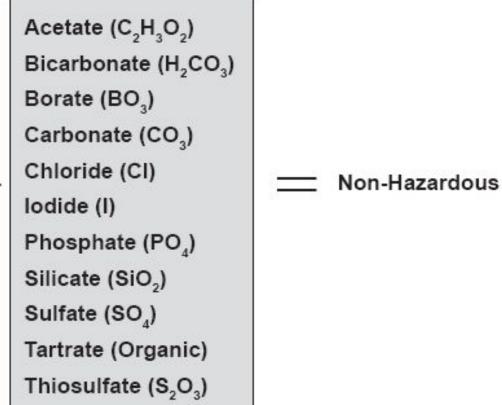
- Ignitable (<140 degree flash point)
- Oxidizer (nitrates, chlorates, chromates, "per-" inorganics)
- Corrosive (pH < 2.0 or pH > 12.5)
- Reactive (w/ air or H₂O or produces cyanide or sulfide gas when acidified)
- Toxic (Listed heavy metals, pesticides and organic toxins)

Hazardous Waste Cheat Sheet

Non-Hazardous Combinations



Must be combined to be accurate Calcium + Chloride = $CaCl_2$



Hazardous Waste Cheat Sheet -- pt. 2

P- List Chemicals

```
Arsenic Trioxide (AsO<sub>3</sub>)
Adrenaline / Epinephrine (C<sub>9</sub>H<sub>13</sub>NO<sub>3</sub>)
All Pure Cyanide (first name, space,
cyanide)
Beryllium Powder (Be)
Carbon Disulfide (CS<sub>2</sub>)
Dinitrophenol (C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>O<sub>5</sub>)
Endothall
Nicotine (C<sub>10</sub>H<sub>14</sub>N<sub>2</sub>)
Nitric Oxide/Nitrogen Oxide (NO)
Osmium Tetroxide (OsO,)
Sodium Azide (NaN<sub>2</sub>)
Strychnine (C<sub>21</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>)
Vanadium Pentoxide (V2O5)
Warfarin (C<sub>19</sub>H<sub>16</sub>O<sub>4</sub>)
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Potential Explosives

Bouin's Solution (dry) Collodion (dry) Dinitrophenol Ethyl Ether Isopropyl Ether Nitroglycerin Picric Acid Potassium (discolored) Tetrahydrofuran Dioxane Trinitro - anything Cumene Cyclohexene

TCLP Metals

Arsenic (As) Barium (Ba) Cadmium (Cd) Chromium (Cr) Lead (Pb) Mercury (Hg) Silver (Ag) Selenium (Se)

Can it go down the drain?







Sewer Regulations

- Treatment plant regulates, link with them
- pH limits usually 6 to 9
- Low PPM local metals limits
- No haz waste allowed without approval
- No post-process dilution
 - Unless you have written OK from sewer utility

Heavy Metals Sewer Limits Can dilute copper sulfate go down the drain? No...

- $0.1 \text{ M CuSO}_4 = 6.35 \text{ g/L Copper} = 6530 \text{ mg/L (ppm)}$
- Sewer limit is 8.0 mg/L copper = 0.0001 M Cu^{+2}
- Arsenic limit = 4.0 mg/L
- Cadmium = 0.6 mg/L
- Chromium = 5.0 mg/L
- Lead = 4.0 mg/L
- Mercury = 0.2 mg/L
- Nickel = 5.0 mg/L
- Silver = 3.0 mg/L
- Zinc = 10.0 mg/L



Treatment of Acids & Bases

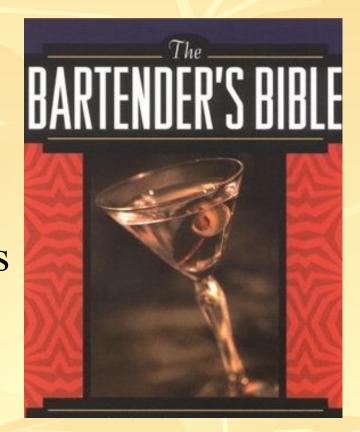
- Elementary neutralization of waste acids and bases is allowed
- Must be tracked on log sheet each batch
- Must be counted toward generator status
- Must meet sewer limits before discharge
 - Can't do it with hydrofluoric, perchloric acids due to toxic by-products from neutralization
- Not recommended for glacial acetic acid or ammonium hydroxide due to fumes

Alcohol Management

Ignitable if >24%
Not allowed down drain
Martini is about 35%

Returned drink = Haz Waste?

Dilution just to get to <24% is not allowed



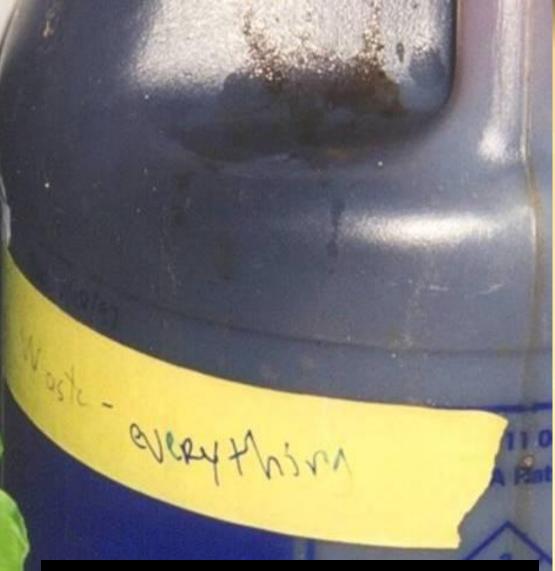
Does It Go Up the Fume Hood?



Yep.

- OK if it's water or an empty container
- Empty = can't pour more out of it
- The always empty collection bottles

If liquids are collected, they must be segregated by hazard class



How to turn \$200 worth of disposal costs into \$1200, just by not segregating waste

Haz Waste Disposal Getting started

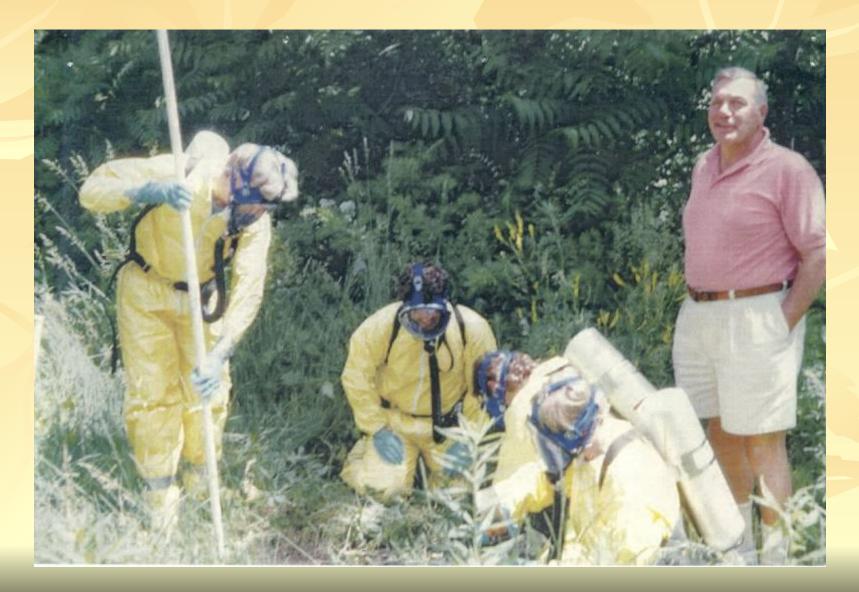
 Start by linking with the Nebraska School Chemical Cleanout Campaign (NE SC3)

Keep Nebraska Beautiful 3201 Pioneers Blvd., Ste 118 Lincoln, NE 68502 402.486.4562

Wash Your Hands Before Leaving



Don't get complacent out there



Questions?

Dave Waddell

waddellenviro@yahoo.com

